Astron. Astrophys. 324, 237–248 (1997)

ASTRONOMY
AND
ASTROPHYSICS

Chemistry in oxygen-rich circumstellar envelopes

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Received 9 December 1996 / Accepted 27 January 1997

Abstract. We have considered the chemistry occuring in the circumstellar envelope surrounding an oxygen-rich AGB star and have specifically modelled 4 sources; R Dor, TX Cam, OH231.8+4.2 and IK Tau. Methane has been assumed to be a parent molecule and the resulting carbon chemistry is investigated. We find that carbon chain molecules up to C_2H_4 can be abundant as can CH_3CN and CH_3OH. Our model extends previous work by including the chemistry of silicon, chlorine and phosphorus. The presence of CH_4 as a parent and hence its daughter species CH_3 and CH_3^+ leads to other carbon-bearing species such as H_2CS, $SiCH_2$, H_2CN and CCl.

Sulphur is an important source of electrons in some regions of the envelope. Its main effect is on the abundance of CH_3^+ and molecules formed from this radical e.g. CH_3OH.

Where possible we have compared our results to observations and in general there is good agreement. A notable exception is the case of OCS in OH231.8+4.2 whose calculated abundance is roughly 10^4 times lower than observed.

Key words: stars: abundances – stars: circumstellar matter – stars: late type

1. Introduction

LTE calculations of the chemistry of the circumstellar envelopes (CSEs) surrounding oxygen-rich late type stars show the carbon to be tied up in CO with the excess oxygen forming other molecules such as H_2O (Tsuji 1973). So the first observations of other carbon-bearing molecules in such sources were somewhat unexpected. Several carbon-bearing molecules have now been observed: HCN, HCO^+, CS, OCS, HNC, CN (Deguchi & Goldsmith 1985; Jewell, Snyder & Schenework 1986; Omont et al. 1986; Lindqvist et al. 1988, 1992; Nercessian et al. 1989; Olofsson et al. 1991; Bujarrabal, Fuente & Omont 1994). It has been suggested that such molecules arise from the breakdown of CH_4 which is assumed to be a parent molecule, formed in the inner envelope, possibly by grain surface reactions (Nejad & Millar 1988) or by UV/shock chemistry (Nercessian et al 1989). The presence of methane has also been used by Millar & Olofsson (1993) to account for observations of H_2CO in OH231.8+4.2 (Lindqvist et al. 1992). Charnley, Tielens & Kress (1995) have predicted that the inclusion of CH_4 in the chemistry will result in high abundances of CH_3OH, C_2H and C_2 with C_2H_4, C_2H_2 and CH_3CN also being present.

In this paper we extend the previous models to include the chemistry of silicon, phosphorus and chlorine. We investigate the effects of CH_4 on the carbon chemistry. We model four sources in detail and compare our results to the available observations.

2. The model

The model is based on that of Nejad & Millar (1988) and involves 200 species linked by 1909 reactions. The reaction rates are taken from the UMIST database RATE95 (Millar, Farquhar & Willacy 1996) with additional phosphorus reactions from Charnley & Millar (1994). Cosmic ray ionization processes are included. For those neutral species without a tabulated photodestruction rate, a rate of $1.1 \times 10^{-9} exp(-2A_V)$ is used. Because of its effective self-shielding, H_2 is assumed to remain unaffected by photodissociation over the region of the envelope which we consider. The photodissociation of CO is treated using the approximation of Morris & Jura (1983). The initial abundances of the parent species are given in Table 1.

The CSE is assumed to be spherically symmetric with an expansion velocity, v_e, and a constant mass loss rate, $\dot{M}$. We have modelled 4 sources, 3 of which are well observed, with different values of $\dot{M}$. The physical parameters are given in Table 2. There is some debate in the literature as to the exact values of these parameters. We have used the values given in Bujarrabal et al (1994) for IK Tau and TX Cam and in Omont et al (1993) for OH231.8+4.2. In each case the chemical abundances are calculated as a function of radius, beginning at an inner radius, r_0, of 2×10^{15} cm and continuing outwards until all the molecules have been destroyed by photodissociation. The radial number density of H_2 is given by

$$n(r) = \dot{M}/(4\pi r^2 v_e m) \quad (1)$$

where m is the mass of molecular hydrogen.

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Table 1. The fractional abundances (relative to H_2) taken for the parent species

Parent species	Fractional abundance	Parent species	Fractional abundance
H_2O	3.0 (-4)	CH_4	3.0 (-5)
SiS	3.5 (-6)	H_2S	1.27 (-5)
NH_3	1.0 (-5)	CO	4.0 (-4)
N_2	5.0 (-5)	SiO	3.15 (-5)
He	0.1	PH_3	3.0 (-8)
HCl	4.4 (-7)		

Table 2. The physical parameters used to model each source. The values are taken from (1) Omont et al 1993; (2) Bujarrabal et al (1994); (3) Lindqvist et al (1992)

Source	$\dot{M}$ ($M_\odot$ yr^{-1})	v_e (kms^{-1})	D (pc)
OH 231.8+4.2[1]	1.0 (-4)	30.0	1300
IK Tau[2]	4.5 (-6)	20.0	270
TX Cam[2]	3.0 (-6)	18.0	350
R Dor[3]	1.0 (-7)	6.0	230

The temperature is described by a power law

$$T(r) = T(r_0)\left(\frac{r_0}{r}\right)^{0.6} \quad (2)$$

where $T(r_0)$ is taken to be 100 K for those sources with $\dot{M} > 5 \times 10^{-6}\ M_\odot$ and 300 K otherwise (Millar & Olofsson 1993). This is an approximation to the temperature profile in the envelope. In the outermost parts the temperature will be higher than given by this equation since the influence of photoelectric heating by the external interstellar radiation field becomes important. However at this distance from the star the density is low and the chemistry is driven by the UV photons rather than by collisions. In addition the major chemical reactions have rates which are either independent of temperature or which depend on $T^{-0.5}$ so that the rate is only weakly dependent on the radius. Hence in the region of the CSE that we are considering the chemistry is relatively temperature independent and the exact nature of the power law is unimportant.

3. The chemistry of the circumstellar envelope

The envelope chemistry can roughly be divided into 3 zones: an inner region where the parent molecules begin to break down, a peak region where the daughter molecules reach their peak abundances and an outer region where the photons finally photodissociate all the molecules. The abundance distributions are illustrated by the case of TX Cam. The chemistry in the three zones does not vary with mass loss rate. Therefore the discussion which follows is valid for all 4 models. What does vary with $\dot{M}$ are the radii at which the various regions arise, with r increasing with $\dot{M}$.

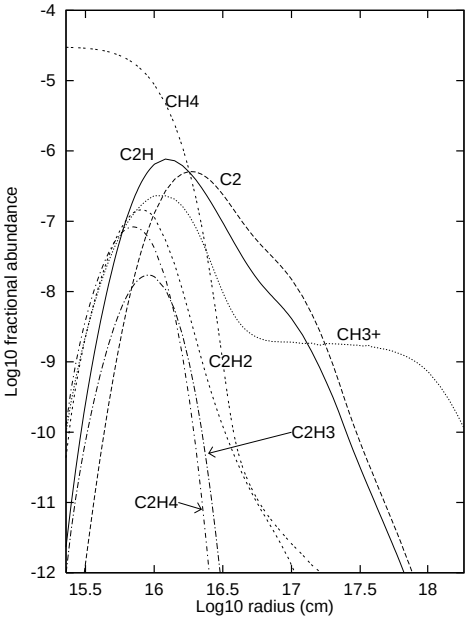


Fig. 1. The fractional abundance of the carbon-chain molecules as a function of radius for TX Cam.

3.1. Initiating the chemistry

At very small radii, ions as well as photons are important in driving the chemistry by breaking down the parent molecules. Cosmic rays produce H_3^+ by

$$H_2 \xrightarrow{cr} H_2^+ \xrightarrow{H_2} H_3^+ \quad (3)$$

Once this is present other ions can be formed e.g.

$$H_2O + H_3^+ \longrightarrow H_3O^+ + H_2 \quad (4)$$

$$CO + H_3^+ \longrightarrow HCO^+ + H_2 \quad (5)$$

The role played by these ions in the chemistry is discussed below.

3.2. Carbon chain chemistry

Carbon is contained in two parent molecules, CO and CH_4. Previous work (Nejad & Millar 1988) has shown that carbon is not released from CO in sufficient quantities to drive the carbon chemistry. So the presence of carbon chains in our model is due to the breakdown of CH_4.

The fractional abundance of the carbon chain molecules as a function of radius is shown in Fig. 1. It can be seen that, except in the outer region, the distributions of the chain molecules follow that of CH_3^+.

3.2.1. The inner region

The main destruction processes for CH_4 are photodissociation to CH_2 and reaction with H_3^+ forming CH_5^+. Some CH_4 is also broken down into CH_3 and CH_3^+ by

$$CH_4 + h\nu \longrightarrow CH_3 + H \quad (6)$$

$$CH_4 + He^+ \longrightarrow \begin{cases} CH_3 + H^+ + He \\ CH_3^+ + H + He \end{cases} \quad (7)$$

$$CH_4 \xrightarrow{He^+} CH_2^+ \xrightarrow{H_2} CH_3^+ \quad (8)$$

and

$$CH_4 + H^+ \longrightarrow CH_3^+ + H_2 \quad (9)$$

The reaction of CH_3^+ with H_2 is much slower than for the other CH_n^+ species. Hence it has the opportunity to react with other molecules, initiating a rich chemistry.

In the inner zone the chemistry is driven by

$$CH_4 + CH_3^+ \longrightarrow C_2H_5^+ + H_2 \quad (10)$$

$$C + CH_3^+ \longrightarrow C_2H^+ + H_2 \quad (11)$$

$$CH_4 + C^+ \longrightarrow \begin{cases} C_2H_2^+ + H_2 \\ C_2H_3^+ + H \end{cases} \quad (12)$$

These ions can then react with the most abundant neutral species, H_2O, NH_3 or H_2:

$$C_2H_5^+ + NH_3 \longrightarrow C_2H_4 + NH_4^+ \quad (13)$$

$$C_2H_5^+ + H_2O \longrightarrow C_2H_4 + H_3O^+ \quad (14)$$

and

$$C_2H_2^+ + H_2O \longrightarrow C_2H + H_3O^+ \quad (15)$$

$$C_2H_2^+ + H_2 \longrightarrow C_2H_4^+ + h\nu \quad (16)$$

Only those C_2H_n molecules with $n \leq 4$ are abundant. In these cases the ion chains build up by

$$C_2H_n^+ + H_2 \longrightarrow C_2H_{n+1}^+ + H \quad (n \leq 3) \quad (17)$$

and the ions are converted into neutrals by proton transfer reaction with the parent molecules NH_3 and H_2O.

The addition of H_2 to form $C_2H_n^+$ with $n > 4$ does not occur and C_2H_5 and C_2H_6 are formed by

$$C_2H_4^+ + SiH_4 \longrightarrow \begin{cases} C_2H_5 + SiH_3^+ \\ C_2H_6 + SiH_2^+ \end{cases} \quad (18)$$

Since SiH_4 has a very low abundance, these processes are inefficient and C_2H_5 and C_2H_6 are not present in the gas to any significant degree.

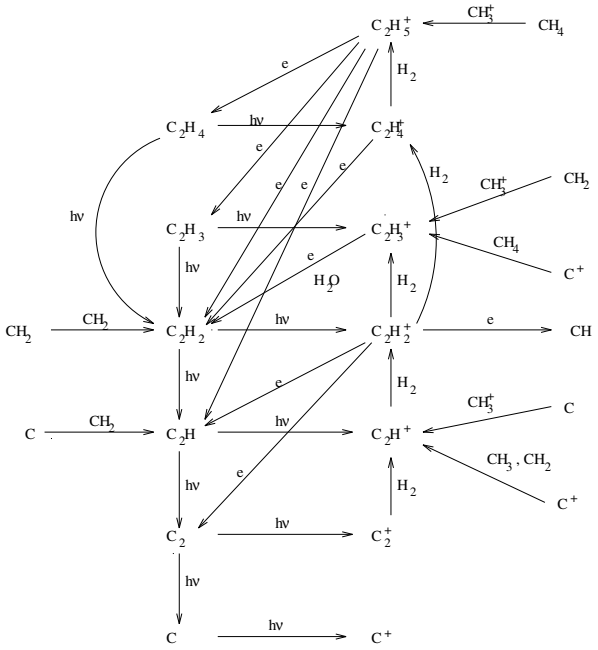


Fig. 2. The carbon chain chemistry in the peak region. Here destruction by photons rather than by reaction with ions is the major means of removing the neutral species.

3.2.2. The peak region

As the radius increases so does the importance of the photodestruction of the carbon chain neutrals, converting them into ions (see Fig. 2). The ions are now mainly destroyed by dissociative recombination with electrons e.g.

$$C_2H_5^+ + e \longrightarrow \begin{cases} C_2H_4 + H \\ C_2H_3 + H_2 \\ C_2H_2 + H_2 + H \\ C_2H + H_2 + H_2 \end{cases} \quad (19)$$

although reaction with H_2O is still important in the formation of C_2H_4 (from $C_2H_5^+$) and C_2H_2 (from $C_2H_3^+$).

There are still several routes into the chemistry from the reactions

$$CH_n + C^+ \longrightarrow \begin{cases} C_2H_{n-1}^+ + H \\ C_2H_{n-2}^+ + H_2 \end{cases} \quad (20)$$

for n = 0, 1...4 and from CH_3^+ reacting with CH_4 and CH_2 to form $C_2H_5^+$ and $C_2H_3^+$ respectively.

3.2.3. The outer region

The chemistry in this region is similar to that at the smaller radii except that photoreactions are now of increased importance. Molecules are destroyed and most of the carbon is in C^+. One change in the chemistry is that the reaction of C_2H with Si^+ followed by dissociative recombination

$$C_2H \xrightarrow{Si^+} SiC_2^+ \xrightarrow{e} C_2 \quad (21)$$

is now a major source of C_2, producing more of this molecule than the direct conversion from C_2H by photoprocessing.

3.3. Other carbon-bearing molecules

At small radii the parent molecules are generally destroyed by reactions with ions rather than by interactions with photons. One of these ions is HCO^+ which is formed by

$$CO + H_3^+ \longrightarrow HCO^+ + H_2 \quad (22)$$

The first carbon-oxygen bearing molecule to be formed is CO_2 from the reaction of OH and CO

$$OH + CO \longrightarrow CO_2 + H \quad (23)$$

Cosmic rays can also destroy CO producing CO^+.

Methanol is formed entirely from

$$H_2O \xrightarrow{CH_3^+} CH_3OH_2^+ \xrightarrow{e} CH_3OH \quad (24)$$

once again demonstrating the importance of the presence of CH_3^+ for the carbon chemistry. This ion also aids the formation of CH_2CO:

$$CO \xrightarrow{CH_3^+} CH_3CO^+ \xrightarrow{e} CH_2CO \quad (25)$$

H_2CO on the other hand is formed from neutral-neutral reactions

$$\left.\begin{array}{l} OH + CH_2 \\ O + CH_3 \end{array}\right\} \longrightarrow H_2CO + H \quad (26)$$

Fig. 3 shows the abundances of various carbon-bearing species.

3.4. Nitrogen chemistry

3.4.1. The inner region

At this low value of the radius photodestruction of the strongly bound parent N_2 is not important. Instead it is destroyed by:

$$N_2 + He^+ \longrightarrow N + N^+ + He \quad (27)$$

N^+ reacts with H_2 to form the nitrogen hydride ions

$$N^+ \xrightarrow{H_2} NH^+ \xrightarrow{H_2} NH_2^+ \xrightarrow{H_2} NH_3^+ \xrightarrow{H_2} NH_4^+ \quad (28)$$

while the nitrogen atoms react with OH forming NO.

The first daughter species to appear is NH_2. It is formed from the breakdown of NH_3 which occurs mainly by reaction with ions:

$$NH_3 \xrightarrow{H_3^+, H_3S^+} NH_4^+ \xrightarrow{e} NH_2 \quad (29)$$

There is also a small ($\sim 10\%$) contribution from the direct photodissociation of NH_3

$$NH_3 + h\nu \longrightarrow NH_2 + H \quad (30)$$

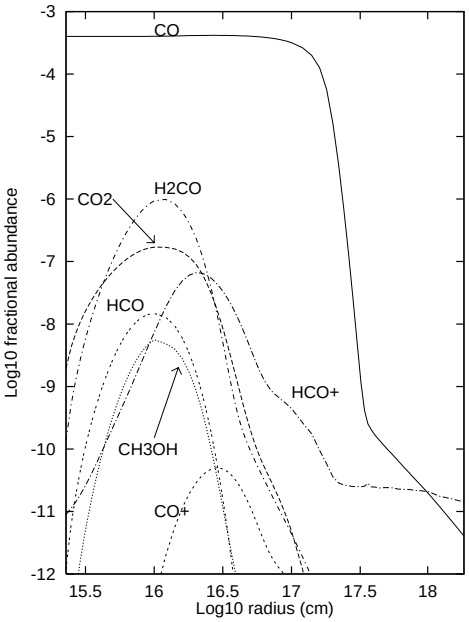


Fig. 3. The radial distribution of carbon- and oxygen-bearing molecules in TX Cam.

The formation of HCN and related compounds depends on the reactions of NH_3 as shown in Fig. 5. The C^+ ion is important in destroying NH_3 and hence in the formation of HNC and CN. At all points in the envelope CH_3CN is formed by

$$HCN \xrightarrow{CH_3^+} CH_3CNH^+ \xrightarrow{e} CH_3CN \quad (31)$$

and destroyed by photons.

3.4.2. The peak region

Moving out from the star the gas density is reduced and the interstellar radiation field is able to penetrate leading to an increased importance of photoreactions. The main destruction process for N_2 is now photodissociation resulting in two nitrogen atoms. A small amount of N_2 is still converted into N^+ by reaction with He^+ and continues to contribute to the formation of NH_n^+ (reaction 28). The formation route of HCN has however changed (Fig. 6).

HCN and CN are now produced by neutral-neutral reactions, with HNC mainly formed by ion-molecule reactions. HCN is formed directly from the reaction of NO with CH or from

$$N \xrightarrow{CH_3} H_2CN \xrightarrow{h\nu} HCN \quad (32)$$

It is rapidly dissociated into CN and then into its constituent atoms. NO, the most abundant nitrogen-bearing molecule in this region, is also involved in the formation of CN by its reaction with carbon atoms. Another route to CN is via the reaction of carbon atoms with NH. HNC on the other hand is a result of either

$$NH_3 \xrightarrow{C^+} H_2NC^+ \xrightarrow{e} HNC \quad (33)$$

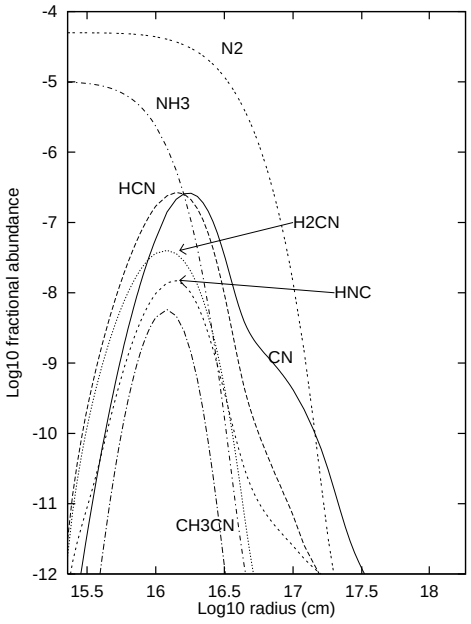


Fig. 4. The radial distributions of some nitrogen-bearing molecules in TX Cam.

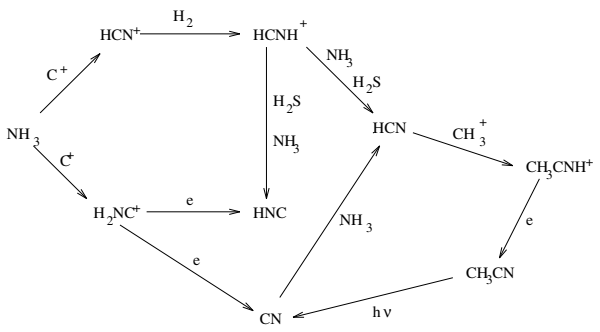


Fig. 5. The main reactions forming carbon-nitrogen compounds in the inner region.

or

$$\mathrm{NH} \xrightarrow{\mathrm{CH_3^+}} \mathrm{HNCH^+} \xrightarrow{\mathrm{e}} \mathrm{HNC} \quad (34)$$

The recombination of $HCNH^+$ with electrons can also result in HCN and CN but for these molecules the other formation routes mentioned above are more efficient. About 30% of the HNC is formed by the neutral-neutral reaction between carbon atoms and NH_2.

3.4.3. The outer region

Fig. 7 shows the nitrogen-carbon chemistry at large radii.

The abundance of ammonia is now too low to play a part in the chemistry but its daughter species N and NH are important. HCN is now produced by the reaction of nitrogen atoms with either CH_2 or $SiCH_2^+$. The dominant route to HNC is through H_2NC^+, with only a small ($\sim 6\%$) contribution from $HCNH^+$.

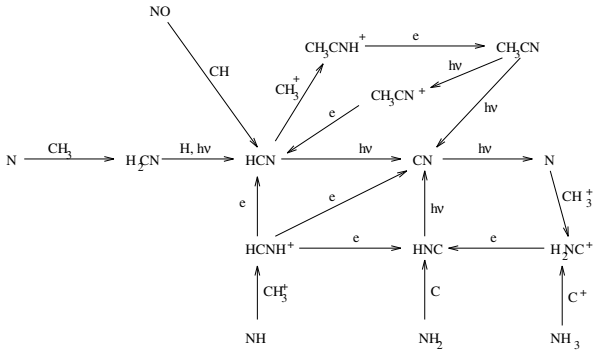


Fig. 6. The nitrogen chemistry in the peak region. The reactions of nitrogen atoms are now more important than those of NH_3 in forming nitrogen-carbon compounds.

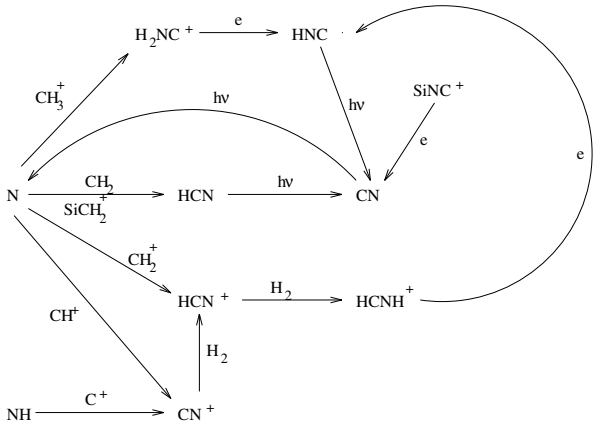


Fig. 7. The nitrogen-carbon chemistry in the outer region. At this point there is net destruction of the molecules due to the photon field.

Overall the molecules are destroyed by the photon field and abundances are very low.

3.5. Silicon chemistry

The parent molecules for silicon are SiS and SiO. The radial distributions of some important molecules are shown in Fig. 8. SiO_2 is the most abundant of the silicon bearing molecules formed in our model which also predicts high abundances of $SiCH_2$, HCSi, SiC and SiN.

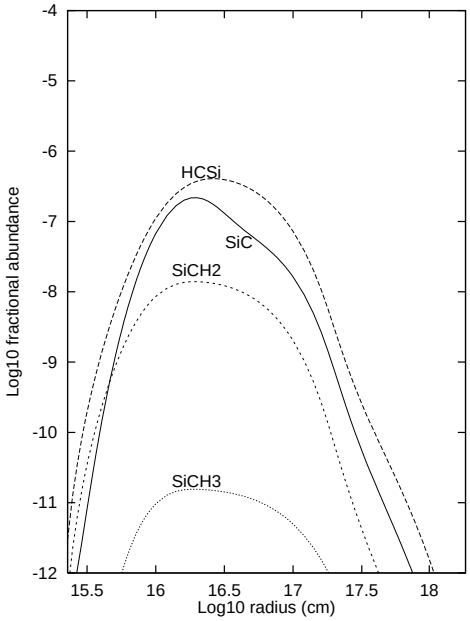
3.5.1. Initiating the chemistry

The parent molecules are not destroyed by photons at small radii. Instead reactions with ions are important:

$$\mathrm{SiS} \xrightarrow{\mathrm{H_3^+}} \mathrm{HSiS^+} \xrightarrow{\mathrm{e}} \mathrm{Si} \quad (35)$$

$$\mathrm{SiS} \xrightarrow{\mathrm{HCO^+}} \mathrm{HSiS^+} \xrightarrow{\mathrm{e}} \mathrm{Si} \quad (36)$$

$$\mathrm{SiO} \xrightarrow{\mathrm{H_3O^+}} \mathrm{SiOH^+} \xrightarrow{\mathrm{e}} \mathrm{Si} \quad (37)$$



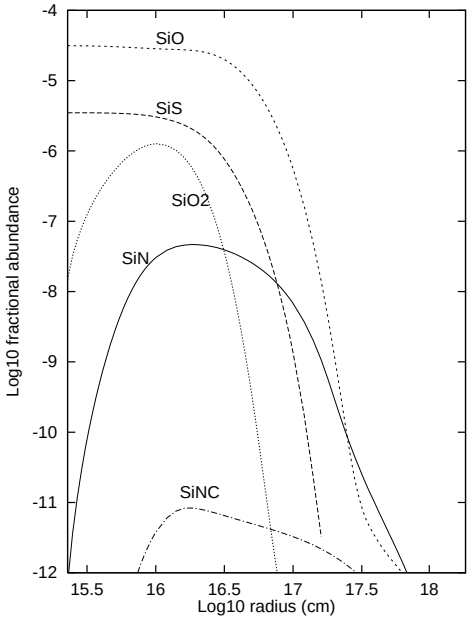


Fig. 8. The radial distributions of some important silicon-bearing molecules in TX Cam.

Initially silicon ions are formed by the reactions of SiS or SiO with He^+ and C^+ but as the radius increases photodissociation becomes more important:

$$\left.\begin{matrix}\mathrm{SiO}\\ \mathrm{SiS}\end{matrix}\right\} \xrightarrow{h\nu} \mathrm{Si} \xrightarrow{h\nu} \mathrm{Si^+} \tag{38}$$

Once the silicon atoms and ions are present other silicon-bearing molecules can be formed.

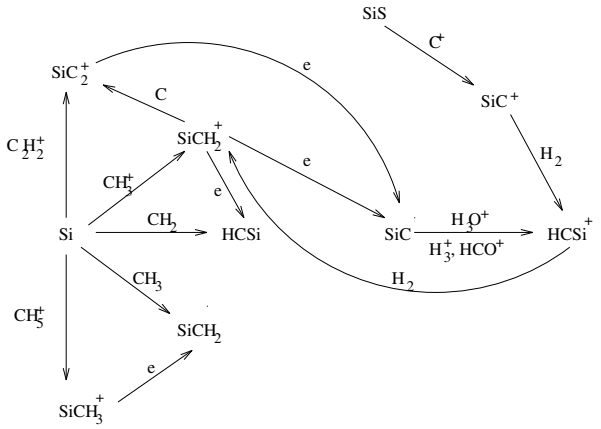


Fig. 9. The silicon and carbon chemistry in the inner region.

3.5.2. Silicon-carbon compounds

The main processes involving silicon and carbon molecules in the inner region are shown in Fig. 9.

HCSi and SiC are the silicon-carbon bearing molecules with the highest abundances. Both form from the dissociative recombination of $SiCH_2^+$ which can only be produced if CH_4 is present as a parent:

$$\mathrm{Si + CH_3^+ \longrightarrow SiCH_2^+ + H} \tag{39}$$

$$\mathrm{SiCH_2^+ + e \longrightarrow} \begin{cases}\mathrm{SiC + H_2}\\ \mathrm{HCSi + H}\end{cases} \tag{40}$$

HCSi is also formed directly from

$$\mathrm{Si + CH_2 \longrightarrow HCSi + H} \tag{41}$$

Larger silicon-carbon molecules can also form in appreciable quantities e.g.

$$\mathrm{Si + CH_3 \longrightarrow SiCH_2 + H} \tag{42}$$

$$\mathrm{Si + CH_5^+ \longrightarrow} \begin{cases}\mathrm{SiCH_3^+} \xrightarrow{\mathrm{H_2O,e}} \mathrm{SiCH_2}\\ \mathrm{SiCH_4^+} \xrightarrow{\mathrm{e}} \mathrm{SiCH_3}\end{cases} \tag{43}$$

As the radius increases, the chemistry is driven more by reactions of Si^+ than by reactions of Si. Si^+ can react with CH_n:

$$\mathrm{Si^+ + CH \longrightarrow SiC^+ + H} \tag{44}$$

(which is now the main route to SiC^+ with virtually no contribution from the SiS + C^+ reaction which dominates at small radii),

$$\mathrm{Si^+ + CH_2 \longrightarrow HCSi^+ + H} \tag{45}$$

$$\mathrm{Si^+ + CH_3 \longrightarrow HCSi^+ + H_2} \tag{46}$$

$$\mathrm{Si^+ + CH_3 \longrightarrow SiCH_2^+ + H} \tag{47}$$

In the outer layers of the CSE, SiC is mainly formed by the SiC_2^+ route (see Fig. 9). Its conversion into SiC^+ is achieved by reaction with C^+ which is now the dominant ion.

3.5.3. Other silicon compounds

Si^+ reacts with NH_3 to form $SiNH_3^+$. From this, dissociative recombination produces SiN and HNSi while reaction with carbon atoms results in SiNCH. At small radii HNSi is mainly destroyed by

$$HNSi + He^+ \longrightarrow SiN^+ + H + He \quad (48)$$

but as the radius increases and the abundance of C^+ rises

$$HNSi \xrightarrow{C^+} SiNC^+ \xrightarrow{e} Si + CN \quad (49)$$

becomes more important.

SiN is destroyed by reaction with oxygen atoms in the peak region forming SiO. Again reaction with C^+ becomes significant at larger radii producing SiC^+ or SiN^+.

SiO_2 is formed at all radii by

$$SiO + OH \longrightarrow SiO_2 + H \quad (50)$$

and destroyed mainly by photodissociation.

Of the silicon hydrides only SiH is abundant. In the inner region it is formed by one of three routes:

$$Si^+ \xrightarrow{H_2} SiH_2^+ \xrightarrow{e} SiH \quad (51)$$

$$Si \xrightarrow{H_3O^+} SiH^+ \xrightarrow{H_2} SiH_3^+ \xrightarrow{e} SiH \quad (52)$$

or

$$SiCH_2^+ + O \longrightarrow SiH + HCO^+ \quad (53)$$

As the radius increases reaction 53 becomes the only important route until the abundance of $SiCH_2^+$ drops after which, in the outer region, reaction 51 is the major formation process. Destruction is by photodissociation into Si and H.

3.6. Sulphur chemistry

Several sulphur-bearing molecules have high fractional abundances as can be seen in Fig. 10. Initially sulphur is contained in SiS and H_2S. The first molecules to appear are HS and CS. HS arises from the breakdown of the parent molecules by reaction with ions e.g.

$$H_2S \xrightarrow{H_3O^+} H_3S^+ \xrightarrow{e} HS \quad (54)$$

or by photodissociation

$$H_2S + h\nu \longrightarrow \begin{cases} HS + H \\ S + H_2 \end{cases} \quad (55)$$

HS is also a product of reaction 36.

Both S and S^+ are unreactive with H_2 but they can react with other molecules, e.g. with OH to form SO. However in this region the major route to SO is by the reaction of HS with oxygen atoms.

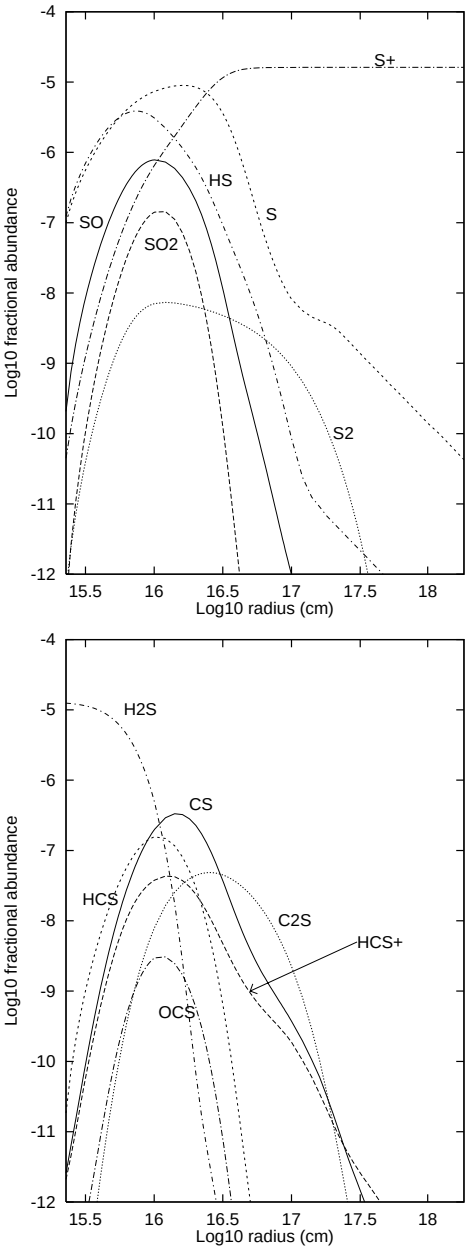


Fig. 10. The abundances of important sulphur-bearing molecules in the circumstellar envelope of TX Cam.

The carbon sulphides are formed by

$$H_2S \xrightarrow{C^+} HCS^+ \xrightarrow{NH_3,e} CS \quad (56)$$

and

$$S^+ \xrightarrow{C_2H_2} HC_2S^+ \xrightarrow{e} C_2S \quad (57)$$

while HCS arises either from the dissociative recombination of HC_2S^+ or from the reaction of S with CH_2.

The main chemical pathways involving sulphur and oxygen are shown in Fig. 11.

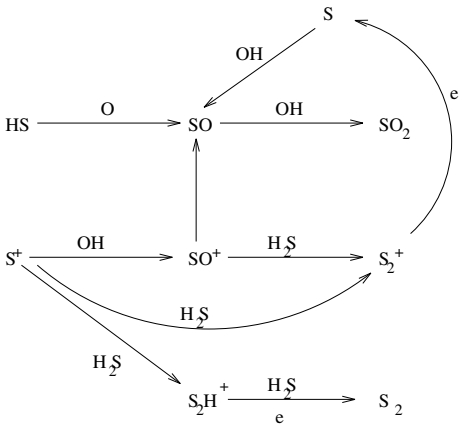


Fig. 11. The sulphur and oxygen chemistry in the inner region.

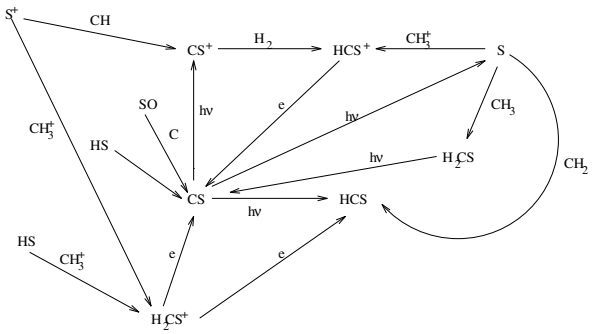


Fig. 12. The sulphur and carbon chemistry in the peak region.

3.6.1. The peak region

As the abundance of sulphur atoms rises so does the importance of the S + OH route to SO and in this region of the CSE it is the main formation process of this molecule. In addition, there is now a sizeable contribution from the photodissociation of SO_2. SO is itself photodissociated into its constituent atoms, either directly or via SO^+.

H_2S is now longer the most abundant sulphur species and its importance is diminished with the chemistry now being driven by S, S^+ and HS (see Fig. 11). HCS^+ is formed by the two stage process

$$S^+ \xrightarrow{CH} CS^+ \xrightarrow{H_2} HCS^+ \quad (58)$$

The recombination of HCS^+ with electrons is still the most efficient way of forming CS but, in addition, the reactions of SO and HS with carbon atoms are now important.

$$SO + C \longrightarrow CS + O \quad (59)$$

$$HS + C \longrightarrow CS + H \quad (60)$$

3.6.2. Other sulphur-bearing molecules

OCS has been observed in one source, OH231.8+4.2. It is produced by

$$SO \xrightarrow{CH_3^+} HOCS^+ \xrightarrow{e} OCS \quad (61)$$

with

$$HCS + O \longrightarrow OCS + H \quad (62)$$

also being an important mechanism. Where CH_3^+ is not abundant OCS arises from the radiative association of CO and S.

At all radii NS can be produced by

$$N + HS \longrightarrow NS + H \quad (63)$$

At the abundance peak there is a second formation process

$$S + NH \longrightarrow NS + H \quad (64)$$

It is destroyed by oxygen atoms forming NO, with reactions with C^+ (leading to NS^+ and CS^+) and photodissociation (into its constituent atoms) becoming more important as the radius increases.

S_2 is quite abundant in the outer layers of the CSE where it is produced by

$$H_2S \xrightarrow{S^+} S_2H^+ \xrightarrow{e} S_2 \quad (65)$$

Near the radius corresponding to its peak abundance it is partly destroyed by reaction with oxygen atoms forming SO. Moving further out photon reactions become the major source of destruction.

H_2CS is another molecule whose distribution depends on the presence of CH_4 as a parent molecule. Near its peak it is produced by

$$S + CH_3 \longrightarrow H_2CS + H \quad (66)$$

At very small or very large radii it arises from

$$SiCH_2^+ + S \longrightarrow H_2CS + Si^+ \quad (67)$$

It is destroyed by photoreactions producing CS and H_2.

3.6.3. The effect of the sulphur chemistry on other molecules

Sulphur can be an important source of electrons, thereby increasing the influence of ion-molecule reactions on the chemistry. We have run our models for two sources, R Dor and OH231.8+4.2 excluding sulphur. The effect of this on the abundance of the carbon-bearing molecules is shown in Table 3.

The removal of sulphur from the model causes an increase in the peak abundance of CH_3^+ of about 60%. This causes a corresponding increase in the abundances of those carbon bearing molecules which depend on the presence of CH_3^+ for their existence e.g. C_2H_4. The effect is most marked in the higher mass loss rate model. CH_3 is not affected by the presence of sulphur and its abundance and that of molecules such as H_2CN remains

Table 3. The peak fractional abundances of selected molecules for the models of R Dor and OH231.8+4.2. Two values are given for each model, where the sulphur chemistry has been included or excluded.

Species	R Dor		OH231.8+4.2	
	with S	without S	with S	without S
CH_3^+	3.1 (-7)	5.0 (-7)	8.2 (-8)	1.3 (-7)
CH_3	2.2 (-6)	2.2 (-6)	2.0 (-6)	2.2 (-6)
C_2	4.2 (-7)	5.9 (-7)	2.0 (-7)	2.8 (-7)
C_2H	6.2 (-7)	8.2 (-7)	2.0 (-7)	3.0 (-7)
C_2H_2	1.0 (-7)	1.2 (-7)	3.2 (-8)	4.4 (-8)
C_2H_3	1.8 (-8)	2.3 (-8)	8.6 (-9)	1.1 (-8)
C_2H_4	3.8 (-8)	5.8 (-8)	3.5 (-8)	4.9 (-8)
CH_3OH	1.2 (-8)	1.6 (-8)	3.5 (-8)	5.1 (-8)
H_2CO	9.3 (-7)	9.5 (-7)	5.0 (-7)	5.1 (-7)
C_2H^+	1.1 (-11)	1.7 (-11)	3.6 (-12)	5.6 (-12)
$C_2H_5^+$	4.0 (-9)	6.8 (-9)	1.4 (-9)	2.5 (-9)
H_2CN	4.8 (-8)	5.0 (-8)	2.2 (-8)	2.3 (-8)
CH_3CN	5.0 (-9)	8.3 (-9)	1.4 (-9)	2.4 (-9)
$SiCH_2$	9.5 (-9)	8.8 (-9)	7.0 (-9)	6.4 (-9)
$SiCH_2^+$	9.9 (-9)	1.4 (-8)	4.1 (-9)	5.4 (-9)
$HCSi^+$	1.4 (-11)	9.3 (-12)	5.2 (-12)	3.4 (-12)
CCl	9.8 (-9)	1.5 (-8)	4.2 (-9)	6.3 (-9)

the same. The smaller carbon chain molecules (C_2H_n where n = 0, 1, 2) are also relatively unaffected by the presence of sulphur. They have alternative formation processes which do not depend on CH_3^+ and these become more important in the presence of sulphur.

3.7. Chlorine chemistry

The formation of ClO is inhibited by the presence of high activation energy barriers and we have therefore assumed it is not present in the gas. Instead we have considered the parent molecule to be HCl.

The chlorine chemistry does not change much with radius and is shown in Fig. 13. The most abundant molecule formed in the CSE is CCl which arises from:

$$HCl \xrightarrow{CH_3^+} CCl^+ \xrightarrow{e} CCl \tag{68}$$

At low radii there is a route from HCl to Cl^+ by reaction with He^+ in addition to the photodestruction process shown in Fig. 13. At large radii HCl is still abundant. Its formation, by reactions of H_2 with chlorine-bearing ions:

$$Cl^+ \xrightarrow{H_2} HCl^+ \xrightarrow{H_2} H_2Cl^+ \xrightarrow{e} HCl \tag{69}$$

and destruction (by photons) are almost in equilibrium. The abundance of HCl will fall off as the photon field destroys H_2.

3.8. Phosphorus chemistry

The only phosphorus-bearing species with fractional abundances greater than 10^{-10} are P, PH, PH_2, PH_3 and PO. Their distributions are shown in Fig. 14. The chemistry is driven by

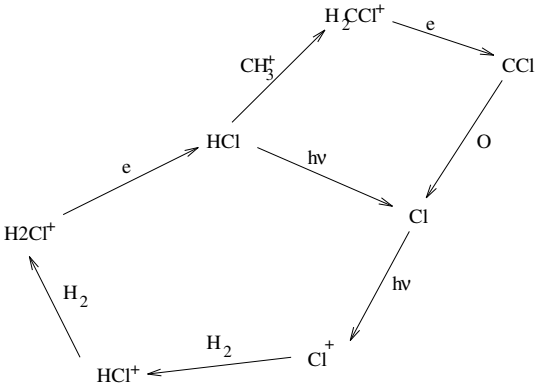


Fig. 13. The chlorine chemistry in a circumstellar envelope. The reactions do not vary with radius other than for the photoreactions to assume an increased importance as the radius increases.

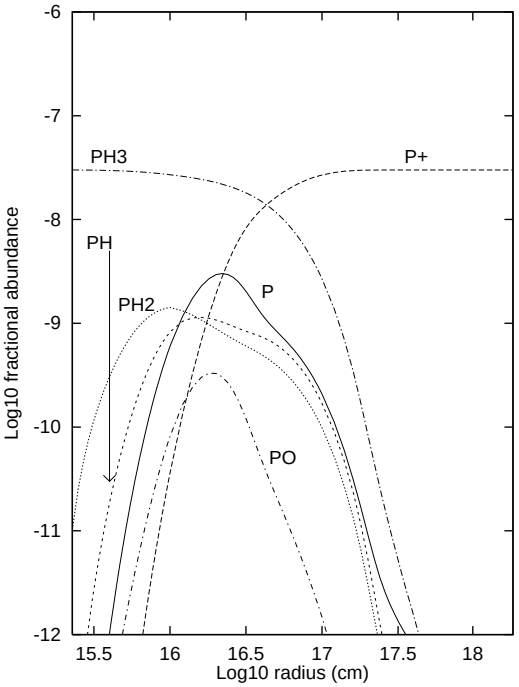


Fig. 14. The radial distribution of the phosphorus molecules in OH231.8+4.2

the destruction of the parent molecule, PH_3, by reaction with ions:

$$PH_3 + H_3O^+ \longrightarrow PH_4^+ + H_2O \tag{70}$$

$$PH_3 + H_3^+ \longrightarrow PH_4^+ + H_2 \tag{71}$$

$$PH_3 + C^+ \longrightarrow PH_3^+ + C \tag{72}$$

with reaction 72 becoming more important as the radius increases. Photodissociation is not important even at large radii. The other hydride molecules are formed by recombination

$$PH_4^+ \xrightarrow{e} PH_2 \xrightarrow{H} PH \tag{73}$$

Table 4. A comparison of the observed peak fractional abundances with those calculated in the model for OH231.8+4.2. The observations are taken from (1) Morris et al (1987); (2) Bujarrabal et al (1994); (3) Lindqvist et al (1992); (4) Charnley & Latter (1996). The observed values vary greatly. This is probably due to different assumtions as to the excitation temperature and the radial extent of the emission.

Species	Model	Observations			
		1	2	3	4
HCN	1.0 (-7)	3.9 (-7)	4.4 (-6)	3.0 (-7)	
HNC	1.8 (-8)	1.8 (-7)	7.9 (-7)		
CS	2.4 (-7)	2.8 (-7)	7.5 (-7)		
SiO	3.2 (-5)	7.8 (-8)	7.7 (-7)		
SO	1.0 (-6)	2.1 (-6)	4.0 (-6)		
SiS	3.5 (-6)	$<$ 1.4 (-7)	$<$ 5.0 (-7)		
SO_2	3.0 (-7)	1.3 (-5)			
H_2S	1.3 (-5)	7.5 (-7)			
H_2CO	5.0 (-7)			4.0 (-8)	
CO	4.0 (-4)	2.8 (-4)			
HCO^+	3.0 (-8)	8.4 (-8)			
OCS	9.0 (-10)	1.1 (-6)			
CN	2.3 (-7)	$<$ 2.0 (-7)			
N_2H^+	4.9 (-11)	$<$ 1.6 (-8)			
HCS^+	2.0 (-8)	$<$ 1.5 (-7)			
NH_3	1.0 (-5)	1.0 (-6)			
CH_3OH	3.5 (-8)				$<$ 4.1 (-8)
C_2H	1.9 (-7)				$<$ 1.8 (-7)

Table 5. A comparison of the peak calculated fractional abundances in the model for TX Cam with the observations of this region. The references for the observations are (1) Bujarrabal et al (1994); (2) Olofsson et al (1991); (3) Lindqvist et al (1988); (4) Charnley & Latter (1996).

Species	Model	Observations			
		1	2	3	4
HCN	2.7 (-7)	2.2 (-6)	1.0 (-6)	1.4 (-6)	
HNC	1.4 (-8)	1.3 (-7)			
SiS	3.5 (-6)	1.5 (-6)		1.2 (-6)	
CS	3.3 (-7)	4.6 (-7)	1.0 (-6)	5.0 (-7)	
SiO	3.2 (-5)	3.0 (-5)			
SO	7.8 (-7)	1.8 (-6)			
CN	2.6 (-7)		2.0 (-7)	$<$ 5.0 (-6)	
NO	4.4 (-6)		$<$ 8.0 (-5)		
HCO^+	6.6 (-8)			$<$ 4.0 (-7)	
CH_3OH	1.4 (-8)				$<$ 4.3 (-7)
C_2H	7.7 (-7)				$<$ 8.7 (-7)

$$PH_3^+ \xrightarrow{e} \begin{cases} PH_2 + H \\ PH + H_2 \end{cases} \quad (74)$$

and destroyed by photons.

PO is formed by the reaction of oxygen atoms with either PH or PH_2. Destruction is by photodissociation.

Carbon-phosphorus molecules are not formed because of the lack of formation routes involving CH_3 and CH_3^+.

Table 6. The peak fractional abundances calculated in the model of IK Tau compared with the observations. The references are (1) Bujarrabal et al (1985); (2) Omont et al (1993); (3) Lindqvist et al (1988); (4) Charnley & Latter (1996)

Species	Model	Observations			
		1	2	3	4
HCN	1.4 (-7)	9.8 (-7)		6.0 (-7)	
HNC	2.0 (-8)	5.2 (-8)		$<$ 2.0 (-7)	
SiS	3.5 (-6)	4.4 (-7)		$<$ 7.0 (-7)	
CS	2.9 (-7)	1.0 (-7)		3.0 (-7)	
SiO	3.2 (-5)	1.7 (-5)	3.0 (-6)		
SO	9.1 (-7)	2.6 (-6)	1.8 (-6)		
SO_2	2.2 (-7)		4.1 (-6)		
H_2S	1.3 (-5)				
HCO^+	3.9 (-8)		-		
CH_3OH	4.5 (-8)				1.2 (-7)
C_2H	2.3 (-7)				-

4. A comparison with observations

Observations are available for 3 of our sources, the exception being RDor.

OH231.8+4.2 is an unusual source with a strong bipolar outflow in which there is likely to be shocks which will affect the chemistry. We have not attempted to model this but instead have concentrated on the CSE itself. In view of this, the model gives surprisingly good agreement for a number of molecules: CS, SO, HCO^+, CO, CN, N_2H^+ and HCS^+ (see Table 4). Only an upper limit is available for the last 3 of these molecules. The available data for HCN show a considerable degree of variation with a fractional abundance of $\sim$ 3-4 $\times$ 10^{-7} being found by Morris et al (1987) and Lindqvist et al (1992), and a value about 10 times higher determined by Bujarrabal et al (1994). Our model agrees with the lower value. HNC is a factor of 10 lower than the observations but the ratio of HCN/HNC agrees with that found by Bujarrabal et al.

SiO, SiS, CO, H_2S and NH_3 have been assumed to be parent molecules. Any differences between the model and the observations for these species therefore reflects a problem with the input abundances. CO is in agreement with the observations but the others show some discrepancies. SiO, SiS and NH_3 are calculated to have abundances considerably larger than observed. H_2S is in agreement with the observations of Omont et al (1993) (who find that f(H_2S) may be as large as 10^{-5} at $R = 10^{16}$ cm) but is considerably larger than the abundance found by Morris et al (1987). As stated in the introduction no attempt has been made here to customize the input abundances for a particular source and it may be that for OH231.8+4.2 the abundances of silicon and nitrogen are lower than we have assumed due to a greater incorporation into dust grains.

The calculated abundance of OCS shows poor agreement with the observations. SO_2 is also underabundant in our models. The observed abundance for SO_2 of 1.3 $\times$ 10^{-5} means that it contains 80 % of the solar abundance of sulphur. It is possible that the SO_2 arises in a different part of the source that the other

sulphur molecules and is formed for example in the shocks in the bipolar outflow (Jackson & Nguyen-Q-Rieu 1988).

Recently Charnley & Latter (1996) have undertaken a search for CH_3OH and C_2H in CSEs in order to place limits on the amount of CH_4 which could be present in the envelope as a parent molecule. Neither of these molecules were detected in any of the sources observed but upper limits were obtained. Our model results are in accord with their upper limits in contrast to the model of Charnley & Latter which predicted an overabundance of these two molecules. In the next section we consider the differences between the two models and the implications of these observations for the chemistry of CSEs.

Of the 11 molecules for which data is available, our model can reproduce the peak fractional abundances of all but 3 of them in TX Cam. HCN and HNC are again too low but their ratio is correct. For NO, HCO^+, CH_3OH and C_2H upper limits only are available with which our model is consistent. Bujarrabal et al (1994) find a value for SO which is 3 times higher than our model and other observations by Sahai & Wannier (1992) put the fractional abundance even higher at 3.2 - 6.5 $\times$ 10^{-6}.

IK Tau is the only source for which the calculated abundance of HNC agrees with the observations. However in this case the abundance of HCN is too low. CS and SO are also in good agreement with SiO fitting the observations of Bujarrabal et al (1994) but not those of Omont et al (1993). SiS is calculated to be about 10 times higher than observed and this may argue for its abundance at the start of the model to be reduced. The SO_2 abundance is too low to account for the observations.

We conclude this section with a listing of the calculated column densities for a variety of species (Table 7).

Table 7. The calculated column densities in each model for a variety of species.

Species	OH231.8+4.2	IK Tau	TX Cam	R Dor
N_2H^+	6.4 (10)	5.7 (9)	6.6 (9)	1.1 (9)
NH_3	1.8 (17)	1.1 (16)	8.0 (15)	2.0 (14)
HCN	8.8 (13)	2.4 (13)	4.5 (13)	1.2 (13)
HNC	1.5 (13)	3.4 (12)	2.4 (12)	7.1 (11)
CN	1.7 (14)	3.9 (13)	3.1 (13)	1.0 (13)
H_2CN	1.9 (13)	6.2 (12)	8.4 (12)	2.1 (9)
CH_3CN	9.9 (11)	3.2 (11)	7.9 (11)	1.6 (11)
SiN	3.8 (13)	1.2 (13)	1.2 (13)	3.1 (12)
SiS	6.8 (16)	4.8 (15)	3.6 (15)	2.3 (14)
SiO	6.1 (17)	4.5 (16)	3.4 (16)	2.7 (15)
SiO_2	1.1 (15)	3.9 (14)	4.6 (14)	4.2 (13)
HCSi	1.4 (14)	5.0 (13)	7.3 (13)	2.5 (13)
$SiCH_2$	6.5 (12)	2.0 (12)	3.5 (12)	6.4 (11)
CS	2.1 (14)	4.8 (13)	5.6 (13)	1.3 (13)
H_2CS	8.0 (12)	2.1 (12)	3.9 (12)	5.2 (11)
SO	9.4 (14)	2.6 (14)	2.0 (14)	3.1 (13)
SO_2	2.1 (14)	4.6 (13)	2.8 (13)	3.4 (12)
H_2S	2.3 (17)	1.3 (16)	8.8 (15)	1.2 (14)
CO	7.9 (18)	6.2 (17)	4.8 (17)	4.6 (16)
CO^+	1.2 (10)	6.0 (9)	3.9 (9)	1.2 (9)
CO_2	3.0 (14)	9.4 (13)	6.4 (13)	7.0 (12)
HCO^+	2.5 (13)	6.1 (12)	7.4 (12)	2.6 (12)
H_2CO	4.8 (14)	1.4 (14)	2.2 (14)	4.0 (13)
OCS	6.2 (11)	1.9 (11)	5.5 (11)	8.6 (10)
C_2H	1.9 (14)	5.1 (13)	1.5 (14)	3.0 (13)
C_2H_2	1.9 (13)	9.4 (12)	3.6 (13)	3.7 (12)
C_2H_3	4.9 (12)	2.3 (12)	3.8 (12)	6.8 (11)
C_2H_4	1.7 (13)	1.3 (13)	2.4 (13)	1.2 (12)
CH_3^+	6.7 (13)	2.6 (13)	6.6 (13)	1.7 (13)
CH_3	2.0 (15)	7.3 (14)	5.9 (14)	1.1 (14)
CH_4	5.6 (17)	3.5 (16)	2.5 (16)	6.4 (14)
CH_3OH	2.7 (13)	1.2 (13)	3.6 (12)	5.3 (11)
CH_2CO	1.2 (12)	2.8 (11)	2.7 (11)	5.1 (10)
H_3O^+	3.1 (13)	1.8 (13)	2.4 (13)	3.3 (12)
H_2O	5.6 (18)	3.7 (17)	2.8 (17)	1.2 (16)
OH	1.2 (17)	3.5 (16)	2.7 (16)	6.6 (15)

4.1. Is the presence of CH_4 as a parent molecule compatible with the observations?

Charnley & Latter (1996) found upper limits to the abundance of CH_3OH and C_2H in several CSEs and modelled 3 of them including TX Cam and IK Tau. Their calculations produced abundances which are too high (in some cases as much as an order of magnitude too high) to fit the observations. In addition they cannot reproduce the observed CS/SO ratio which is always less than 1. Our model can fit both these observational facts.

The models differ in that they use different versions of the UMIST ratefile but apart from that appear to be essentially the same. The updates in the rate coefficients in the ratefile used in our calculations are not sufficient to account for the variations in the results and we have no explanation for this. Here we present the differences between our models but without any attempt to account for them.

We have found a difference in the chemistry of CS and SO. In the model of Charnley & Latter CS and SO are closely linked, with CS forming from

$$C + SO \longrightarrow CS + O \quad (75)$$

In our model this reaction does make a contribution but it is not the principal formation route for CS. Instead CS forms from the reaction of HCS^+ with electrons

$$HCS^+ + e \longrightarrow CS + H \quad (76)$$

This is in agreement with Nejad & Millar (1988). However, in their model HCS^+ forms from

$$C^+ + H_2S \longrightarrow HCS^+ + H \quad (77)$$

Charnley & Latter pointed out that H_2S and C^+ exist in spatially distinct regions and therefore this reaction is unlikely to produce sufficient HCS^+ to account for the abundance of CS. In our model we find that HCS^+ forms from

$$S \xrightarrow{h\nu} S^+ \xrightarrow{CH} CS^+ \xrightarrow{H_2} HCS^+ \quad (78)$$

thereby eliminating the problem.

In conclusion, we find that the presence of CH_4 as a parent molecule is not inconsistent with a CS/SO ratio of less than one and the upper limits of CH_3OH and C_2H.

5. Conclusions

Overall our model produces results which are in good agreement with the observations. In particular we have found that the presence of CH_4 as a parent molecule can account for the observations of carbon-bearing molecules in oxygen-rich CSEs and is not inconsistent with any of the available data. The chemistry of HCN and HNC is still not entirely clear with the calculated abundances of these molecules varying by up to an order of magnitude from the observed value.

The results for OH231.8+4.2 are the most unexpected as this is a complicated source and we have modelled just one part of it. Even so our model is very successful. An exception is SO_2 whose calculated abundance is too low in all the sources with the discrepancy being most marked for OH231.8+4.2. This may indicate that some of the emission for this molecule arises in the outflow region rather than the circumstellar envelope itself. The results for other sulphur molecules agree with the observations and in particular we can account for the observed ratio of CS/SO which is always < 1.

Phosphorus-carbon species are not formed in appreciable quantities because of the lack of formation reactions involving either CH_3 or its ion.

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