OXYGEN CHEMISTRY IN THE CIRCUMSTELLAR ENVELOPE OF THE CARBON-RICH STAR IRC +10216

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ABSTRACT

In this paper we study the oxygen chemistry in the C-rich circumstellar shells of IRC +10216. The recent discoveries of oxygen-bearing species (water, hydroxyl radical, and formaldehyde) toward this source challenge our current understanding of the chemistry in C-rich circumstellar envelopes. The presence of icy comets surrounding the star or catalysis on iron grain surfaces have been invoked to explain the presence of such unexpected species. This detailed study aims at evaluating the chances of producing O-bearing species in the C-rich circumstellar envelope only by gas-phase chemical reactions. For the hot inner envelope we show that although most of the oxygen is locked in CO near the photosphere (as expected for a C/O ratio greater than 1), for radial distances larger than ~15 stellar radii, species such as H2O and CO2 have a large abundance under the assumption of thermochemical equilibrium. It is also shown how non-LTE chemistry makes the CO → H2O, CO2 transformation predicted in LTE very difficult. Concerning the chemistry in the colder, outer envelope, we show that formaldehyde can be formed through gas-phase reactions. However, in order to form water vapor, it is necessary to include a radiative association between atomic oxygen and molecular hydrogen with quite a high rate constant. The chemical models explain the presence of HCO+ and predict the existence of SO and H2CS (which has been detected in a 3 mm line survey to be published). We have modeled the line profiles of H2CO, H2O, HCO+, SO, and H2CS using a nonlocal radiative transfer model and the abundance profiles predicted by our chemical model. The results have been compared to the observations and discussed.

Subject headings: astrochemistry — circumstellar matter — molecular processes — stars: AGB and post-AGB — stars: individual (IRC +10216)

Online material: machine-readable table, color figure

1. INTRODUCTION

IRC +10216 is a low-mass AGB star losing mass at a rate of (2–4) × 10^{-5} M_☉ yr^{-1} in the form of a molecular and dusty wind that produces an extended circumstellar envelope (CSE). The processes of dredge-up that occurs during this late evolutionary stage alter the elemental composition in the stellar surface (which is roughly solar, C/O < 1, during the main-sequence phase) resulting, in the case of IRC +10216, in a C/O ratio greater than 1, in what is known as a carbon star.

The physical conditions in the vicinity of the photosphere of an asymptotic giant branch (AGB) star (typical temperatures of ~2500 K and densities of ~10^{14} cm^{-3}) make the material mainly molecular, with a composition determined by local thermochemical equilibrium (LTE). It is now well established since the pioneering work of Tsuji (1973) that the C/O ratio completely determines the kind of chemistry taking place. The high stability of CO causes this molecule to have a large abundance, locking almost all of the limiting reactant and allowing for the reactant in excess to form either carbon-bearing molecules when C/O > 1 and the opposite, i.e., oxygen-bearing molecules, when C/O < 1. This has been extensively confirmed by observations. A look to the list of molecules detected in IRC +10216 confirms that they are mostly C-bearing species (see Table 1 in Cernicharo et al. 2000; see also §3). The only O-bearing molecule in C-rich AGB stars with a significant abundance, apart from CO, is SiO (Morris et al. 1975).

However, some other O-bearing molecules such as H2O (Melnick et al. 2001; Hasegawa et al. 2006), OH (Ford et al. 2003), and H2CO (Ford et al. 2004) have recently been detected in IRC +10216. The existence of such molecules has been interpreted as the result of evaporation of comet ices from a Kuiper belt analog in IRC +10216 (Ford & Neufeld 2001). The luminosity increase of the star, intrinsic to the red giant phase, would have caused the ice sublimation and subsequent release of water vapor to the gas phase in the circumstellar shells. OH would be produced when water is photodissociated by the interstellar ultraviolet field in the unshielded outer envelope, and H2CO would be the photodissociation product of an unknown parent molecule produced by sublimation of the ice mantles of these comets.

An alternative explanation has been proposed by Willacy (2004), in which H2O would be produced through Fischer-Tropsch catalysis on the surface of iron grains, which would be present in the expanding envelope due to condensation from the gas phase of some fraction of the available iron. Fischer-Tropsch catalysis breaks the CO bond and produces H2O and hydrocarbons such as CH4.

Oxygen-bearing species have also been detected in the C-rich proto–planetary nebula CRL 618 (Herpin & Cernicharo 2000). However, the production of these species has been interpreted by Cernicharo (2004) as the result of a rich photochemistry in a region of high density (~10^7 cm^{-3}) and temperature (200–300 K) where large complex C-rich molecules are also produced (Cernicharo et al. 2001).

The aim of this paper is to investigate whether O-bearing molecules could be produced in the C-rich expanding gas of AGB stars by non-LTE mechanisms. LTE calculations provide a good estimation of molecular abundances in the vicinity of the photosphere, but as the gas expands the temperature and density decrease significantly and the chemical timescale increases, making
chemical kinetics dominant in determining the molecular abundances. We describe the model of the circumstellar envelope in § 2. The reaction network is discussed in § 3. The results of the chemical model are presented in § 4 together with comparisons of radiative transfer calculations with available observations. The conclusions are given in § 5.

2. THE CIRCUMSTELLAR ENVELOPE

We assume spherical symmetry for the circumstellar envelope. In order to calculate the molecular abundances at different radii in the CSE, we follow the history of a volume element of gas with a given chemical composition traveling from the photosphere \( r = R_\odot \) to the end of the envelope \( r \sim 10^{18} \) cm. We build a system of differential equations, integration of which yields the temporal evolution of the density of each gas species. The time must be interpreted as radial position, provided the gas travels outward at a given velocity. Different processes are considered during this travel depending on the position in the CSE. Kinetic temperature (which determines the reaction rate constants) and total gas density radial profiles are needed to solve the system of equations. The values adopted for the different parameters used to model the CSE are given in Table 1. For model purposes the CSE is believed to consist of three different regions: the innermost region, the inner envelope, and the intermediate and outer envelopes.

2.1. The Innermost Region

This zone corresponds to the region between the photosphere and \( r_0 \) (see Fig. 1a). The adopted physical conditions are

1. The temperature is considered to vary as a power law of the radius \( r \),
   \[
   T(r) = T_\odot \left( \frac{r}{R_\odot} \right)^{-\alpha},
   \]  
   where \( T_\odot \) is the temperature at the photosphere and \( R_\odot \) is the star radius.

\[  \begin{array}{|c|c|c|}
\hline
\text{Parameter} & \text{Values} & \text{Ref.} \\
\hline
R_\odot \ (\text{cm}) & 6.5 \times 10^{13} & 1 \\
M_\odot \ (M_\odot) & 2 & 2 \\
r_0 \ (R_\odot) & 1.2 & 2 \\
r_c \ (R_\odot) & 5 & 1 \\
T_\odot \ (K) & 2320 & 1 \\
\alpha & 0.6 & 3 \\
n(r_0)_{\text{MH,ML}} \ (\text{cm}^{-3}) & 3.7 \times 10^{14} & 2 \\
n(r_0)_{\text{ML}} \ (\text{cm}^{-3}) & 1.2 \times 10^{12} & 2 \\
K_{\text{ML,ML}} & 1 & 1 \\
K_{\text{MH}} & 1.8565 & 4 \\
P \ (\text{days}) & 650 & 3 \\
\gamma(r < r_c) \ (\text{amu}) & 0.89 & 3 \\
\mu(r < r_c) \ (\text{amu}) & 1.7 & 3 \\
v_{\text{exp}} \ (\text{km s}^{-1}) & 14.5 & 5 \\
M \ (M_\odot \text{ yr}^{-1}) & 3 \times 10^{-5} & 6 \\
\text{Distance} \ (\text{pc}) & 150 & 7 \\
\tau_{\text{1006}}(r = 10^{16}) & 12.7 & 8 \\
\hline
\end{array} \]

References.—(1) Ridgway & Keady 1988; (2) Willacy & Cherchneff 1998; (3) Cherchneff et al. 1992; (4) Witteborn et al. 1980; (5) Cernicharo et al. 2000; (6) Glassgold 1996; (7) Crosas & Menten 1997; (8) Doyt & Leung 1998.

![Fig. 1.](image)

2. The density profile is given by hydrostatic equilibrium. Considering the above temperature law, the gas density can be expressed as follows in terms of the value at \( r_0, n(r_0) \),

\[ n(r) = n(r_0) \left( \frac{r}{r_0} \right)^\alpha \exp \left[ \frac{-GM_\odot m_{\text{HI}} \mu}{kT_\odot R_\odot^2 (1 - \alpha) \left( r_0^\alpha - r^\alpha \right)} \right], \]

where \( k \) is the Boltzmann constant, \( G \) is the gravitational constant, \( M_\odot \) is the mass of the star, \( m_{\text{HI}} \) is the mass of a hydrogen atom, and \( \mu \) is the mean molecular weight of gas.

The high densities and temperatures in this region allow one to assume that molecular abundances are given by a LTE calculation.

2.2. The Inner Envelope

The gas travels from \( r_0 \) to \( r_c \) (see Fig. 1a), where \( r_c \) stands for condensation radius. At this distance grain formation is supposed to occur. Radiation pressure on grains, together with momentum coupling of gas and grains, make the gas accelerate up to a terminal expansion velocity, which remains constant beyond \( r_c \). The mechanism responsible for the transport of the gas from \( r_0 \) to \( r_c \) is somewhat controversial. Hydrodynamical models (Bowen
1988) have shown that pulsational driven shocks can gradually move the gas up to $r_c$. Willacy & Cherchneff (1998) have applied this approach for modeling the chemistry in the inner envelope. An alternative mechanism could be that the gas close to the photosphere pulsates around an equilibrium position with an associated radial velocity very similar to the escape velocity. This could lead to a scenario in which shells of gas that are in levitation can eventually escape from the surroundings of the photosphere, and some of them could reach $r_c$.

1. The temperature profile in this region is given by equation (1).

2. For the density profile we follow the treatment of a shocked extended region of a C–rich CSE of Cherchneff et al. (1992),

$$n(r) = n(r_0) \exp \left[ -Kn \frac{GM_n m_n \mu (1 - \gamma^2)}{kT_n R_n^2 (1 - \alpha)} \left( \frac{r}{r_0} \right) \right],$$

(3)

where $\gamma$ is defined in Cherchneff et al. (1992) and $K_n$ is explained in the next paragraph.

The reference value $n(r_0)$ is evident neither from observations nor from models. Previous models of the inner envelope of IRC +10216 (Cherchneff et al. 1992; Willacy & Cherchneff 1998) have used high values of $n(r_0)$ based on hydrodynamical models for periodically shocked Mira-like stars, which have density profiles as an output. However, with such high $n(r_0)$ values, the extrapolation to larger radii produces densities for the outer envelope much higher than those obtained from the law of conservation of mass, in which the absolute density is well determined by the mass-loss rate and the expansion velocity (see eqs. [5] and [6] in § 2.3). To reconcile the outer envelope density law with the high values in the inner regions, we introduce the arbitrary factor $K_n$ in equation (3). We consider three different density laws for the inner envelope (shown in Fig. 1a) whose parameters $n(r_0)$ and $K_n$ are given in Table 1: MI (I for intermediate density); MH (H for high density); and ML (L for low density). We point out that the chemical timescale of these two magnitudes is detailed in Appendix A.

Another issue is how the gas travels from $r_0$ to $r_c$. As discussed above, different mechanisms could be operating. The simplest assumption to model the chemistry is to consider that the gas travels at constant velocity in this inner envelope. When using this approach we assume a velocity of 1 km s$^{-1}$.

SiO condensation onto SiC grains.—Considering non-LTE effects, we investigated whether deposition of SiC species (that are specially refractory) on SiC grains could affect the oxygen chemistry, because SiO is the second most abundant O-bearing molecule. The model for grain formation in IRC +10216 could be as follows. The major type of grains is carbonaceous, most probably amorphous carbon (AC), as indicated by fitting the infrared spectrum (Bagnulo et al. 1995). These grains would originate in condensation processes involving $C_2H_2$ (the most abundant C-bearing molecule after CO) that would take place at ~1000 K (~4R$\_c$). A minor type of grains would be SiC, as indicated by the 11.3 $\mu$m feature in the IR spectrum (Lorenz-Martins & Lefèvre 1993), which would condense at ~1500 K (~2R$\_c$). This condensation sequence is due to an inverse greenhouse effect in both types of grains (see McCabe [1982] for a theoretical approach and Frenklach et al. [1989] for experimental evidence). Although a more correct approach would be a chemical mechanism leading to the formation of grains from gaseous molecules, for our purposes we describe the condensation of SiC grains (AC grains are not considered, because we are just interested in deposition of Si species on SiC grains) as a two-step process: (1) nucleation from SiC gas molecules in the context of homogeneous nucleation theory, which is basically described by the nucleation rate $J_n$ (number of condensation nuclei formed per unit time and unit volume), and (2) growth of grains by accretion of gas-phase molecules, which is described by the grain radius $a_g$. The calculation of these two magnitudes is detailed in Appendix A.

Shocks.—An alternative to the mechanism of the gas traveling at constant velocity in the inner envelope is to consider the effect of gas driven by shocks. Molecular abundances are considerably affected by the steep changes in temperature and density associated with the shocks. We follow the approach of Willacy & Cherchneff (1998), but in a more simplistic way. The history of a volume element of gas to reach $r_c$ from $r_0$ after a certain number of shocks is represented in Figures 2a, 2b, and 2c, and is described below. With one shock and subsequent relaxation the gas moves from a position $r_1$ to $r_2$ ($r_2 > r_1$) following a harmonic trajectory. The gas in $r_1$ with temperature $T_1$ and density $n_1$ suffers a shock, and we assume that the immediately postshocked gas increases its temperature by a factor of 2 and its density by a factor of 10 (typical values obtained by Willacy & Cherchneff [1998] from hydrodynamical considerations). Then the gas relaxes its temperature and density exponentially until reaching the new radius $r_2$ (with temperature $T_2$ and density $n_2$) in a time interval equal to the period of pulsation of the star $P$. In this way the gas progressively moves outward until reaching $r_c$, beyond which an expansion at constant velocity $v_{exp}$ takes place.

In Figure 2 we plot the trajectory, temperature, and the three density laws introduced previously. Note that again the H/H$_2$ ratio strongly depends on the total gas density (see Figs. 2d, 2e, and 2f).

2.3. The Intermediate and Outer Envelopes

The intermediate and outer envelopes begin at $r_c$. The gas expands adiabatically at constant velocity $v_{exp}$. The molecules in the very outer envelope are no longer shielded by the dust of the CSE against the interstellar UV field, and are then photodissociated. Cosmic rays also play a role by ionizing some species.

1. The temperature profile is taken from the fit of Manon et al. (1988) to the results of Kwan & Linke (1982) for the outer envelope of IRC +10216,

$$T(r) = \max \left[ 10, 14.6 \left( \frac{r}{9 \times 10^{16}} \right)^{-p} \right],$$

(4)

where $r$ is expressed in centimeters and $p$ takes values of 0.72 for $r < 9 \times 10^{16}$ and 0.54 for $r > 9 \times 10^{16}$.

2. The density profile is given by the law of conservation of mass,

$$\dot{M} = n(r)m_{H_2}v_{exp}4\pi r^2,$$

(5)

which, with the values given in Table 1 and assuming that hydrogen is mostly molecular ($\mu \sim 2$ amu), results in

$$n(r) = \frac{3.1 \times 10^{37}}{r^2(\text{cm})} \text{cm}^{-3}.$$
3. The photodissociation rate $\Gamma_i$ for a molecule $i$ at a radius $r$ depends on the UV field at that radius,

$$\Gamma_i(r) = \int_{\lambda_1}^{\lambda_2} 4\pi J_i(r) \sigma_i(\lambda) d\lambda,$$

where $4\pi J_i(r)$ is the UV field at $r$ in photons cm$^{-2}$ s$^{-1}$ nm$^{-1}$, $\sigma_i(\lambda)$ is the photodissociation cross section, and the integral extends from 91.2 nm (Lyman cutoff) to a threshold value $\lambda_i$ that depends on each molecule. The calculation of each $\Gamma_i(r)$ involves the knowledge of the cross section and the solution of the UV radiative transfer for calculating $J_i$ at each radius $r$, which will depend in a first approximation on the amount of dust that surrounds the point $r$. In practice, photodissociation rates are usually expressed in the literature (Le Teuff et al. 2000) for plane-parallel geometry as a function of the visual extinction $A_v$ (in magnitudes) measured along the direction normal to the infinite plane,

$$\Gamma_i(A_v) = A_v \exp(-C_i A_v),$$

where $A_i$ and $C_i$ are specific parameters for each molecule. For our purposes we have adopted this simple approach by merely correcting for the geometrical difference from plane parallel to spherical. The procedure used for such correction as well as the resulting $A_v$ radial profile are detailed in Appendix B.

3. THE CHEMISTRY

We consider solar elemental abundances (oxygen from Allende Prieto et al. [2001] and the rest from Cox [2000]) and assume a C/O ratio of 2. The chemistry in IRC +10216 is dominated by C-bearing molecules. For carbon chain radicals $C_n$H see Tucker et al. (1974), Thaddeus et al. (1985), Guélin et al. (1978, 1987a, 1997), Cernicharo et al. (1986), and Cernicharo & Guélin (1996). For carbon chain radicals $C_n$N see Wilson et al. (1971), Guélin & Thaddeus (1977), and Guélin et al. (1998). For cyanopolyynes $HC_2n$+$1$N see Morris et al. (1971, 1976), Winnewisser & Walmsley (1978), and Bell et al. (1982). For sulfur-carbon chain molecules $C_n$S see Wilson et al. (1971), Cernicharo et al. (1987), and Bell et al. (1993). Finally, for silicon-bearing molecules $SiC_n$ see Cernicharo et al. (1989), Thaddeus et al. (1984), Apponi et al. (1999), and Ohishi et al. (1989). However, since we are just interested in oxygen chemistry, in our model we do not include very long carbon chains, only the 65 neutral molecules given in Table 2.

As initial abundances for the inner envelope we take those given by LTE at $r_0$, while for the outer shells we adopt initial abundances for some parent molecules taken from the literature or from a LTE calculation when no data are available (see Table 3). This procedure is motivated by the processes occurring in the intermediate envelope (especially on grain surfaces) that presumably alter the molecular abundances (hydrides such as CH$_4$, NH$_3$, SiH$_4$, and H$_2$S are believed to form via such processes).

Different types of reactions dominate the chemistry depending on the region of the CSE considered. The temperatures in the

![Figure 2](image_url)

**Fig. 2.** Parameters for a volume element of gas that suffers a history of five shocks: (a) trajectory; (b) temperature history; (c) density histories for models MH, MI, and ML. Panels (d), (e), and (f) show the H and H$_2$ abundances, relative to total number of hydrogen nuclei, calculated by chemical kinetics for the three density laws shown in (c).
inner envelope are not high enough to make ions abundant but allow for reactions with activations energies of up to a few 10,000 K to occur. Therefore, important processes are termolecular reactions, its reverse (thermal dissociation), and bimolecular reactions between neutrals. The outer envelope chemistry is dominated by photodissociation, radical-molecule reactions without activation energy, and radiative associations. Although all the species detected in IRC +10216 except HCO$^+$ are neutral, ionic chemistry energy, and radiative associations. Although all the species tions between neutrals. The outer envelope chemistry is dominated to occur. Therefore, important processes are termolecular reac-
tions, its reverse (thermal dissociation), and bimolecular reac-
tions, (assuming an expansion at constant velocity of 1 km s$^{-1}$) with those of chemical equilibrium, (2) we discuss the effects that SiO depletion from the gas phase could have on oxygen chemistry, and (3) we consider the chemistry with shocks.

4. RESULTS AND DISCUSSION

4.1. Oxygen Chemistry in the Inner Envelope

In this section we (1) compare the results of chemical kinetics (assuming an expansion at constant velocity of 1 km s$^{-1}$) with the CO case specifically for IRC +10216. For H$_2$ we use the same result, correcting for the different unattenuated photodissociation rate.

The most important reactions for oxygen chemistry are shown in Table 4. Table 5 contains the complete set of reactions.

4.1.1. Results of Chemical Kinetics

The densities considered in the inner envelope affect, among other parameters, the H$_2$/H$_2$ ratio. Figures 1b, 1c, and 1d show the H$_2$ and H abundances for models MH, MI, and ML, respectively. The high densities of model MH make the chemical timescale lower than the dynamical timescale associated with an expansion at 1 km s$^{-1}$; therefore, reactions (R1)–(R6),

\[
\begin{align*}
H + H + M &\rightarrow H_2 + M \quad (R1, R2, R3) \\
H_2 + M &\rightarrow H + H + M \quad (R4, R5, R6)
\end{align*}
\]

are rapid enough to produce LTE abundances for H and H$_2$. The steep decay in density of model MI causes the reactions (R1)–(R6) to become so slow at $\sim 2R_*$ that the H abundance is frozen at a value of $5 \times 10^{-2}$. Models MH and MI both allow hydrogen to enter the intermediate shells and outer envelope mostly as H$_2$. Model MI has a low photospheric density, and therefore, hydrogen exists in atomic form rather than molecular. For larger radii the decrease in temperature makes molecular the most stable form. However, chemical kinetics does not allow for a H $\rightarrow$ H$_2$ transformation, and hydrogen enters the outer envelope in atomic form. One can see how both the density at the photosphere and the density radial profile affect the H$_2$/H$_2$ ratio. There are observational constraints about this ratio that suggest that hydrogen is mainly molecular in the CSE (based on an upper limit for the H$_2$ mass in the CSE and on an estimation of the hydrogen mass from observations of the 21 cm line; see discussion in Glassgold 1996). This suggests a high-density scenario, such as the one of models MH or MI, for the inner envelope.

In what concerns oxygen chemistry, according to chemical equilibrium, for the densities and temperatures prevailing in the inner envelope, almost all the oxygen available in a C-rich gas is locked in CO, with SiO being 2–5 orders of magnitude less abundant. Any other O-bearing molecule has an LTE abundance that is always below $10^{-10}$. However, several stellar radii away from the photosphere, where the temperature has decreased below $\sim 700$ K, the chemical system experiences a significant change, and molecules such as H$_2$O and CO$_2$ become very abundant in LTE (see dashed lines in Figs. 3a, 3b, and 3c). This is related to the fact that the most stable form for both carbon and oxygen is the CO molecule in a high-temperature regime, whereas for a low-temperature regime carbon is preferably locked in CH$_4$ and

| Species | Abundance | Notes |
|---------|-----------|-------|
| H$^+$   | $4.5 \times 10^{-3}$ | 1     |
| He$^+$  | $2.0 \times 10^{-1}$ | 2     |
| CO$^+$  | $6.0 \times 10^{-4}$ | 3     |
| C$_2$H$_2$ | $8.0 \times 10^{-5}$ | 4     |
| HCN$^+$ | $4.9 \times 10^{-5}$ | 4     |
| N$_2$   | $8.0 \times 10^{-5}$ | 2     |
| C$_2$H$_4$ | $2.0 \times 10^{-8}$ | 5     |
| CH$_4$  | $3.5 \times 10^{-6}$ | 6     |
| NH$_3$  | $1.7 \times 10^{-7}$ | 6     |
| SiH$_4$ | $2.2 \times 10^{-7}$ | 6     |
| H$_2$S  | $6.0 \times 10^{-10}$ | 7     |
| CS$^+$  | $1.2 \times 10^{-7}$ | 8     |
| SiS$^+$ | $4.3 \times 10^{-6}$ | 9     |
| SiC$_2$ | $5.0 \times 10^{-8}$ | 10    |
| SiO$^+$ | $8.0 \times 10^{-7}$ | 6     |

Notes: (1) Upper limit by Bowers & Knapp (1987); (2) calculated according to LTE, solar elemental abundances and a C/O ratio of 2; (3) data from Crosas & Menten (1997); (4) data from J. P. Fonfría et al. (2006, in preparation); (5) data from Golddhaber et al. (1987); (6) data from Keady & Ridgway (1993); (7) abundance derived from the T$_{12}$=10 line of ortho-H$_2$S observed in Cernicharo et al. (2000) in the optically thin and LTE limit assuming $T_{\text{rot}} = 20$ K and considering that H$_2$S is present for $r > 50 R_*$; (8) data from Henkel et al. (1985); (9) data from Boyle et al. (1994); (10) upper limit by Genesheimer et al. (1995).
TABLE 4
REACTIONS RELEVANT FOR OXYGEN CHEMISTRY

| Reaction Number | Reaction                                      | A       | n  | C  |
|-----------------|-----------------------------------------------|---------|----|----|
| R1              | H + H + H2 → H2 + H2                         | 8.6 × 10^{-33} | -0.60 | 0  |
| R2              | H + H + H → H2 + H                           | 8.8 × 10^{-33} | 0.00 | 0  |
| R3              | H + H + He → H2 + He                         | 6.1 × 10^{-33} | -0.13 | -39|
| R4              | H2 + H2 + H + H2 + H2                       | 8.4 × 10^{-09} | -0.24 | 52043|
| R5              | H2 + H + H + H + H                          | 8.6 × 10^{-09} | 0.36  | 52043|
| R6              | H2 + He + H + H + H                         | 5.9 × 10^{-09} | 0.23  | 52003|
| R7              | SiO + CO → SiO + C                           | 1.3 × 10^{-09} | 0.00  | 34513|
| R8              | SiO + C → Si + CO                            | 1.0 × 10^{-09} | -0.23 | 1291|
| R9              | C + H2 → CH + H                             | 3.1 × 10^{-10} | 0.16  | 11894|
| R10             | OH + Si → SiO + H                            | 1.0 × 10^{-10} | 0.00  | 0  |
| R11             | OH + H2 → H2O + H                            | 2.2 × 10^{-12} | 1.43  | 1751|
| R12             | SiO + CO → CO2 + Si                          | 4.2 × 10^{-13} | 0.67  | 32225|
| R13             | CO2 + H2 → H2O + CO                          | 3.2 × 10^{-7}  | 1.53  | 56906|
| R14             | OH + CO → CO2 + H                            | 1.2 × 10^{-13} | 0.95  | -73a|
| R15             | O + H2 → OH + H                             | 3.5 × 10^{-13} | 2.60  | 3241|
| R16             | CO2 + Si → SiO + CO                          | 2.7 × 10^{-11} | 0.00  | 282 |

Important Reactions in the Inner Envelope

| Reaction Number | Reaction                                      | A       | n  | C  |
|-----------------|-----------------------------------------------|---------|----|----|
| R17             | O + NH4 → OH + NH                            | 1.2 × 10^{-11} | 0.00 | 0  |
| R18             | O + CH3 → H2CO + H                           | 1.4 × 10^{-10} | 0.00 | 0  |
| R19             | OH + S → SO + H                              | 6.6 × 10^{-11} | 0.00 | 0  |
| R20             | O + SH → SO + H                              | 1.2 × 10^{-10} | 0.00 | -74b|
| R21             | O + NH → NO + H                              | 1.2 × 10^{-10} | 0.00 | 0  |
| R22             | CN + OH → NCO + H                            | 1.4 × 10^{-10} | 0.00 | 0  |
| R23             | S + CH3 → H2CS + H                           | 1.4 × 10^{-10} | 0.00 | 0  |
| R24             | O + OH → O2 + H                              | 1.8 × 10^{-11} | 0.00 | -175c|
| R25             | O + CH3 → HCO + H                            | 5.0 × 10^{-11} | 0.00 | 0  |
| R26             | 13C + 12C + 12CO → 12C + 13CO               | 3.4 × 10^{-10} | -0.50 | 1.3|
| R27             | SiO + C → Si + CO                            | 5.4 × 10^{-10} | 0.00 | 0  |
| R28             | H2 + H2 → H2 + H                            | 2.1 × 10^{-9}  | 0.00 | 0  |
| R29             | H2 + CO → HCO + H                            | 1.7 × 10^{-9}  | 0.00 | 0  |
| R30             | HCO + HCN → CO + HCNH+                      | 3.1 × 10^{-9}  | 0.00 | 0  |
| R31             | HCO + C2H2 → CO + C2H2                      | 1.4 × 10^{-9}  | 0.00 | 0  |
| R32             | SiS + C → SiS + C                            | 2.3 × 10^{-9}  | 0.00 | 0  |
| R33             | SiS + H → SH + Si                             | 1.9 × 10^{-9}  | 0.00 | 0  |
| R34             | SiS + S → SiS + S                            | 3.2 × 10^{-9}  | 0.00 | 0  |
| R35             | SiO + CO → CO2 + Si                          | 7.9 × 10^{-10} | 0.00 | 0  |
| R36             | O + H → OH + h                             | 9.9 × 10^{-19} | -0.38 | 0  |
| R37             | S + CO → OCS + h                             | 1.6 × 10^{-17} | -1.50 | 0  |
| R38             | HCO + e → CO + h                             | 1.1 × 10^{-7}  | -1.00 | 0  |
| R39             | H2CS + e → H2CS + h                         | 3.0 × 10^{-7}  | -0.50 | 0  |
| R40             | H2CO + e → HCO + h                          | 1.0 × 10^{-7}  | -0.50 | 0  |
| R41             | SiO + h → Si + O                            | 1.0 × 10^{-10} | 0.00 | 2.3|
| R42             | H2O + h → OH + H                            | 5.9 × 10^{-10} | 0.00 | 1.7|
| R43             | CH4 + h → CH3 + H                           | 2.2 × 10^{-10} | 0.00 | 2.2|
| R44             | H2 + CR → H2 + e                            | 1.2 × 10^{-17} | 0.00 | 0  |

Reactions Not Considered in Previous Chemical Modelsd

| Reaction Number | Reaction                                      | A       | n  | C  |
|-----------------|-----------------------------------------------|---------|----|----|
| R45             | O + H2 → H2O + h                             | 1.0 × 10^{-18} | 0.00 | 0  |
| R46             | HCO + H2 → H2CO + h                          | 5.0 × 10^{-15} | 0.00 | 0  |

Notes.—Rate constants for termolecular and bimolecular reactions are given by $k = A(T/300)^{n} \exp(-C/T)$, constants for photodissociations (hv) are given by $k = A \exp(-CA_{s})$, while constants for reactions with cosmic rays (CR) are given by $k = A$. Units are cm$^{3}$/s$^{4}$ for termolecular reactions, cm$^{3}$/s$^{3}$ for bimolecular reactions, and s$^{-1}$ for photodissociations and reactions with cosmic rays.

a $k(T < 80 K) = k(T = 80 K)$.

b $k(T < 298 K) = k(T = 298 K)$.

c $k(T < 167 K) = k(T = 167 K)$.

d See text for a discussion on these rate constants.
oxygen in H₂O (Tsuji 2000), as is easily seen from the analysis of the equilibrium constant of this reaction,

\[ \text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}, \]  

which can be fitted by the expression

\[ K_{eq}(T) = 1.58 \times 10^{-50} \left( \frac{T}{300} \right)^{0.09} \exp \left( \frac{24427}{T} \right) \]  

for a temperature interval of 200–2000 K \([K_{eq} \text{ with units of (molecules cm}^{-3})^{-2}]\). The formation of CH₄ and H₂O from CO and H₂ is exothermic and involves fewer particles, so according to Le Chatelier’s principle, the CH₄/H₂O mixture dominates over the CO/H₂ mixture at low temperatures and high densities. In our case, as temperature decreases so does density. Thus, a total CO → H₂O transformation is only produced for \(T \leq 400\) K \((r \gtrsim 18R_\odot)\) in model MH (see Fig. 3a) and for larger radii in models MI and ML. Despite a total CO → H₂O transformation that only takes place beyond \(~20R_\odot\), the three models show a considerably increase in the LTE abundance of H₂O beyond \(~10R_\odot\).

In order to have LTE abundances in the inner envelope, the chemical timescale \(r_{\text{chem}}\) must be shorter than the dynamical timescale \(r_{\text{dyn}}\) associated with the expansion for the gas being able to readapt its molecular abundances to the actual physical conditions (temperature and density) as it expands. The situation in the inner envelope of IRC +10216 is such that \(r_{\text{chem}} < r_{\text{dyn}}\) in the vicinity of the photosphere, but as temperature and density fall with radial distance, chemical reactions become slower, and for a certain ratio (which depends on the chemical species) \(r_{\text{chem}} > r_{\text{dyn}}\). There, molecular abundances “freeze,” and the LTE scenario disappears.

The LTE abundance of CO remains constant from the photosphere to \(~20R_\odot\). Thus, whether chemical kinetics is rapid (LTE is reproduced) or slow (“freezing” effect) the CO abundance will

| N | Reaction | \(A\) | \(n\) | \(C\) | \(T_1\) | \(T_2\) | \(T_{\text{range}}\) | Ref. |
|---|----------|------|------|------|------|------|----------------|-----|
| 1 | H + H + H₂ ⇌ H₂ + H₂ | 8.640E−33 | −0.60 | 0.60 | 50 | 5000 | ALL \_T | NIST |
| 2 | H + H + He ⇌ H₂ + He | 6.070E−33 | −0.13 | −39.00 | 77 | 2000 | ALL \_T | NIST |
| 3 | H + H + H ⇌ H₂ + H | 8.820E−33 | 0.00 | 0.00 | 50 | 5000 | ALL \_T | NIST |
| 4 | CH + He ⇌ C + H + He | 3.160E−10 | 0.00 | 33704.00 | 2500 | 3800 | LOW \_T | NIST |
| 5 | CH + H₂ ⇌ C + H + H₂ | 8.830E−10 | 0.00 | 33704.00 | 2500 | 3800 | LOW \_T | NIST |

Note.—Table 5 is also available in machine-readable form in the electronic edition of the Astrophysical Journal.

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TABLE 5

FIRST FIVE REACTIONS OF THE FULL CHEMICAL KINETICS MECHANISM

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Fig. 3.—Abundances, relative to total number of hydrogen nuclei, of some O-bearing molecules. (a), (b), and (c) Abundances given by LTE (dotted and dashed lines) and by chemical kinetics (solid lines) assuming a constant velocity expansion of 1 km s\(^{-1}\) and the density profiles (a) MH, (b) MI, and (c) ML. (d) Abundances of CO and H₂O for a CO, H₂, CH₄, and H₂O system with \(k_{r}\) (see text) equal to 10\(^{−15}\) and 10\(^{−16}\) cm\(^3\) s\(^{-1}\). (e) and (f) Abundances given by chemical kinetics with the density profile MH when we consider that 90% of SiO gas is deposited onto SiC grains and that the corresponding oxygen is released to the gas phase either as (e) atomic oxygen or as (f) CO₂. The nucleation rate of SiC grains \(J_\text{SiC}\), (with units of nuclei cm\(^{-3}\) s\(^{-1}\)) and its abundance \(x_{\text{SiC gr}}\), relative to total number of hydrogen nuclei, are also plotted as dotted lines. [See the electronic edition of the Journal for a color version of this figure.]
not be modified. The situation is different for SiO (see Figs. 3a, 3b, and 3c). Its LTE abundance at $n_0$ is $\sim 10^{-8}$, while at $\sim 3-5 R_\odot$, it increases to $\sim 10^{-3}$. For this abundance enhancement to occur as the gas expands, SiO must take the oxygen from CO via reaction (R7),

$$Si + CO \rightarrow SiO + C,$$

which has a low rate, and the above considerations about $\tau_{\text{chem}}$ and $\tau_{\text{dyn}}$ apply. Only high densities and/or low expansion velocities will make SiO reach this abundance of $\sim 10^{-3}$. For the three density models considered and the expansion velocity of 1 km s$^{-1}$ assumed, only the MH model makes SiO reach an abundance near its LTE value, whereas MI and ML lead to a non-LTE situation in which SiO abundance remains low. The abundance of atomic carbon has a great impact on SiO. In models MI and ML, this abundance remains well above its LTE value, while in MH it follows the decreasing LTE profile, being destroyed by reaction (R9),

$$C + H_2 \rightarrow CH + H.$$  \hspace{1cm} (R9)

The hydrogen freezing effect of models MI and ML causes the reverse of reaction (R9) to proceed at a higher rate that in a LTE situation, making carbon overabundant, which, through reaction (R8),

$$SiO + C \rightarrow Si + CO,$$  \hspace{1cm} (R8)

destroy SiO, making it underabundant with respect to a LTE situation. Again, a high-density scenario is required for explaining the SiO observational abundance of $8 \times 10^{-7}$ (estimated by Keady & Ridgway [1993] through IR rovibrational lines), which could be due either to this freezing effect or to depletion on SiC grains after reaching its LTE abundance of $\sim 10^{-5}$. Neither of the models run caused any other O-bearing molecule to have a significant abundance. In this high-temperature regime H$_2$O is related to SiO by two routes: (1) competition for OH via reactions (R10) and (R11),

$$OH + Si \rightarrow SiO + H,$$  \hspace{1cm} (R10)

$$OH + H_2 \rightarrow H_2O + H,$$  \hspace{1cm} (R11)

and (2) through CO$_2$, directly, via reactions (R12) + (R13),

$$SiO + CO \rightarrow CO_2 + Si,$$  \hspace{1cm} (R12)

$$CO_2 + H_2 \rightarrow H_2O + CO,$$  \hspace{1cm} (R13)

or involving OH that is converted into CO$_2$ via reaction (R14),

$$OH + CO \rightarrow CO_2 + H.$$  \hspace{1cm} (R14)

The following scheme shows these relations,

$$\begin{array}{cccccc}
& \text{SiO} & \text{R10} & \text{OH} & \text{R11} & \text{H}_2\text{O} \\
\downarrow \text{R12} & \downarrow \text{R14} & \text{R13} & \text{CO}_2 \\
& \text{CO}_2 & \\
\end{array}$$

where the connection between the species is produced by the reactions shown above and also by their reverse processes, so we have a reversible system. Nevertheless, these mechanisms are not efficient in producing H$_2$O from SiO. For H$_2$O to take the oxygen from CO, the chances are scarce, because when the LTE abundance of H$_2$O increases, the temperatures (<700 K) make the possible chemical routes for a CO $\rightarrow$ H$_2$O conversion too slow due to the large activation energy for breaking the CO bond. At this point we would like to know if we miss some important reactions, rapid enough for allowing this CO $\rightarrow$ H$_2$O transformation in the conditions of the inner envelope of IRC +10216. We consider an scenario given by model MH (high density in order to have a short $\tau_{\text{chem}}$) and the chemical reaction given by equation (9). This reaction can be decomposed in several elementary reactions, for example,

$$\begin{align*}
\text{CO} + H_2 & \rightarrow CH + OH (S), \\
\text{OH} + H_2 & \rightarrow H_2O + H, \\
\text{CH} + H_2 & \rightarrow CH_2 + H, \\
\text{CH}_2 + H_2 & \rightarrow \text{CH}_3 + H, \\
\text{CH}_3 + H_2 & \rightarrow \text{CH}_4 + H, \\
2(H + H_2 & \rightarrow H_2 + H_2), \\
\text{CO} + 3H_2 & \rightarrow \text{CH}_4 + H_2O (G). \\
\end{align*}$$

In any mechanism composed of elementary reactions, the rate of the global reaction (G) will be given by the rate of the slowest elementary reaction (S). In this case the slowest elementary step will be the break of the CO bond, since it has the largest activation barrier. The number of H$_2$O molecules produced or the number of CO molecules destroyed in the global reaction, per unit time and unit volume, is equal to the number of CO molecules destroyed in the slowest elementary reaction, per unit time and unit volume. We assign a rate constant $k_S$ for G, calculate the reverse rate constant via detailed balance, and run the model for a CO, H$_2$, CH$_4$, and H$_2$O system in which only G and its reverse operate. Then, we vary $k_G$ until some significant fraction of CO is transformed into H$_2$O and CH$_4$. Models for $k_G$ equal to $10^{-42}$ and $10^{-46}$ cm$^9$ s$^{-1}$ are shown in Figure 3d. One can see that above a threshold value of $\sim 10^{-44}$ cm$^9$ s$^{-1}$ for $k_G$, the CO $\rightarrow$ H$_2$O transformation is significant. The rate of destruction of CO molecules given by reaction G is $k_G x_{CO} n_4$ (where $x_{CO}$ is the CO abundance relative to H$_2$ and $n$ is the density of H$_2$), while the rate of destruction of CO molecules by reaction S is $k_S x_{CO} n^4$. Since both rates must be equal, we arrive at $k_S = k_G n^3$. Taking $10^{-44}$ for $k_S$ and a density of $10^{10}$ cm$^{-3}$ (roughly the value in the region 10–20 $R_\odot$, where the discussed process should take place) results in $k_S = 10^{-24}$ cm$^3$ s$^{-1}$. Therefore, we need a bimolecular reaction similar to reaction S with a rate constant greater than $10^{-24}$ cm$^3$ s$^{-1}$ for temperatures lower than ~700 K. There is no data in the literature about a rate constant for a reaction such as S. Nevertheless, we can estimate an upper limit for $k_S$ if we assume a maximum temperature-independent value of $10^{-9}$ cm$^3$ s$^{-1}$ for the reverse reaction and apply a detailed balance. This results in an activation energy of ~80,000 K for $k_S$, which implies a rate constant well below $10^{-24}$ cm$^3$ s$^{-1}$ for temperatures below ~700 K. So we do not expect a chemical route that is able to convert CO into H$_2$O in the inner envelope within the gas phase and during an adiabatic expansion.

4.1.2. Effects of SiO Depletion

Such a CO $\rightarrow$ H$_2$O process seems too slow, but there is another O-bearing molecule that locks some important amount of oxygen, SiO, which is expected to condense onto SiC grains. How could H$_2$O abundance be affected by SiO condensation during the expansion? When we consider such a process in our model, H$_2$O abundance remains low, because, as explained above, H$_2$O
is related to SiO in such a way that H$_2$O becomes abundant when SiO becomes abundant but not when SiO depletes. Then, we consider in model MH (in which SiO is formed with a significant abundance) a speculative process that can be summarized as follows. A SiO molecule condenses onto a SiC grain, and the Si atom incorporates into the grain lattice, while the oxygen atom is released to the gas phase,

$$\text{SiO}_{\text{gas}} + \text{grain} \rightarrow \text{grain} - \text{Si} + O_{\text{gas}}.$$  

We assume that 90% of the SiO formed in the gas phase is deposited onto SiC grains, and that all that oxygen, formerly contained in SiO, is released to the gas phase as atomic oxygen (see Fig. 3e). One can see that molecules like H$_2$O and CO$_2$ increase their abundances. H$_2$O takes efficiently the oxygen when it is in atomic form via reactions (R15) + (R11),

$$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}, \quad \text{(R15)}$$
$$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}, \quad \text{(R11)}$$

although some important fraction of the atomic oxygen returns to SiO from OH via reaction (R10),

$$\text{OH} + \text{Si} \rightarrow \text{SiO} + \text{H}, \quad \text{(R10)}$$

and through CO$_2$ via reactions (R14) + (R16),

$$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}, \quad \text{(R14)}$$
$$\text{CO}_2 + \text{Si} \rightarrow \text{SiO} + \text{CO}. \quad \text{(R16)}$$

It is known in materials science that oxidation of solid SiC through a flow of O$_2$ at temperatures of $\sim$1000 K produces solid SiO$_2$ and also CO and CO$_2$ molecules that diffuse through the lattice and are released to the gas phase (see Wang et al. 2001 and references therein). Therefore, some fraction of the oxygen entering solid SiC grains begin to build the SiO$_2$ lattice while the rest is released as CO and CO$_2$. In the region of the CSE where SiC grain formation occurs, the temperatures are similar to those described above, but the conditions are somewhat different, since it is an oxygen-deficient environment. Nevertheless, if SiO depletes on SiC grains, some fraction of the oxygen can be processed in the grain and released as CO and CO$_2$. We have run our model assuming that the oxygen of the SiO depleted on SiC grains is released to the gas phase as CO$_2$ instead of atomic oxygen. Both H$_2$O and SiO compete for the oxygen contained in the CO$_2$ molecules through reactions (R13) and (R16), respectively,

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}, \quad \text{(R13)}$$
$$\text{CO}_2 + \text{Si} \rightarrow \text{SiO} + \text{CO}. \quad \text{(R16)}$$

but the high activation energy of (R13) prevents water from reaching a high abundance.

4.1.3. Chemistry with Shocks

Now we consider the effect that shocks have on oxygen chemistry. In Figure 4 we plot the evolution of some abundances as the gas moves along the temperature and density profiles given by model MH (see Fig. 2), in order to compare with Willacy & Cherchneff (1998), who used high density values. We also plot the LTE abundances expected for the temperature and density profiles used, so we can see how the abundances predicted by chemical kinetics deviate from the LTE ones. Within the time interval associated with one shock plus relaxation, the immediately postshocked gas has dissociated a certain fraction of CO, releasing atomic oxygen, which has a large abundance during the first stages. This atomic oxygen is progressively returned to CO during the relaxation time, but also to OH, which has an appreciable abundance during these first stages. Reaction (R11) (OH + H$_2$ → H$_2$O + H), which forms water from OH, operates, but at these high temperatures the reverse reaction immediately destroys the H$_2$O formed, returning oxygen into OH and, some time later, into CO. Indeed, shocks are a very good mechanism for dissociating CO and releasing atomic oxygen. This CO → O process occurs preferably during the first shocks due to the high temperatures, which also make the kinetics of the O → H$_2$O process fast, but since water is not thermodynamically abundant at high temperatures in a C-rich gas (it is at low temperatures), other reactions are faster and return the atomic oxygen to CO.

SiO is strongly affected by the high nonequilibrium chemistry, driven by shocks, and ends this phase with a very low abundance, mainly due to reaction (R8), which was not included by Willacy & Cherchneff (1998). Note that either considering 5 or 15 shocks to reach $r_c$ from $r_0$, the abundances do not appreciably change. We show that this mechanism decreases rather than enhances oxygen chemistry.

Concerning the H/H$_2$ ratio, shocks favor a large value, since H$_2$ is dissociated in the postshocked gas (due to the high temperatures reached), and depending on the density, it can regenerate during the relaxation time via the three body reactions (R1),

![Fig. 4.](image-url)
(R2), and (R3) (with high densities; see Fig. 2d) or freeze its abundance at some moment during the relaxation (with low densities; see Figs. 2e and 2f). Again, with a shock mechanism, a high-density scenario is required to have hydrogen in molecular form.

In summary, O-bearing species are not produced efficiently by gas-phase chemistry in the inner envelope, neither by considering an expansion at constant velocity nor by assuming shocks. Nevertheless, the high water abundance obtained under the LTE assumption suggests that grains may be playing an important role in the recycling of oxygen from CO to H₂O.

4.2. Oxygen Chemistry in the Outer Envelope

The chemistry in the outer envelope is mainly driven by the photodissociation of molecules by the interstellar UV field followed by rapid neutral-neutral-reactions. This mechanism forms species such as polyynes and cyanopolyynes from photodissociation of parent species such as C₂H₂ and HCN (Millar & Herbst 1994). Concerning oxygen, the photodissociation of CO occurs at the very outer edge of the envelope due to self-shielding (much farther away than the photodissociation of C₂H₂ and HCN), so atomic oxygen is abundant only at large radii in the CSE, where the density has decreased considerably and reactions are very slow. This fact makes oxygen chemistry much poorer than carbon chemistry, since oxygen stays locked into CO along most of the envelope. The inclusion of the isotopologue \(^{13}\)CO, \(\sim 45\) times less abundant than parent CO (Cernicharo et al. 2000), which does not self-shield due to its lower abundance, can enhance oxygen abundance at shorter radii. This allows for the formation of some O-bearing species with moderate abundances through rapid neutral-neutral-reactions and radiative associations.

Ionic chemistry is triggered by cosmic-ray ionization. Cosmic rays can penetrate deeper than UV photons in the CSE, since they are not affected by opacity. Ions can react very rapidly via ion-molecule reactions, but the chemistry they can induce is limited by the low abundance of ions in the CSE except at the very outer edge (where, for example, all the carbon is converted into \(C^+\)). In our model, ionic chemistry does not noticeably affect the abundances of the O-bearing species formed except for SO, whose abundance is greatly enhanced, and for HCO⁺, produced with a low abundance but enough for being detected due to its large dipole moment (4.07 D). Another important effect of ionic chemistry is the fractionation of CO through the exchange reaction (R26),

\[
^{13}\text{C}^+ + ^{12}\text{CO} \rightarrow ^{12}\text{C}^+ + ^{13}\text{CO},
\]

which is known to be exothermic by 35 K. Below this temperature the reverse reaction does not operate, and \(^{12}\)CO is effectively transformed into \(^{13}\)CO. The net effect is a delay in the destruction of \(^{13}\)CO; its abundance remains nearly constant due to a steady state in which it is formed by the mentioned exchange reaction while it is destroyed by UV photodissociation.

The abundances predicted in the outer envelope for CO, \(^{13}\)CO, O, SiO, and HCO⁺ (usual O-bearing species in a C-rich star) are shown in the left column of Figure 5. The second column of panels show the abundances predicted for H₂O, OH, and H₂CO (the three “unexpected” oxygen species), while the rest of the panels to the right show the abundances for some other O-bearing species. The H₂CS abundance distribution is also shown together with those of C₂H and CN, peaking at \(\sim 15''\) and \(\sim 20''\), respectively (see Appendix B). We now describe individually the reactions that lead to their abundances, which are expressed relative to total number of hydrogen nuclei rather than relative to H₂.

1. SiO is formed in the inner envelope, and its abundance remains nearly constant throughout the outer envelope until it is dissociated by UV photons (R41). Ionic chemistry destroys SiO at a shorter radius by reacting with \(C^+\) via (R27),

\[
\text{SiO} + C^+ \rightarrow \text{Si}^+ + \text{CO}. \tag{R27}
\]

However, we point out that SiO could enter the outer envelope with a much lower abundance due to condensation on grain surfaces.

2. HCO⁺ is produced by the same sequence of reactions that forms it in dark clouds.

\[
\begin{align*}
\text{H}_2 + \text{cosmic ray} & \rightarrow \text{H}_2^+ + e^- \tag{R44} \\
\text{H}_2^+ + \text{H}_2 & \rightarrow \text{H}_3^+ + \text{H}_2 \tag{R28} \\
\text{H}_3^+ + \text{CO} & \rightarrow \text{HCO}^+ + \text{H}_2. \tag{R29}
\end{align*}
\]

First, \(\text{H}_2\) is ionized by cosmic rays (R44), then \(\text{H}_2^+\) reacts with \(\text{H}_2\), producing \(\text{H}_3^+\) (R28), which in turn reacts rapidly with CO through a proton transfer reaction (R29). The origin of \(\text{HCO}^+\) is different with respect to the rest of O-bearing species commented in this section, because its formation does not require the photodissociation of CO but the presence of \(\text{H}_2^+\), the formation of which is related to cosmic rays. The species \(\text{HCO}^+\) is abundant at shorter radii than the rest of the O-bearing species with a peak abundance of \(4.5 \times 10^{-10}\) at \(3 \times 10^{16}\) cm and a corresponding column density of \(1.1 \times 10^{12}\) cm⁻². The abundance profile sharply falls after its peak, mainly due to dissociative recombination (R38) (electron density becomes important beyond \(5 \times 10^{16}\) cm) and, to a less extent, due to proton transfer with HCN and C₂H₂ (reactions [R30] and [R31], respectively).

\[
\begin{align*}
\text{HCO}^+ + e^- & \rightarrow \text{CO} + \text{H} \tag{R38} \\
\text{HCO}^+ + \text{HCN} & \rightarrow \text{CO} + \text{HCNH}^+, \tag{R30} \\
\text{HCO}^+ + \text{C}_2\text{H}_2 & \rightarrow \text{CO} + \text{C}_2\text{H}_3^+. \tag{R31}
\end{align*}
\]

3. H₂O formation in C-rich environments, where atomic oxygen is available from the photodissociation of CO, is possible through the route of reaction (R15) followed by reaction (R11),

\[
\begin{align*}
\text{O} + \text{H}_2 & \rightarrow \text{OH} + \text{H} \tag{R15} \\
\text{OH} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H}. \tag{R11}
\end{align*}
\]

This is the mechanism that forms water in the C-rich protoplanetary nebula CRL 618 (see Cernicharo 2004), where temperatures in the inner, slowly expanding envelope are \(\sim 300\) K. However, in the outer envelope of IRC +10216, such high temperatures are not expected, and this route does not work, since both reactions (R15) and (R11) have activation energies that result in negligible rates. In our model water forms through the radiative association between atomic oxygen and molecular hydrogen (R45),

\[
\text{O} + \text{H}_2 \rightarrow \text{H}_2\text{O} + h\nu. \tag{R45}
\]

To our knowledge neither experimental nor theoretical studies have made an estimation of this rate. We have assumed a temperature-independent rate constant of \(10^{-18}\) cm³ s⁻¹, typical of radiative
associations between neutral species. Reaction (R45) implies breaking the H₂ bond so that atomic oxygen can be inserted, which will result on some activation energy. However, similar reactions, e.g., H₂ + C (Le Teuff et al. 2000) and H₂ + CH (Brownsword et al. 1997), take values 10⁻¹⁷–10⁻¹⁸ cm³ s⁻¹. Water is produced over an extended region from 4 × 10¹⁶ to 6 × 10¹⁷ cm with a peak abundance of 10⁻¹⁰ and a column density of 4 × 10¹¹ cm⁻². These values are far below the abundance estimated from the observations of the Submillimeter Wave Astronomy Satellite (SWAS) [(2–12) × 10⁻⁷; Melnick et al. 2001] or Odin (1.2 × 10⁻⁶; Hasegawa et al. 2006) by at least 3 orders of magnitude. We discuss in §4.3 if water originated in this way can or cannot explain the observations.

4. OH is produced from the photodissociation of water (R42) and from atomic oxygen through both the bimolecular reaction (R17),

\[ \text{O} + \text{NH}_2 \rightarrow \text{OH} + \text{NH}, \tag{R17} \]

and the radiative association between O and H (R36). As the gas expands reaction (R36) becomes slower due to the decrease in density, although it is compensated by the increase in atomic oxygen abundance. The result is an increase of OH abundance only at the very outer envelope, shown in Figure 5 as a peak at 6 × 10¹⁷ cm. In fact, the O-bearing molecules formed by radiative associations show an extended distribution (reactants such as atoms increase their abundances while expanding), whereas those formed by bimolecular reactions show a peak distribution (reactions only proceed in a shell where reactants are abundant before they are photodissociated). OH could also be produced in reactions of oxygen with several abundant hydrocarbons (e.g., C₄H₂, C₅H, HC₂N) through hydrogen abstraction. However, the reactions of atomic oxygen with closed-shell species such as C₂H₂, C₄H₂, and HCN have activation barriers whereas in reactions with radicals the hydrogen abstraction channel seems to proceed slowly. For example, the reaction O + CH → C + OH has been studied by Murrell & Rodriguez (1986), who estimated a negligible reaction rate at low temperatures, while the reaction of O with C₂H produces mainly CO and CH. OH is predicted to have a very extended distribution from 4 × 10¹⁰ to 10¹⁶ cm with a peak abundance of 7 × 10⁻¹⁰ at the very outer edge and a column density of 2 × 10¹¹ cm⁻². Ford et al. (2003) have derived an OH abundance of 4 × 10⁻⁸, assuming that all OH is produced from the photodissociation of H₂O, which is formed through comet evaporation in the inner envelope. The spatial distribution they obtain ranges from 3 × 10¹⁶ cm to 7 × 10¹⁶ cm. If OH follows the more extended radial distribution calculated by us, then the beam-filling factors and physical conditions of the emitting gas are very different from those assumed by Ford et al. (2003), and we would expect a considerable decrease of the OH estimated abundance.

5. H₂CO is produced through reaction (R18),

\[ \text{O} + \text{CH}_3 \rightarrow \text{H}_2\text{CO} + \text{H}, \tag{R18} \]

the source of CH₃ being the photodissociation of CH₄ (R43) while atomic oxygen is provided by CO and ¹³CO photodissociation.
The rate for (R18) is well known for a temperature range of 259–2500 K, in which it does not show a temperature dependence, suggesting a similar value at low temperatures. The peak abundance is $1.4 \times 10^{-9}$, reached at $4 \times 10^{10}$ cm. The abundance derived by Ford et al. (2004) from millimeter observations of pure rotational transitions is a factor of 5 higher than the one we get with the model. We discuss in § 4.3 the compatibility of the abundance predicted by our model with the lines observed.

6. SO can be formed from OH + S (R19) and from O + SH (R20),

\begin{align*}
    \text{OH} + \text{S} & \rightarrow \text{SO} + \text{H}, & \text{(R19)} \\
    \text{O} + \text{SH} & \rightarrow \text{SO} + \text{H}. & \text{(R20)}
\end{align*}

For (R19) we take the rate constant measured at 298 K. The rate of reaction (R20) has been measured at 298 K and at high temperatures (1100–2000 K) and does not show temperature dependence, so we assume the same value at low temperatures. In our model the abundance of OH is low in most of the CSE. On the other hand, SH abundance is relatively high due to a sequence of ion-molecule reactions that begin with the charge transfer of C$^+$ to SiS (R32). The SiS$^+$ formed this way reacts with hydrogen via reaction (R33) and produces SH,

\begin{align*}
    \text{SiS} + \text{C}^+ & \rightarrow \text{SiS}^+ + \text{C}, \quad \text{(R32)} \\
    \text{SiS}^+ + \text{H} & \rightarrow \text{SH} + \text{Si}^+. \quad \text{(R33)}
\end{align*}

The peak abundance predicted for SO is $1.1 \times 10^{-9}$ with a column density of $4.7 \times 10^{11}$ cm$^{-2}$. However, we point out that SO abundance is greatly influenced by hydrogen abundance, for which we have taken an upper limit given by Bowers & Knapp (1987). A process of H$_2$ formation on grains surfaces, not considered in this model, could reduce the abundance of atomic hydrogen, thus decreasing the amount of SO in the outer envelope.

7. OCS forms by radiative association of S and CO (R37). The predicted peak abundance is $6 \times 10^{-12}$ with a quite low column density of $7.4 \times 10^9$ cm$^{-2}$.

8. NO is formed by the bimolecular reaction (R21) involving atomic oxygen and NH, which in turn comes from photodissociation of NH$_3$,

\begin{align*}
    \text{O} + \text{NH} & \rightarrow \text{NO} + \text{H}. \quad \text{(R21)}
\end{align*}

The rate for this reaction is a temperature-independent estimation for the 250–3000 K range and is assumed to also apply at low temperatures. The predicted abundance is $2 \times 10^{-10}$ with a column density of $2 \times 10^{11}$ cm$^{-2}$, although its low dipole moment (0.159 D) makes its detection difficult.

9. NCO forms by reaction (R22), the rate of which is based on an experimental measurement at low pressure and 292 K and the assumption that formation of NCO is the main channel,

\begin{align*}
    \text{CN} + \text{OH} & \rightarrow \text{NCO} + \text{H}. \quad \text{(R22)}
\end{align*}

Its predicted abundance is $10^{-11}$. The relatively low dipole moment (0.6 D), the large partition function, and the low predicted abundance will make its detection very difficult.

10. H$_2$CS abundance is also shown in Figure 5. Although it is not an O-bearing species, it is formed through the sulfur-analogous reaction that forms H$_2$CO (R23),

\begin{align*}
    \text{S} + \text{CH}_3 & \rightarrow \text{H}_2\text{CS} + \text{H}. \quad \text{(R23)}
\end{align*}

The rate of this reaction has not been measured, and therefore, it is assumed equal to the oxygen-analogous case. Atomic sulfur is necessary, instead of oxygen, and it is provided by the photodissociation of SiS and CS. Ionic chemistry slightly enhances H$_2$CS abundance, since atomic S is released at short radii through ion-molecule reactions such as (R34),

\begin{align*}
    \text{SiS} + \text{S}^+ & \rightarrow \text{SiS}^+ + \text{S}, \quad \text{(R34)}
\end{align*}

and because more chemical routes for thioformaldehyde formation appear, e.g., from H$_2$CS$^+$, through dissociative recombination (R39),

\begin{align*}
    \text{H}_2\text{CS}^+ + e^- & \rightarrow \text{H}_2\text{CS} + \text{H}. \quad \text{(R39)}
\end{align*}

The peak abundance is $10^{-9}$ with a distribution similar to that of formaldehyde, and the resulting radial column density is $6.2 \times 10^{11}$ cm$^{-2}$. The predicted abundance profile produces line shapes in reasonable agreement with observations (see § 4.3.5).

11. CO$_2$ is formed through reaction (R35), which involves SiO$^+$, which is formed with an abundance of $\sim 10^{-11}$ from several ion-molecule reactions,

\begin{align*}
    \text{SiO}^+ + \text{CO} & \rightarrow \text{CO}_2 + \text{Si}^+. \quad \text{(R35)}
\end{align*}

We point out that CO$_2$ could be also a product of evaporation of cometary ices and will have a large abundance in the cometary scenario. However, an Infrared Space Observatory (ISO) spectrum of IRC +10216 in the mid-IR with a very large signal-to-noise ratio (Cernicharo et al. 1999) only shows C$_2$H$_2$ and HCN lines in the 13–16 $\mu$m range and no evidence for CO$_2$.

12. O$_2$ formation is strongly related to the presence of OH, from which it is formed through reaction (R24)

\begin{align*}
    \text{O} + \text{OH} & \rightarrow \text{O}_2 + \text{H}. \quad \text{(R24)}
\end{align*}

Its spatial distribution follows that of OH with an abundance 2 orders of magnitude smaller.

13. HCO is produced with quite a low abundance ($\sim 10^{-12}$), mainly from atomic oxygen, by reaction (R25),

\begin{align*}
    \text{O} + \text{CH}_2 & \rightarrow \text{HCO} + \text{H}. \quad \text{(R25)}
\end{align*}

Dissociative recombination of H$_2$CO$^+$ (R40) also contributes to HCO formation.

4.3. Comparison with Observations

In order to compare with available observations, we have performed Monte Carlo radiative transfer calculations for H$_2$CO, H$_2$O, HCO$^+$, SO, and H$_2$CS with the code described in González-Alfonso & Cernicharo (1993). The CSE has been simulated by a spherically distributed expanding gas with the radial profiles for density, temperature, and abundance of each species taken from the chemical model. Line profiles and intensities for several transitions are then generated after convolution of the radiative transfer results with the main beam of the selected telescope.

4.3.1. H$_2$CO

Ford et al. (2004) have observed four pure rotational lines of ortho-H$_2$CO: 2$_{1,2-1,1}$ (140.840 GHz), 2$_{1,1-1,0}$ (150.498 GHz),
31_2–21_1, 31_3–20_2 (211.211 GHz), and 31_2–21_1 (225.698 GHz) with antenna temperatures of ~30, ~20, ~20, and ~20 mK, respectively; observed one line of para-H_2CO, 30_3–20_2 (218.222 GHz) with T^* ~ 20 mK; and failed to detect the low-excitation transition of para-H_2CO 10_1–00_0 (72.838 GHz) at a sensitivity of ~10 mK. They also conducted 17'' offset observations for the 21_1–10_0 line with an average line intensity reduced by a factor of 3–4, which nevertheless indicates an extended H_2CO distribution. We have used the abundance profile obtained from our chemical model to predict the expected line intensities in order to see if the formaldehyde formed through these chemical routes can account for the observed lines. The collisional coefficients, needed for solving the statistical equilibrium, are taken from Green (1991; corrected for H_2 as the collider instead of He) and the normal ortho-to-para ratio of 3 : 1 has been assumed.

The resulting lines are less intense than those observed by a factor of 4–10, depending on the line. Nevertheless, one has to keep in mind that the abundances resulting from such a simple chemical model are affected by uncertainties due to missing reactions, uncertain rates, and also errors in physical parameters (kinetic temperature, mass-loss rate, etc.). Formaldehyde is formed from O and CH_3 by reaction (R18),

\[
O + CH_3 \rightarrow H_2CO + H, \quad (R18)
\]

so the abundances of the two reactants together with the rate of (R18) directly affect the abundance that H_2CO may reach. The rate constant for reaction (R18) is known down to 259 K, but not for the much lower temperatures that are present in the outer envelope of IRC +10216. We could expect a higher rate constant at very low temperatures, a behavior experimentally observed in many other radical-molecule reactions without activation energy (see Smith et al. 2004 and references therein). Another important parameter is the branching ratio for CH_3 production in methane photodissociation by the interstellar UV field, for which Le Teuff et al. (2000) give a value of 15%. For the solar UV field, values of up to 44% are commonly used (see the chemical model of Saturn’s atmosphere by Moses et al. [2000]). Although the energy distribution of the interstellar and solar UV field are somewhat different, we could expect larger uncertainties in the former.

Fig. 6.—Calculated line intensities and profiles for pure rotational transitions of ortho-H_2CO and para-H_2CO. The lines should be compared with the observations reported by Ford et al. (2004). The IRAM 30 m beam size has been considered and the lines have been smoothed to a resolution of 1 MHz. The H_2CO abundances, relative to total number of hydrogen nuclei, are plotted in the bottom right panel. Solid lines: H_2CO abundance resulting from the chemical model with two parameters slightly changed. The (R18) rate constant is increased by a factor of 3, and the CH_3-branching ratio in methane photodissociation is increased from 15% to 30%. Light dotted line: H_2CO produced from photodissociation of an unknown parent species, which would be released by sublimation of the mantles of comets, assumed to be present in the inner envelope; best model in Ford et al. (2004). Heavy dotted lines: H_2CO abundance resulting from the chemical model including reaction (R46) in order to increase formaldehyde abundance in the inner regions.
When we increase the (R18) rate constant by a factor of 3 and the CH3 branching ratio by a factor of 2, the resulting H2CO abundance (see Fig. 6, bottom right, solid line) increases by a factor of ~6 with respect to the former model (that of Fig. 5). A comparison of the spectral lines resulting from such abundance profile with the lines observed by Ford et al. (2004) give us several conclusions. (1) The line intensities agree quite well for the ortho-H2CO lines, whereas for the para-H2CO the agreement is worse; the 72.838 GHz line is predicted to be a factor of ~3 more intense than the observed upper limit, and the 218.222 GHz line is predicted to be a factor of 2–3 less intense than the observation. Uncertainties in the collisional coefficients, ortho-to-para ratio, or in the temperature and density profiles used could explain the discrepancies between model and observations. (2) The ratio of the integrated intensity between the 17th offset position and the centered position in the 150.498 GHz line is 0.87, in contrast with the value of 0.4 obtained from the observations. Sources for the disagreement could be errors in the pointing, the uncertainty in the distance to the star, or the depart from spherical symmetry in H2CO emission. (3) One last aspect to point out is the different shapes of the observed and predicted 1.3 mm lines of ortho-H2CO (at 211.211 and 225.698 GHz). The predicted lines have pronounced double-peak shapes with almost no emission at zero velocity, as corresponds to a shell with a certain size (diameter of ~400µm in the model) observed with a smaller telescope beam (~11″ for IRAM 30 m at those frequencies). On the other hand, the observed lines show substantial emission at zero velocity and a less pronounced double-peak profile. Neither an error of up to 4% in the pointing observations nor a larger distance to the star of up to 200 pc (more will make IRC +10216 to be overluminous for its type according to Crosas & Menten [1997]) will appreciably change the predicted line profiles.

Ford et al. (2004) interpret the presence of formaldehyde as a direct product from the photodissociation of an unknown parent molecule released in the inner envelope by cometary sublimation. Such an interpretation is supported by the observation of extended emission of formaldehyde toward the comet P/Halley (Meier et al. 1993). Ford et al. (2004) constructed a simple model with the following parameters: initial abundance of the parent species relative to H2 of 8 × 10⁻⁸, unattenuated photodissociation rate of the parent species producing H2CO of A_p = 1.6 × 10⁻¹⁰ s⁻¹, and unattenuated photodissociation rate of formaldehyde A_H2CO = 7.81 × 10⁻¹⁰ s⁻¹, which reproduced the observed line intensity of the 150.498 GHz line and the ratio (\int T_A d\Omega (T_A d\Omega) / (\int T_A d\Omega) of 0.4 for this line. We have run a model with the same parameters to obtain the abundance distribution and the expected line profiles (Fig. 6, light dotted lines). One can see that the abundance distribution is more extended than the previous distribution, although the 1.3 mm line profiles of ortho-H2CO still show an emission at zero velocity that is too low when compared with the observations. The abundance distribution of H2CO with a cometary origin is somewhat similar to the one we get with the chemical model, because in both cases formaldehyde is produced in the region where interstellar UV photons penetrate.

From the above considerations it follows that an increase of the formaldehyde abundance in the inner regions of the CSE is needed for producing some emission at zero velocity and matching the observations. Formation of H2CO in inner regions can be explained by hydrogenation of CO on grain surfaces followed by photodesorption (species such as CH4, NH3, and H2S are thought to be formed by similar processes). Since this possibility is very complex to model, we have investigated if some missing gas-phase reactions can enhance formaldehyde abundance at short radii. At this point it is worth noting that HCO+ has an abundance distribution peaking closer to the star than that of H2CO (see Fig. 5) and that produces double-peaked spectral lines but with substantial emission at zero velocity (see Fig. 8). As discussed for HCO+ formation, ionic chemistry is initiated by cosmic rays at shorter distances than photochemistry is, since the CSE is not opaque to cosmic rays. Formaldehyde can also be formed from H2CO (through charge transfer with several species) and H3CO+ (through dissociative recombination), but in our model these routes are not important, since both H2CO+ and H3CO+ are not abundant enough. Looking at exothermicity, we can examine possible missing reactions that can contribute to the formation of these two species (heats of formation have been taken from NIST Chemistry Web Book⁴ and Le Teuff et al. 2000). One possibility is the reaction H3+ + CO, for which the only exothermic channels are the well-known proton transfer, giving HCO+, and the radiative association, which produces H3CO+. Another possibility is the reaction HCO+ + H2, but all the investigated channels are highly endothermic due to the high stability of both reactants, and only the radiation association producing H3CO+ is exothermic by 123 kJ mol⁻¹. We find that including the reaction HCO+ + H2 → H2CO + hν with a rate constant of 5 × 10⁻¹⁵ cm³ s⁻¹ (R46), the formaldehyde abundance is enhanced at the inner regions, producing rotational lines in agreement with the observations, i.e., with significant emission at zero velocity (Fig. 6, heavy dotted lines). All the lines except the one at 218.222 GHz of para-H2CO (predicted to be a factor of 2 less intense than observed) agree very well with the observations in intensity and profile. The required rate constant is typical of other ion-neutral radiative associations (Le Teuff et al. 2000).

Finally, it is worth noting that three of the four unidentified lines in Ford et al. (2004) can be assigned as follows: U150 is the 71.17−61.16 transition of Si13CC at 150,385.281 MHz (Cernicharo et al. 1991, 2000), U218b is the N = 23−22 J = 45/2−43/2 transition of CC13CCH at 218,103.281 MHz (Cernicharo et al. 2000), and U218a is one component of the 2Π1/2 J = 45/2−43/2 transition in the ν3 = 1 vibrational state of C2H at 218,287.460 MHz (Guélin et al. 1987b; Yamamoto et al. 1987; Cernicharo et al. 2000).

4.3.2. H2O

The evidence for water presence in IRC +10216 comes from the detection of the ortho transition 1_1,0−1_0,1 at 556.936 GHz with the telescopes SWAS (T_A ~ 20 mK; Melnick et al. 2001) and Odin (T_A ~ 50 mK; Hasegawa et al. 2006). In order to model the radiative transfer of water throughout the CSE we consider the lowest lying 8 rotational levels in the vibrational ground state level (ν1, ν2, ν3 = (0, 0, 0), in the first excited bending mode (0, 1, 0), and in the first excited asymmetric stretching mode (0, 1, 1). The ortho-H2O−He collisional rates from Green (1993), corrected for H2 as collider, are adopted for all the transitions within the same vibrational level, whereas for rovibrational transitions, collisions are not considered important.

Excitation to the ν3 = 1 state occurs by absorption of λ ~ 6 µm photons, whereas excitation to the ν3 = 1 state corresponds to λ ~ 3 µm. Photons at these two wavelengths are abundant within the CSE due to the presence of the central star and dust, so these excited vibrational levels can be easily populated. Furthermore, since our chemical model predicts water to be abundant in the outer CSE, where densities range from 10⁵ to 10² cm⁻³ (n_e ~ 10⁶ cm⁻³ for the 556.936 GHz transition), collisional excitation is not effective to populate the 1_0 state, and the dominant excitation

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⁴ The NIST Chemistry Web Book is available on the World Wide Web at http://webbook.nist.gov/chemistry/.
mechanism is radiative pumping to the $\nu_2 = 1$ and $\nu_3 = 1$ vibrational excited states followed by radiative decay to several rotational levels of the vibrational ground state, including the $1_{1,0}$ state.

In our chemical model water is formed through the radiative association (R45),

$$O + H_2 \rightarrow H_2O + h\nu,$$

with an assumed rate constant of $10^{-18}$ cm$^3$ s$^{-1}$. As noted in §4.2 the abundance reached with such a rate constant is not enough to explain the observed 556.936 GHz line. Since the rate constant for this reaction is not known and water abundance approximately scales with this rate, we have fitted the (R45) rate to get a 556.936 GHz line intensity in agreement with the observations. We find that it is necessary to increase the rate constant up to $\sim 10^{-15}$ cm$^3$ s$^{-1}$. The peak abundance obtained then is $\sim 10^{-7}$ (as shown in Fig. 7, left). With such an abundance profile, we have performed Monte Carlo radiative transfer calculations. We show in the right panel of Figure 7 the lines predicted for Odin in different scenarios in which the fluxes at $\lambda = 3$ and 6 $\mu$m vary. On the left side of the right panel, the central star has been considered as a blackbody at $T = T_*$ with and without dust throughout the CSE. We consider carbonaceous grains with sizes between 0.01 and 1 $\mu$m and a gas-to-dust mass ratio of 500 (Knapp 1985). One can see that the presence of dust enhances the 556.936 GHz line intensity since grains absorb the photons from the star (its maximum is at $\lambda = 2$ $\mu$m) and reemits at longer wavelengths, thus enhancing the flux at $\lambda = 6$ $\mu$m and exciting the bending mode of H$_2$O. In fact, the IR spectrum of IRC +10216 as observed by ISO (Cernicharo et al. 1999) peaks at 10 $\mu$m due to the presence of dust and approximately corresponds to a blackbody of radius 20$R_*$, with a temperature of $\sim$500 K. We can therefore simulate the IR flux that water in the outer envelope would receive by putting such a blackbody instead of the star. On the right side of the right panel of Figure 7 we see how the 556.936 GHz line intensity increases when the flux at 6 $\mu$m is enhanced by considering a blackbody with increasing temperature. These radiative transfer models show the importance of the IR pumping of the excited vibrational levels of H$_2$O for the intensities of pure rotational lines in the ground vibrational state.

In summary, assuming a rate constant of $10^{-15}$ or a few $10^{-16}$ cm$^3$ s$^{-1}$ for (R45), we can reproduce the water line observed by Odin. Now the question is how reasonable is such a high rate constant for a radiative association between neutrals. This reaction is spin-forbidden according to Wigner-Witmer rules, since the potential energy surfaces (PESs) of reactants and products in their ground electronic states, H$_2$(1$^1S$) + O($^3P$) → H$_2$O(1$^3A$) + $h\nu$, are not connected adiabatically. For the reaction to proceed, an intersystem crossing between PESs with different total electronic spin must occur during the reaction. A spin-forbidden reaction is likely to have a small rate constant; however, some other reactions in which reactants and products do not adiabatically correlate have been found to be very rapid. For example, the bimolecular reaction C($^3P$) + C$_2$H$_2$(1$^1S$) → C$_3$(1$^3S$) + H$_2$(1$^1S$) may have a rate constant of several $10^{-10}$ cm$^3$ s$^{-1}$ at very low temperatures (Clary et al. 2002), while the radiative association HS$^+$(1$^3S$) + H$_2$(1$^1S$) → H$_2$S$^+$(1$^3A$) + $h\nu$ has a rate constant of $7 \times 10^{-16}$ cm$^3$ s$^{-1}$ at 80 K (Herbst et al. 1989).

A high rate constant for reaction (R45) would also have consequences for the chemistry in dark clouds. If $k_{R45} = 10^{-15}$ cm$^3$ s$^{-1}$, and with a typical density of $10^4$ cm$^{-3}$, the chemical timescale to produce water from atomic oxygen would be as short as $3 \times 10^3$ yr. Chemical models without this radiative association predict H$_2$O abundances somewhat higher than the observational upper limits imposed by SWAS (Roberts & Herbst 2002). Nevertheless, depletion on grains at late times would reduce the water vapor abundance so that models could match the observations. In diffuse clouds, with lower visual extinctions ($A_v \sim 1$) and densities ($n_H \sim 100$ cm$^{-3}$), reaction (R45) would also produce water in timescales of $3 \times 10^5$ yr, with an abundance relative to H$_2$ of $3 \times 10^{-7}$ in steady state. This value is 1–2 orders of magnitude higher than the scarce observational estimations available (Spaans et al. 1998; Neufeld et al. 2002). Nevertheless, in diffuse

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$^5$ The H$_2$O abundance reaches the steady state when the formation and destruction rates become equal. If we assume that reactions (R45) and (R42) are the main formation and destruction routes, then $n$(H$_2$O)/$n$(H$_2$) = $[k_{R45} n$(H$_2$)]/(G5.9 × 10$^{-10}$ exp(−1.7$A_v$)), where $x_O$ is the oxygen abundance relative to H$_2$ and G is the UV field relative to that of the interstellar standard field (see Appendix B). If we take $A_v = 1$, $G = 1$, $x_O = 6 \times 10^{-4}$, $k_{R45} = 10^{-15}$ cm$^3$ s$^{-1}$, and $n$(H$_2$) = $n$(H) = 100/2 cm$^{-3}$ (assuming hydrogen is mainly molecular), we get $n$(H$_2$O)/$n$(H$_2$) = $3 \times 10^{-7}$. 

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![Diagram](image-url)
clouds a significant fraction of hydrogen is not in molecular form; therefore, the rate of water formation through reaction (R45) would be lower than our estimation. Furthermore, since the observations of interstellar water ice bands do not discriminate between different types of clouds, dense or diffuse, present along the line of sight (e.g., Schutte et al. 1998; Moneti et al. 2001), it is highly uncertain whether the amount of water as solid ice is important or not.

There are other clues, apart from the 556.936 GHz line, that will help in understanding the water origin in this late-type C-rich star. (1) If water is formed in the outer envelope, it will have a spherical shell-like distribution, while Fischer-Tropsch and cometary hypotheses will produce a solid sphere-like distribution, since both require water to be formed much closer to the star. The Herschel Space Observatory will be able to distinguish between these two possibilities, since its beam size will be much narrower than those of SWAS and Odin. (2) The absence of pure rotational and rovibrational lines of water in the ISO far-IR spectrum analyzed by Cernicharo et al. (1996) discards the presence of a significant amount of water in the inner envelope. (3) As noted by Rodgers & Charnley (2002), the cometary origin implies the presence of HDO with an abundance $\sim 0.06\%$ relative to H$_2$O. HDO detection would demonstrate that water is not formed from material ejected by the star, and the cometary hypothesis would be the only one reasonable.

4.3.3. HCO$^+$

Its presence in IRC +10216 has been debated for years. Chemical models (Glassgold et al. 1986) predicted it with an abundance high enough to allow its detection with available millimeter or submillimeter telescopes. On the other hand, observations did not clearly probe its existence. The $J = 1–0$ line (with an intensity of $T_A = 20$ mK with the IRAM 30 m telescope; see Fig. 8) often has been observed as a weak feature at the noise level (Lucas & Guélin 1990). The $J = 4–3$ line was observed as a weak feature of $T_A \sim 25$ mK with the James Clerk Maxwell Telescope (JCMT) by Avery et al. (1994). However, they failed to detect the $J = 3–2$ line at a noise level of $\sim 10$ mK,
which was predicted with $T_d^* \sim 45$ mK on the basis of a rotational temperature of 17 K obtained from the intensities of the $J = 1-0$ and $J = 4-3$ lines. These considerations led these authors to conclude that the feature at the $J = 4-3$ frequency was not arising from HCO$^+$, and they calculated an upper limit for its column density of $1.4 \times 10^{11}$ cm$^{-2}$. Our Monte Carlo radiative transfer calculations show that the excitation temperatures of each line are significantly different, thus a prediction of the expected intensities of other lines with a unique $T_{\text{rot}}$ should be taken with care. To calculate the line profiles of HCO$^+$, we have decreased by a factor of 2 the abundance profile obtained with the chemical model in order to match the observed $J = 1-0$ line. HCO$^+$ is formed through the sequence of reactions R44 + R28 + R29, and therefore, its abundance basically depends on the rates of these reactions as well as on the destruction rates. The most uncertain of all them is the ionization by cosmic rays of H$_2$ (R44), which depends on the cosmic ray field in the surroundings of IRC +10216. The abundance of HCO$^+$ approximately scales with (R44) rate. Therefore, a decrease by a factor of 2 in the cosmic-ray field would explain the decrease in abundance needed to match the $J = 1-0$ observed line.

The predictions for the first four pure rotational transitions are shown in Figure 8. One can see that the excitation conditions are such that the $J = 3-2$ line is expected with a slightly higher intensity than the $J = 4-3$ line, both being $\sim 10$ mK in $T_d^*$ for the JCMT. This suggests that the 25 mK feature observed by Avery et al. (1994) at the frequency of $J = 4-3$ is indeed not arising from HCO$^+$, because the $J = 3-2$ was not detected above a 10 mK noise level. Future long time-integrated observations of these two lines will definitively establish the excitation conditions of HCO$^+$ in IRC +10216.

4.3.4. SO

The abundance reached by SO in the chemical model is enough to produce some lines with intensities of a few millikelvins. Figure 8 shows the $N_{J} = 2_1-1_2$ and $3_2-2_3$ expected line intensities together with a feature at 99.300 GHz of a spectrum, obtained with the IRAM 30 m telescope (J. Cernicharo et al. 2006, in preparation), which could correspond to the $2_1-1_2$ transition. A higher signal-to-noise ratio for this spectrum is needed to claim detection. Long time-integrated observations at the frequencies of other SO transitions (e.g., the $3_2-2_3$) would decide about the existence of SO in IRC +10216 formed through the ion-molecule chemical sequence of (R32) + (R33) followed by the neutral-neutral reaction (R20).

4.3.5. H$_2$CS

The chemical model predicts that this molecule is produced with a moderate abundance, both through neutral chemistry (from S + CH$_3$; [R23]) and through ionic chemistry (from H$_3$CSS$^-$; [R39]). The abundance reached is within the same order of magnitude than for H$_2$CO, but less intense rotational lines are expected due to its smaller dipole moment (1.649 vs. 2.331 D of formaldehyde). We have also assumed an ortho-to-para ratio of 3:1. Figure 8 shows the expected line profiles of ortho- and para-H$_2$CS, together with some features from a 3 mm spectrum taken with the IRAM 30 m telescope (J. Cernicharo et al. 2006, in preparation). The features have intensities somewhat higher than the predicted ones but with the right order of magnitude.

5. CONCLUSIONS

LTE chemical models predict that O-bearing species such as water are very abundant in the inner envelope of IRC +10216. However, a more realistic non-LTE approach, based on chemical kinetics, indicates that the transformation of CO into H$_2$O within the gas phase is not efficient in the inner layers, because of the high energies required to break the CO bond. On the other hand, the increase of SiO abundance with radius, predicted in LTE, is possible because the reaction Si + CO $\rightarrow$ SiO + C is competitive in a high-density scenario for the inner envelope. An alternative mechanism for water production out of the gas phase could be related to grain surfaces, which can act as a catalyst reducing the activation energy for either a CO $\rightarrow$ H$_2$O process (due to Fischer-Tropsch catalysis according to Willacy [2004]) or a SiO $\rightarrow$ H$_2$O process (on SiC grains).

Concerning oxygen chemistry in the outer envelope, the release of atomic oxygen due to CO photodissociation allows for the formation of some O-bearing species. The abundance predicted for H$_2$CO is a factor of $\sim$5 lower than the observational estimation of Ford et al. (2004). Whether formaldehyde is formed by the reaction O + CH$_3$ $\rightarrow$ H$_2$CO + H or it is produced from photodissociation of an unknown parent species released from comets, as suggested by Ford et al. (2004), the expected shape of the 1.3 mm rotational lines disagrees with the observations. An alternative source of H$_2$CO is suggested to be the radiative association HCO$^+$ + H $\rightarrow$ H$_2$CO$^+$ + hv. The possibility of forming water in the outer envelope depends on the rate constant of the radiative association between atomic oxygen and molecular hydrogen. Nonlocal radiative transfer models show that a rate constant as high as $10^{-13}$ cm$^3$ s$^{-1}$ is needed to reproduce the 556.936 GHz line profile observed by SWAS and Odin telescopes. Quantum chemical calculations of the rate constants of the two radiative associations suggested in this paper, especially the H$_2$ + O reaction, could support or discard them as important reactions in astrochemistry.

Other O-bearing species such as SO could exist with abundances and excitation conditions that would produce rotational lines near the detection limit of the IRAM 30 m telescope. HCO$^+$ is observed with an intensity roughly in agreement with that predicted from chemical and radiative transfer models. Thioformaldehyde formation is also predicted through a chemical route analogous to that of formaldehyde. This is supported by the agreement of the line profiles obtained from radiative transfer models with observations at 3 mm.

Although the evaporation of cometary ices could be the source of water in this late-stage carbon star, other phenomena such as catalysis on grains or the production in the outer envelope through the radiative association of H$_2$ + O could also explain the formation of this O-bearing species in the expanding carbon-rich envelope. Future observations with the Herschel Space Observatory will permit one to distinguish the most plausible chemical processes leading to the formation of water vapor in a carbon-rich environment.

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Here we describe the formation of SiC grains in the inner envelope of IRC +10216 as a two-step process: (1) the formation of condensation nuclei plus (2) the growth of grains from these nuclei by accretion of gas-phase species.

A1. FORMATION OF CONDENSATION NUCLEI

The mathematical description of the nucleation process is mainly taken from Gail et al. (1984). We assume that the expanding gas has at all moments a population of clusters (SiC)$_N$, composed of a different number $N$ of SiC monomers, which in thermal equilibrium is given by

$$n_{(SiC)_N} = n_{SiC} \exp \left[ - \frac{\Delta G(N)}{kT_{gr}} \right], \quad \text{(A1.1)}$$

where $n$ is the numerical density, $T_{gr}$ is the grain temperature, and $\Delta G(N)$ is the free energy of formation of a cluster of size $N$ from the monomers. The temperature of SiC grains $T_{gr}$ is not equal to the kinetic temperature of the gas $T_k$, because the former is affected by an inverse greenhouse effect that causes $T_{gr}$ to be less than $T_k$ (McCabe 1982). To calculate $T_{gr}$, we follow the treatment of this author. The magnitude $\Delta G(N)$ can be expressed as

$$\Delta G(N) = k \theta_N (T_{gr})(N - 1)^{2/3} - kT_{gr}(N - 1) \ln S,$$

where $S$ is the supersaturation ratio (ratio of the SiC vapor pressure to its saturation pressure) that is calculated following McCabe (1982), and the magnitude $\theta_N(T_{gr})$ (described in Draine 1979) is related to the surface tension of solid SiC for large $N$, while for small $N$ it is treated as a free parameter, since it is unknown.

Once we have established a population of clusters (SiC)$_N$, given by thermal equilibrium, nucleation theory says that there exists one critical size $N_c$. Clusters with sizes $N \geq N_c$ will continue accreting growth species (here, SiC molecules), resulting in grains of growing size, while clusters with sizes $N < N_c$ will revert to the monomers. Thus, there exists a bottleneck at $N_c$ in the size spectrum. The critical size $N_c$ is found by maximization of $\Delta G(N)$ with respect to $N$. The steady state rate $J^S_\alpha$ for the transformation “(SiC)$_N$ → nucleus” is given by

$$J^S_\alpha = \sum_{i=1}^{N_c} n_i \left( \frac{kT_k}{2\pi m_i} \right)^{1/2} \frac{\alpha_i}{A_{N_i}} \frac{4\pi a_0^2 N_e^{2/3}}{A_{N_i}} n_{(SiC)_N} Z,$$

where the subscript $i$ refers to the growth species, $n_i$ is the numerical density, $m_i$ is the mass, $\alpha_i$ is the sticking coefficient, and the sum of all contributions, $\beta$, has the meaning of a flux of particles. The subscript $\alpha$ refers to critical clusters; $A_{N_i}$ is the surface area, and $a_0$ is the radius of a monomer in the SiC lattice. The $Z$ term is the Zeldovich factor (see § 2 of Gail et al. 1984 for a detailed explanation).

Once $J^S_\alpha$ is computed for the conditions prevailing at each radius, the temporal evolution of the nucleation rate $J_\alpha$ is obtained from $J^S_\alpha$ by considering a time lag $\tau_\alpha$ (see Gail et al. 1984)

$$\frac{\partial}{\partial t} \left( \frac{J_\alpha}{\beta A_{N_i}} \right) = - \frac{1}{\tau_\alpha} \left( \frac{J_\alpha - J^S_\alpha}{\beta A_{N_i}} \right). \quad \text{(A1.4)}$$

A2. GROWTH OF GRAINS FROM NUCLEI BY ACCRETION

The growth of grains occur by addition of species that incorporate into the grain, resulting in a temporal evolution for the grain radius $a_{gr}$ of

$$\frac{\partial a_{gr}}{\partial t} = \sum_{i=1}^{N_i} \alpha_i \left( \frac{kT_k}{2\pi m_i} \right)^{1/2} \frac{4\pi a_0^2}{3N_i^{2/3}} n_i \frac{a_0}{3N_i^{2/3}}, \quad \text{(A2.1)}$$

where the sum extends to all gaseous species $i$ that produce growth of grains (here only SiC molecules are considered). The parameters $\alpha_i$ and $m_i$ have the same meaning as in equation (A1.3), $a_{0i}$ is the radius of the species $i$ in the lattice, and $N_i$ is the number of monomers of type $i$ forming part of a grain.

The unknown parameters, such as the sticking coefficients and the form of the function $\theta_N$ for low $N$, are chosen for obtaining an abundance and size of SiC grains in agreement with the literature: an abundance relative to H$_2$ of $\sim 10^{-14}$ and a radius of $\sim 0.1$ μm (Knapp 1985; Lorenz-Martins & Lefèvre 1993).
Fig. 9.—The $A_r$ radial profiles obtained from the plane-parallel to spherical correction ($A_{pp}$) and from the standard relation $A_r \propto N_0$ of Bohlin et al. (1978). The inserts show a two-dimensional scheme of plane-parallel and spherical geometries.

APPENDIX B

VISUAL EXTINCTION RADIAL PROFILE

The parameters $A_i$ and $C_i$ in equation (8) are usually given in the literature for plane-parallel geometry. Therefore, the evaluation of the photodissociation rate $\Gamma_i$ of a species $i$ through equation (8) is only valid for a species situated at point $P$ in a plane-parallel layer (see Fig. 9), where the visual extinction measured along the direction perpendicular to the infinite plane is $A_{pp}$. However, we want to know $\Gamma_i$ at the different points $r$ in spherical geometry. The strategy then is to find expressions for the UV field (4$\pi j_{UV}$) at points $P$ and $r$ in plane-parallel and spherical geometries, respectively. Setting both expressions equal, we determine the associated $A_{pp}$ that we insert in equation (8).

The UV field at point $P$ in a constant density plane-parallel layer is given by

$$4\pi j_{UV}(P) = 2\pi G_0 \int_0^\infty \sin \theta \exp[-\tau_{1000}(\theta)] d\theta,$$

$$\tau_{1000}(\theta) = \frac{\tau_{1000}}{\tau_{5500}} \frac{A_{pp}}{1.868 \cos \theta}, \quad (B1)$$

where $G_0$ is the wavelength-integrated specific intensity of the interstellar standard UV field (Draine 1978; i.e., in photons cm$^{-2}$ s$^{-1}$ sr$^{-1}$) and $\theta$ is the angle of the considered direction with respect to the normal to the surface. The UV opacity $\tau_{1000}$ has been expressed as a function of the visual extinction $A_{pp}$ through the ratio of UV-to-visible opacities ($\tau_{1000}/\tau_{5500}$), where the subscript stands for the mean wavelength in angstroms.

The UV field at point $r$ within a sphere with a $r^{-2}$ density law is

$$4\pi j_{UV}(r) = 2\pi G_0 \int_0^\pi \sin \theta \exp[-\tau_{1000}(r, \theta)] d\theta,$$

$$\tau_{1000}(r, \theta) = \frac{\tau_{1000}^*}{\sqrt{1 + \cos^2 \theta}} \left[ \frac{\pi}{2} - \arctan \left( \frac{-\cos \theta}{\sqrt{1 + \cos^2 \theta}} \right) \right], \quad (B2)$$

where it is necessary to define a boundary condition, e.g., the UV optical depth $\tau_{1000}^*$ at point $r^*$ along the radial direction.

We have assumed $\tau_{1000}(r = 10^{16}) = 12.7$ (Doty & Leung 1998), although the opacity at UV wavelengths is highly uncertain for IRC +10216, and a ($\tau_{1000}/\tau_{5500}$) ratio of 3.1 (as measured by Rouleau & Martin 1991) for amorphous carbon grains of 0.05 $\mu$m, although different values up to 8 can be found in the literature depending on grain nature and size. The radial profile $A_r(r)$ obtained is shown in Figure 9, where it is compared to the standard relation $A_r \propto N_0$ found for the interstellar medium by Bohlin et al. (1978).

In the chemical model the interstellar UV field $G$ has been decreased by a factor of 2 with respect to the standard $G_0$ to make the abundance distributions of C$2$H and CN (photodissociation products of C$_2$H$_2$ and HCN, respectively) peak at $\sim 15''$ and $\sim 20''$, respectively, in agreement with interferometric observations (Dayal & Bieging 1995; Guélin et al. 1999). For our assumed distance of the star (150 pc) C$2$H peaks at $3.4 \times 10^{16}$ cm, and CN peaks at $4.5 \times 10^{16}$ cm (see Fig. 5). We point out that this procedure is affected by a degeneracy between at least two parameters, the star distance, which transforms radial distances to angular distances, and the UV field and/or the $A_r$ radial profile, which make molecules photodissociate at a shorter or larger radial distance. Despite the uncertainties in the knowledge of these quantities and even if our assumption of a UV field less intense than standard is not correct, the abundances of the different molecules will be predicted at the right angular positions.

REFERENCES

Allende Prieto, C., Lambert, D. L., & Asplund, M. 2001, ApJ, 556, L63
Apponi, A. J., McCarthy, M. C., Gottlieb, C. A., & Thaddeus, P. 1999, ApJ, 516, L103
Avery, L. W., Bell, M. B., Cunningham, C. T., Feldman, P. A., Hayward, R. H., McLeod, J. M., Matthews, H. E., & Wade, J. D. 1994, ApJ, 426, 737
Bagnulo, S., Doyle, J. G., & Griffin, I. P. 1995, A&A, 301, 501
Bell, M. B., Avery, L. W., & Feldman, P. A. 1993, ApJ, 417, L37
Bell, M. B., Feldman, P. A., Kwok, S., & Matthews, H. E. 1982, Nature, 295, 389
Bohlin, R. C., Savage, B. D., & Drake, J. F. 1978, ApJ, 224, 132
Bowen, G. H. 1988, ApJ, 329, 299
Bowers, P. F., & Knapp, G. R. 1987, ApJ, 315, 305
