Cyanopolyynes and sulphur bearing species in hot cores: Chemical and line excitation models

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ABSTRACT
We present results from a time dependent gas phase chemical model of a hot core based on the physical conditions of G305.2+0.2. While the cyanopolyyne HC\(_5\)N has been observed in hot cores, the longer chained species, HC\(_5\)N, HC\(_7\)N, and HC\(_9\)N have not been considered typical hot core species. We present results which show that these species can be formed under hot core conditions. We discuss the important chemical reactions in this process and, in particular, show that their abundances are linked to the parent species acetylene which is evaporated from icy grain mantles. The cyanopolyynes show promise as ‘chemical clocks’ which may aid future observations in determining the age of hot core sources. The abundance of the larger cyanopolyynes increase and decrease over relatively short time scales, \(\sim 10^5\) years. We also discuss several sulphur bearing species. We present results from a non-LTE statistical equilibrium excitation model as a series of density, temperature and column density dependent contour plots which show both the line intensities and several line ratios. These aid in the interpretation of spectral line data, even when there is limited line information available.

Key words: stars:formation - ISM: molecules.

1 INTRODUCTION
Hot cores are observed in regions of high mass star formation, and are small, hot (\(\sim 200\)K) and dense (\(\sim 10^8\) cm\(^{-3}\)) clumps of gas (e.g., Sweitzer 1978; Pauls et al. 1983, for a review see, e.g., van der Tak 2003). The chemistry of these regions is unique, characterized by unusually high abundances of saturated molecules, such as H\(_2\)O and NH\(_3\) (e.g., Henkel et al. 1987; Walmsley et al. 1987; Olmi et al. 1993). This unique chemistry is believed to be a direct result of grain mantle evaporation due to an event, such as the switching on of a nearby star or a source within the core itself (e.g., Kaufman et al. 1998; Wyrowski & Walmsley 1996). During an earlier high density phase of collapse, these molecules are formed on the surface of dust grains (e.g., Walmsley & Schilke 1991), released into the gas phase during the onset of heating, and are processed into daughter species. Since cores are both hot and dense, the time dependent gas phase chemistry rapidly changes over time scales <100,000 years. Species with time dependent chemistry can be used as ‘chemical clocks’ and may help in determining the age of hot core regions (e.g., Millar, Macdonald & Gibb 1997).

The origins of some interstellar molecules found in hot cores can be separated into the following three groups. Those that are formed in the cold gas:

- e.g., CO, C\(_2\)H\(_2\), C\(_2\)H\(_4\), N\(_2\), O\(_2\), CS

those formed on grain surfaces:

- e.g., H\(_2\)O, CH\(_4\), NH\(_3\), H\(_2\)S, CH\(_3\)OH, H\(_2\)CO, C\(_2\)H\(_5\)OH, CO\(_2\), HCOOH, NH\(_2\)CHO, C\(_2\)H\(_4\), C\(_2\)H\(_6\), H\(_2\)CS, OCS

and those formed in the hot gas (e.g., Charnley 1993):

- e.g., CH\(_3\)OCH\(_3\), CH\(_3\)CHO, HCOOC\(_2\)H\(_5\), CH\(_2\)COCH\(_3\), (C\(_2\)H\(_5\))\(_2\)O, CH\(_2\)OC\(_2\)H\(_5\), C\(_2\)H\(_5\)CN, CH\(_3\)CN, HCN, SO, SO\(_2\), C\(_2\)H\(_5\)CN, H\(_3\)N, CH\(_3\)NH\(_2\), CH\(_2\)NH, SiO.

Observations of hot cores include molecular line and dust continuum emission, and some of the chemical core models, along with radiative transfer calculations, have proven useful in reproducing observed column densities (e.g., Millar, Macdonald & Gibb 1997; Kaufman et al. 1993).
have also been detected in the molecular cloud of Sgr B2. Hydrogenated species such as vinyl cyanide CH₂CHCN and ethyl cyanide CH₃CH₂CN are more likely to be detected (Blake et al. 1987) over the larger cyanopolyynes.

Models of the gas phase chemistry are extremely useful as predictive tools with regards to observations. However, extracting molecular abundances from line emission, suitable for comparison with the model predictions is not a straightforward task. Furthermore, although theoretical models can produce abundances for hundreds of molecules, observations are limited to specific frequency bands, and possibly contain line emission from only a handful of species. A broad understanding of the chemistry is thus not often possible with limited molecular line data for a specific source.

Line surveys of massive star forming regions have been undertaken (e.g., Blake et al. 1987; Sutton et al. 1991; Schilke et al. 2001) however differences between telescopes, beam sizes and excitation conditions make comparisons of abundances between sources difficult. To avoid this problem, Bisschop et al. (2007) performed a partial submillimeter line survey of 7 high mass young stellar objects, and further identified ‘first generation’ species that originate from solid state chemistry, as opposed to species produced in the gas phase chemistry. The ‘first generation’ species observed were H₂CO, CH₃OH, C₂H₂OH, HCOOCH₃, CH₃OCH₃, HNCO, and NH₂CHO.

Modelling tools to aid in the interpretation of spectral line data are especially important for large line surveys, and efficient methods are needed to obtain physical and chemical parameters, such as column densities, relatively easily even with large numbers of species and lines. Currently, collisional rate coefficients are available for approximately 24 species on the Leiden atomic and molecular database (LAMDA) Schilke et al. (2001), with several others in literature (e.g., CH₃CN in Green 1986), and so statistical equilibrium calculations are limited to these. Moreover, observations are limited in frequency, and so limit the process further. The list of species for which collisional rate coefficients are available include CS, OCS, SO, SO₂, SiO, HCO⁺, HC₃N, HCN, HNC, H₂O, OH, CH₃OH, and NH₃. There are many more species of astronomical interest that do not appear in the LAMDA database, or elsewhere in the literature and we will have to wait to see if these will become available in the future.

The aim of this paper is to model the gas phase chemistry of hot cores, and to further aid in the interpretation of spectral line data. In section 2 we present results from a hot core chemistry model which follows the time dependent gas phase chemistry. We concentrate on the cyanopolyynes HC₃(3,5,7,9)N and show that the longer chain species can be produced in appreciable abundances in typical hot core conditions. Several sulphur bearing species are also modelled and discussed. In section 3 we present results from a statistical equilibrium model which produces the line intensity of a molecular line of interest. We present a series of density n(H₂), temperature T and column density Nₖ dependent contour plots which will directly aid in the interpretation of observations. Line ratios are chosen that enable the clearest interpretation of the physical parameters which helps identify useful observable lines and will give direction to future observations.
2 CHEMICAL MODEL

The physical model for the core is similar to that of Millar, Macdonald & Gibb [1997] and Thompson et al. [1999] which assume a spherical core geometry. The density and temperature is constant throughout since we want to examine the general gas phase chemistries. We assume a density of $n_{HI} = 8 \times 10^4 \text{cm}^{-3}$ and a temperature of 200K, which was derived for the core of G305.2+0.2 in [Walsh et al. 2007], with a radius of 1.1pc at a distance of 3.9kpc. The initial abundances are given in table I (e.g., Millar, Macdonald & Gibb [1997], Walsh et al. 2007). The initial abundances are based on previous models of hot cores (e.g., Millar, Macdonald & Gibb [1997], Rodgers & Charnley 2001, Walsh et al. 2007) and the mean interstellar values. The source is assumed to fill the beam, and so beam dilution does not play a large role in the model results. The model contains 245 species, consisting of the 8 elements H, He, C, O, Si, S, Fe, N. Included in the model are the cyanopolyynes $\text{HC}_{2n+1} \text{N}$ ($n=0-4$), the carbon chained molecules $\text{C}_n\text{H}_2$ ($n=3-9$) and the hydrocarbon chains $\text{C}_n\text{H}_n$ ($n=1-9$). The full set of species are given in table II with the initial mantle abundances in table I. The species list includes many previously observed hot core species along with essential species needed for their production.

Discrepancies between models of dense interstellar clouds (Millar, Leung & Herbst 1987) highlight the sensitivity of astrochemical models to the reaction rate coefficients as well as the reaction network. The reaction rates are taken from the most recent UMIST database which includes the latest laboratory data (Woodall et al. 2007). The reaction networks of some of the key core species will be discussed in more detail below. Many of the rate coefficients are temperature dependent and care has been taken when using these outside their specified temperature range. There are a select few reactions with rate coefficients that are ill-defined.
outside their prescribed temperature range, with rate coefficients exponentially increasing with decreasing temperature. In these cases the rate coefficients are kept constant at the lowest or highest temperature range value nearest the temperature of interest. The reaction network is discussed further in section 4.

Numerically, the core is described by a series of 22 concentric shells, with a density and temperature assigned to each. At each depth point or shell, the initial abundances are set and the reaction network is calculated over 10^8 years. However, the chemistry rapidly evolves over much shorter time scales than this. The species abundances are integrated along the line of sight and the column density of a species at time t is

\[ N_j(r, \theta, t) = \int_0^\infty n_j(s, t) ds \]  

(1)

where \( n_j(s, t) \) is the species abundance and s is the depth through the core along the line of sight. The coordinates r and \( \theta \) specify the position of the pencil beam with respect to the centre of the core. We approximate the telescope beam using a Gaussian with an area normalized primary beam:

\[ P(r) = \frac{1}{2\pi \sigma^2} \exp\left(-\frac{r^2}{2\sigma^2}\right), \quad \sigma = \frac{\text{HPBW}}{2\sqrt{2}\ln 2} \]  

(2)

where r is the radius measured from the centre of the gaussian and HPBW is the half power beam width. \( P(r) \) is normalized so that

\[ \int_0^{2\pi} \int_0^\infty P(r) r dr d\theta = 1. \]  

(3)

To evaluate the gaussian beam, column densities are firstly evaluated along pencil beams on grid points through the chemical core model. These column densities are then convolved with the Gaussian, equation (2), giving the beam-averaged or beam diluted column density \( N_j(t) \)

\[ N_j(t) = \frac{1}{2\pi \sigma^2} \int_0^{2\pi} \int_0^\infty N_j(r, \theta, t) \exp\left(-\frac{r^2}{2\sigma^2}\right) r dr d\theta. \]  

(4)

2.1 Carbon bearing species

In a related project, we have begun a survey for HC_3N in methanol-maser selected hot molecular cores from the Purcell et al. 2006 list, using the Tidbinbilla 34m telescope to measure the 31.95 GHz J=12-11 line. These results will be reported separately, when the survey is complete. However, we can report that HC_3N is frequently observed in the cores selected from this list, typically when CH_3CN 5-4 92 GHz line emission was also detected by Purcell et al. 2006. Sources have been found to contain both CH_3CN and HC_3N, or neither at all, suggesting their possible use as chemical clocks. We will explore the chemical pathways below and we show that HC_3N may well be a hot core species. We also discuss the likely role of other carbon bearing molecules.

Fukuzawa, Osamura & Schaefer (1998) have demonstrated the importance of these neutral-neutral reactions:

\[ C_2nH_2 + CN \rightarrow HC_{2n+1}N + H, \]  

(5)

in the formation of cyanopolyynes in the ISM. Cyanoacetylene, HC_3N is often detected in cold gas in molecular clouds, and is formed efficiently via the reaction:

\[ C_2H_2 + CN \rightarrow HC_3N + H \]  

(6)

Lichtin & Lin (1984). Observed abundances of C_2H_2, (as well as CH_3CN and H_2CO) cannot be produced in the hot core gas phase alone, but can be accounted for in the cold phase chemistry where they are frozen out onto the grains before being released into the gas phase (e.g., Brown, Charnley & Millar 1988; Charnley & Tielens 1992; Charnley, Tielens, & Millar 1992). C_2H_2 has long been observed in IR emission features, which provides direct evidence for its existence in the ice mantles of dust grains (Allamandola & Nordsieck 1978). Rodgers & Charnley (2001) have also demonstrated with a gas grain model that high abundances of C_2H_2 may be produced in the gas phase provided that a large enough abundance of methane is ejected from the grain mantles. Inside hot cores, C_2H_2 is released from the grain mantles and reaction (6) proceeds relatively easy for hot core temperatures (100-300K).
Results from the time dependent gas phase chemical model described in section 2 are shown in figure 1. The column density of HC$_3$N rises to a peak above $N=10^{14.5}$ cm$^{-2}$ at $t=10^5$ years, and reaches its steady state abundance after $10^6$ years. The abundance of HC$_3$N initially increases with CN since it is mainly produced via the reaction of CN with C$_2$H$_2$, reaction (7). Also plotted are the larger cyanopolyynes HC$_{5,7,9}$N, whose abundances also peak near $t=10^5$ years. These species are not usually considered hot core species but in figure 1 they are all reach appreciable column densities over $N = 10^{12.5}$ cm$^{-2}$. The peak column densities of the shorter molecules, HC$_5$N and HC$_7$N, are one order of magnitude larger than that of HC$_3$N. Also, all species reach steady state abundances after $10^6$ years.

In the ISM cyanodiacetylene, HC$_3$N is mainly formed in the neutral-neutral reaction

$$\text{CN} + \text{H}_2\text{CCCC} \rightarrow \text{HC}_3\text{N} + \text{H}.$$  

(7)

the rate coefficient for this reaction is $2.55 \times 10^{-10}$ cm$^3$ s$^{-1}$ at a temperature of 300 K (Woodall et al. 2007). This was confirmed as the dominant reaction in the production of HC$_3$N in the hot core results of figure 1. This reaction has not been considered important in the past since it was not thought that H$_2$CCCC was formed on the grain surfaces or very efficiently in the gas phase. However, H$_2$CCCC is formed efficiently via

$$\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{H}_2\text{CCCC} + \text{H}.$$  

(8)

with a rate coefficient of $1.5 \times 10^{-10}$ cm$^3$ s$^{-1}$ at 200K. The column densities of H$_2$CCCC and C$_2$H are plotted in figure 3 reaching peak column densities of $10^{14.8}$ cm$^{-2}$ and $10^{14.5}$ cm$^{-2}$, respectively, near $10^4$ years. Therefore, the abundance of H$_2$CCCC, and thus HC$_3$N, also depend on acetylene C$_2$H$_2$. CN is produced in relatively large quantities, furthering the efficiency of reaction (7). CN is produced mainly by dissociative recombination of H$_2$NC$^+$,

$$\text{H}_2\text{NC}^+ + e^- \rightarrow \text{CN} + \text{H}_2,$$

(9)

and at later times after $10^5$ years by the reaction

$$\text{C} + \text{NO} \rightarrow \text{CN} + \text{O}.$$  

(10)

H$_2$NC$^+$ is formed by

$$\text{He}^+ + \text{CO} \rightarrow \text{O} + \text{C}^+ + \text{He}.$$  

(11)

$$\text{C}^+ + \text{NH}_3 \rightarrow \text{H}_2\text{NC}^+ + \text{H},$$  

(12)

and reaction (10) is preceded by

$$\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}.$$  

(13)

$$\text{H}_2\text{O}^+ + e^- \rightarrow \text{OH} + \text{H} + \text{H}.$$  

(14)

Carbon chained polar molecules of the form H$_2$C=C.C have been detected in the laboratory and have been identified as useful species to radio astronomers being stable under interstellar conditions. Killian et al. (1990) have detected propadienylidene H$_2$CCCC and butatrienylidene H$_2$CCCC in the laboratory, and suggest that the H$_2$C$_n$ cumulene carbones may be an another important sequence of interstellar molecules, comparable with the cyanopolynes (HC$_n$N observed in space up to $n=11$) and the linear hydrocarbon chains C$_n$H$_n$ (observed up to $n=8$). H$_2$CCCC is an isomer of diacetylene HCCCH and has been detected in the dark cloud TMC-1 (Kawaguchi et al. 1991) and the circumstellar shell of IRC +10216 (Cernicharo et al. 1991).

The increase of the abundance of HC$_7$N in figure 1 is due to the reaction network

$$\text{C}_2\text{H}_2 + \text{C}_4\text{H} \rightarrow \text{C}_6\text{H}_2 + \text{H}$$  

(15)

$$\text{CN} + \text{C}_6\text{H}_2 \rightarrow \text{HC}_7\text{N} + \text{H}. $$  

(16)

Once again the abundance of the cyanopolyene HC$_7$N is directly related to acetylene. Similarly, the increase in the abundance of HC$_9$N can be accounted for by the reactions

$$\text{C}_6\text{H}_2 + \text{C}_2\text{H} \rightarrow \text{C}_8\text{H}_2 + \text{H}$$  

(17)

$$\text{CN} + \text{C}_8\text{H}_2 \rightarrow \text{HC}_9\text{N} + \text{H},$$  

(18)

and this can be related to the HC$_7$N reaction network (reaction (15)) via the C$_6$H$_2$ molecule. The column densities of the molecules responsible for the production of the cyanopolynes are plotted in figure 3 and are compared with the daughter species HC$_5$N, HC$_7$N and HC$_9$N in figure 2. The abundance of H$_2$CCCC increases to a peak of $10^{14.8}$ cm$^{-2}$ at 10$^4$ years. The abundance of the daughter species HC$_5$N also increases reaching a peak of $10^{14.2}$ cm$^{-2}$ near $10^5$ years. The peak in HC$_5$N occurs at a later time then its parent H$_2$CCCC. Similar relationships between C$_6$H$_2$ and HC$_7$N, and between C$_8$H$_2$ and HC$_9$N, can also be seen.

The formation of the cyanopolynes, HC$_5$N, HC$_7$N and HC$_9$N, are sensitive to the abundances of CN and the carbon chain molecules H$_2$CCCC, C$_6$H$_2$, and C$_8$H$_2$. Furthermore, the abundance of the carbon chain molecules are dependent on acetylene C$_2$H$_2$. Thus one would expect, that if C$_2$H$_2$ is present in the gas then the larger cyanopolynes may also be present. Figure 4 illustrates this, which shows the resulting abundances when no C$_2$H$_2$ is initially evaporated from grain mantles. The acetylene abundance initially increases to a column density ~ $10^{14}$ cm$^{-2}$ near $10^{13}$ years. HC$_5$N, HC$_7$N, HC$_9$N and HC$_{11}$N reach peak densities of $10^{13.5}$ cm$^{-2}$, $10^{12.7}$ cm$^{-2}$, $10^{11.8}$ cm$^{-2}$, and $10^{10.4}$ cm$^{-2}$, respectively. These column densities are a magnitude (or in some cases less) smaller then those of figure 1.
Figure 3. As for figure 1 but for the parent species of the higher order cyanopolyynes H$_C^n$N (n>3).

Figure 4. As for figure 1, however, C$_2$H$_2$ is assumed to form in the gas only, with no initial abundance related to grain mantle evaporation.

Since CH$_3$CN emission is often used as a signature of the presence of a hot molecular core, we have investigated its relative abundance compared to HC$_5$N as a function of time. CH$_3$CN is efficiently produced via

$$\text{CH}_3\text{CNH}^+ + \text{e}^- \rightarrow \text{CH}_3\text{CN} + \text{H} \quad (19)$$

and the abundance of CH$_3$CNH$^+$ is driven by radiative association:

$$\text{CH}_3^+ + \text{HCN} \rightarrow \text{CH}_3\text{CNH}^+ + \text{h}v. \quad (20)$$

For the first 10$^4$ years, CH$_3^+$ is produced by

$$\text{H}_3^+ + \text{CH}_3\text{OH} \rightarrow \text{CH}_3^+ + \text{H}_2\text{O} + \text{H}_2 \quad (21)$$

and

$$\text{H}_2 + \text{CH}_3^+ \rightarrow \text{CH}_3^+ + \text{H} \quad (22)$$

thereafter. The HCN abundance is driven by

$$\text{NH}_3 + \text{HCNH}^+ \rightarrow \text{HCN} + \text{NH}_3^+ \quad (23)$$

for the first 10$^5$ years and

$$\text{HCNH}^+ + \text{e}^- \rightarrow \text{HCN} + \text{H} \quad (24)$$

after 10$^5$ years. These are preceded by

$$\text{H}_2 + \text{HCN} \rightarrow \text{HCNH}^+ + \text{H} \quad (25)$$

$$\text{C}^+ + \text{NH}_3 \rightarrow \text{HCN}^+ + \text{H}_2 \quad (26)$$

$$\text{C}^+ + \text{NH}_2 \rightarrow \text{HCN}^+ + \text{H}. \quad (27)$$

The methyl cyanide chemistry is shown in figure 5. The destruction of the mantle species NH$_3$ and CH$_3$OH begins near 10$^4$ years, signalling the start of the rapid gas phase chemistry between 10$^4$ and 10$^5$ years. As reaction (25) proceeds, the HCN abundance increases. CH$_3^+$ is strongly dependent on CH$_3$OH which is highly abundant before 10$^4$ years and so remains in the gas phase with a constant column density of 10$^{12}$ cm$^{-2}$ between 10$^2$ and 10$^4$ years. When the abundance of HCN increases, reaction (20) proceeds and the abundance of CH$_3$CNH$^+$ increases, allowing the formation of CH$_3$CN via reaction (19).

The abundances of HC$_5$N and CH$_3$CN are not directly linked via their respective reaction networks, however the abundances of both are strongly dependent on their parent grain mantle species. The abundances of both increase at the onset of the rapid gas phase chemistry caused by the destruction of the grain mantle species. As a useful comparison, we plot the time dependent HC$_5$N/CH$_3$CN ratio in figure 6. The ratio increases considerably between 10$^4$ and
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2.2 Sulphur bearing species

Many sulphur bearing species are easily detectable in the mm and submm wavelengths making these useful observational targets. The collision rates with H$_2$ of several sulphur bearing molecules are available; CS, OCS, SO, SO$_2$ and HCS$^+$ (Schoier et al. 2005). Chemical hot core models have also shown that the sulphur chemistry is highly time dependent, with some species showing promise as chemical clocks (e.g., Millar 1997). Column densities of some sulphur bearing molecules are plotted in figure 7. The grain mantle species H$_2$S and OCS are destroyed after $10^5$ years while the column densities of other species reach a peak between $10^4$ and $10^5$ years.

H$_2$S is destroyed after $10^4$ years, after reacting with H atoms. The resulting HS molecule is further processed through reactions with H, which is responsible for the increase in the S column density (clearly shown in figure 7). At earlier times $t < 10^4$ years, O reacts with HS to produce SO until atomic S is present in the gas. SO is formed via

$$\text{O} + \text{S} \rightarrow \text{SO} + \text{H} \quad (28)$$

At later times, after $10^5$ years the predominant SO producing reaction is

$$\text{OH} + \text{S} \rightarrow \text{SO} + \text{H} \quad (29)$$

At later times, after $10^5$ years, dissociative recombination of HSO$^+$ also contributes to the abundance of SO. As the abundance of SO increases, so does the abundance of SO$_2$ via

$$\text{OH} + \text{SO} \rightarrow \text{SO}_2 + \text{H} \quad (30)$$

The column density of CS increases to a peak near $10^4$ years. Initially, at early times $t < 10^2$ years, CS is formed via dissociative recombination of HOC$^+$. From $10^2$ years until $10^4$ years the CS abundance increases, since ammonia which has been released from the grains, is available for the following ion neutral reaction to proceed

$$\text{NH}_3 + \text{HCS}^+ \rightarrow \text{CS} + \text{NH}_4^+ \quad (31)$$

which is preceded by

$$\text{C}^+ + \text{H}_2\text{S} \rightarrow \text{HCS}^+ + \text{H} \quad (32)$$

After the peak at $10^4$ years, the destruction of CS, via

$$\text{O} + \text{CS} \rightarrow \text{S} + \text{CO} \quad , (33)$$

$10^5$ years and so could prove useful in determining the age of hot cores within this range.
is balanced by
\[ \text{C} + \text{SO} \rightarrow \text{CS} + \text{O} \] (34)
and the column density remains constant at \(10^{14.5}\text{cm}^{-2}\).

OCS was assumed to be released from grain mantles. This assumption was based on the observations of G305.2+0.2 in [Walsh et al. (2007)] in which an initial abundance was needed to reproduce the observed abundance of OCS. Ice absorption spectra have also suggested that OCS is a grain mantle species (Keane et al. 2001). In figure 7, OCS is destroyed after 10\(^5\) years before reaching a constant abundance after 10\(^6\) years. Initially, between 10\(^4\) and 10\(^5\) years, OCS is predominantly destroyed by the ion-neutral reaction;
\[ \text{Si}^+ + \text{OCS} \rightarrow \text{SiS}^+ + \text{CO}. \] (35)
After 10\(^5\) years, the abundance of S\(^+\) increases via
\[ \text{H} + \text{HS}^+ \rightarrow \text{S}^+ + \text{H}_2 \] (36)
and OCS is destroyed further by
\[ \text{S}^+ + \text{OCS} \rightarrow \text{S}_2\text{O} + \text{CO}. \] (37)
The ratios of the parent/daughter species, SO/SO\(_\text{2}\), or SO/CS and CS/OCS are shown in figure 5. The time dependent nature of these ratios suggest these are useful in comparing with observations to determine core ages.

### 3 MOLECULAR LINE EXCITATION MODEL

Models of the gas phase chemistry are useful as predictive tools in regards to observations. However, extracting molecular abundances from line emission data suitable for comparison with model predictions is not a straight forward task. Modeling tools to aid in the interpretation of spectral line data are especially important for large line surveys, and efficient methods are needed to obtain physical and chemical parameters, such as column densities, relatively easily even with a large number of species and lines. In this section, a molecular excitation model is used to calculate the excitation of the species of interest discussed in section 2.

In order to calculate the rotational excitation of a molecule, the collisional rates (per second per molecule) with H\(_2\) are taken from the LAMDA database [Schoier et al. 2002]. The collision rates depend on the cross section of the molecule and the density of H\(_2\). The LAMDA database also contains the relevant transitional frequencies, rotational levels and Einstein A-coefficients compiled from sources such as the JPL Molecular Spectroscopy database [Pickett et al. 1998] and the CDMS catalogue [Muller et al. 2003]. The escape probability method is used to simplify the statistical equilibrium equations (see for example Schoier et al. 2002). The model outputs the intensity of a line for a given density and temperature.

In figure 6 line intensities and line ratios are plotted for the 81.88, 90.98 and 100.08GHz rotational lines of HC\(_\text{3}\)N. The LAMDA database [Schoier et al. 2002] contains collision rates of the first 21 levels (9-18GHz) of HC\(_\text{3}\)N (however the higher transitions are affected by truncation). These plots are useful in interpreting observations since a measured line intensity, or line ratio can directly be compared on the plot, and the column density and/or density may be determined. In the first row, the individual line intensities in units K kms\(^{-1}\) are given for a density of \(n_\text{H}_2 = 8 \times 10^4\text{cm}^{-3}\) as a function of temperature and column density. Each plot shows the same overall trends, with the intensities becoming relatively constant with temperature for given normalised column densities below \(10^{14}\text{cm}^{-2}\). A single observed line intensity could be directly compared to these, after telescope beam dilution effects have been taken into account. Previous analyses (Walsh et al. 2007) have proven that a useful technique is to over plot a number of different lines allowing for the determination of the column density.

We also show in the second row of figure 6 the line ratios as a function of temperature for \(n_\text{H}_2 = 8 \times 10^4\text{cm}^{-3}\), which do not require any correction for beam dilution effects. Again these are useful in determining the column density. In the hot core regime, for temperatures of the order 150K and above, the features are relatively constant with column density and so potentially allowing one to read off the column density directly using an observed line ratio value.

In the third row of figure 6 the line intensities are shown again, but this time as a function of density for \(T=200\text{K}\). Each contour becomes constant with column density as the density increases, and the LTE approximation is approached with increasing \(n_\text{H}_2\). One could safely assume the LTE approximation, and use a rotation diagram, for densities above \(10^6\text{cm}^{-3}\) and if the line width normalised HC\(_\text{3}\)N column density is expected to be in the range \(10^{12}\text{cm}^{-2}\) to \(10^{16}\text{cm}^{-2}\). Finally, in the bottom row of figure 6 the line ratios are plotted as a function of density. As the column density decreases, the contours become constant with density. The trend towards LTE with increasing density is also clear.

Depending on what information is available, either series (row) of plots in figure 6 may be the most useful in interpreting observations. If either the temperature or density is known than the complexity is reduced greatly, and the corresponding plots with the appropriate temperature or density can be produced. Notwithstanding, however, even if these are unknown, the combination of all four plots can still be useful in determining limits on the density, temperature and column density. The collision rates for the larger cyanopolyynes HC\(_\text{5}\)N, HC\(_\text{7}\)N, HC\(_\text{9}\)N etc. have yet to be published. To calculate the excitation of HC\(_\text{5}\)N, we have used the collision rates of HC\(_\text{3}\)N [Schoier et al. 2002], however the cross section for HC\(_\text{5}\)N is scaled by a factor of 1.5 to account for the greater geometric length (e.g., Avery et al. 1974; Snell et al. 1981). The energy levels and Einstein A coefficients for HC\(_\text{7}\)N have been taken from the CDMS database [Muller et al. 2003]. The collision rates for HC\(_\text{5}\)N are available for the first 21 lines and in the case of HC\(_\text{5}\)N this includes all transitions from 2GHz to 54GHz. In figure 10 the corresponding line intensities and line ratios are shown for the 23.96, 26.63 and 29.29GHz lines of HC\(_\text{5}\)N. As expected these show similar characteristics as the HC\(_\text{3}\)N. A similar calculation has also been performed for HC\(_\text{7}\)N, after scaling the collision rates of HC\(_\text{5}\)N by 2 to account for the larger cross section of HC\(_\text{5}\)N (plots not shown here). These plots show similar features as those for HC\(_\text{5}\)N and HC\(_\text{7}\)N.

The sulphur bearing species discussed in section 2.2 proved useful as chemical clocks. Similar plots for species SO, CS and OCS are also shown. The intensities of the 86.09, 99.30 and 109.25 GHz lines of SO (and associated line ra-
Figure 9. Line intensities and ratios of HC$_3$N for the J=9-8 (81.88GHz), J=10-9 (90.98GHz) and J=11-10 (100.08GHz) lines calculated by the excitation model. The first row shows the line intensities in units of K km/s as a function of temperature and column density (normalised by line width) assuming a density of n$_{H_2}$ = 8 × 10$^4$ cm$^{-3}$. In the second row, three line ratios as a function of temperature and column density for constant density 8 × 10$^4$ cm$^{-3}$ are plotted. In the third and fourth rows, the corresponding plots as a function of density for a constant temperature of 200K are shown.

tios) are given in figure 11. The line intensities as a function of temperature (top row) show features that are somewhat constant with column density, which could be particularly useful if only single line data are known, then the column density can easily be read (after including any observational errors). The line ratios as a function of temperature also show these vertical features for column densities between 10$^{14}$ and 10$^{16}$ cm$^{-2}$. The corresponding plots as a function of density are given in the third and fourth rows. The line intensities as a function of density (third row), show that
the LTE approximation is valid for densities greater than $10^7 \text{cm}^{-3}$. With only information on one line, a lower limit of the column density is easily determined. The line ratios as a function of density are a little more complex but limiting values of both column density and/or temperature could still be determined depending on the measured line ratio. The corresponding plots for CS and OCS are given in figures 12 and 13, respectively.

### 4 DISCUSSION

The results from the chemical model in section 2 illustrate the highly time dependent chemistry of hot cores. The column densities of the carbon bearing species shown in figures 6-11 show time dependent features between $10^2$ and $10^6$ years. In particular the cyanopolyynes all switch on after $10^2$ and peak around $10^4$ years, before being rapidly destroyed before $10^5$ years. Acetylene was shown to be a key species.
in the formation of the cumulene carbenes $H_2C_n$, which react with CN to form the cyanopolyynes. Since acetylene is abundant in large quantities, as it has been evaporated from grain mantles, and CN is formed easily in the gas phase, the cyanopolyynes should also be found in hot cores. The formation and subsequent destruction of the longer chain cyanopolyynes are relatively short lived, which may explain why these are not often observed in hot core sources. However, if they are observed, they may prove very useful as chemical clocks, as they could help pinpoint the age of the hot core. Their detection in sources with similar physical conditions to those modelled in section 2 should imply ages of the order of $10^{4.5}$ years.

The sulphur bearing species also show promise as chemical clocks. As the grain mantle species, OCS and $H_2S$, are processed into daughter species, a rapid chemistry follows. The column densities of SO and $SO_2$ increase above...
10^{15}\text{cm}^{-2}$ after $10^{3.5}$ years. The CS abundance follows similar timing, with a peak column density of $10^{14.5}\text{cm}^{-2}$.

The calculated time dependent chemistry in section 2 are for specific physical conditions; $n_{\text{H}_2} = 10^4\text{cm}^{-3}$ and $T=200$K. Since the conditions inside the core are constant throughout, and the source fills the beam and beam dilution effects are not so important, changes in the size of the core, will only scale the column densities and not change the time dependent features. Since the reaction rates are temperature dependent, a change in temperature will effect the model results. The reaction rates for two body reactions are of the form

$$k = \alpha(T/300)^\beta \exp(\gamma/T) \text{cm}^3\text{s}^{-1}$$

(38)

where $\alpha$, $\beta$ and $\gamma$ are constants taken from the UMIST database (Woodall, et al. 2007). The reaction rates for reaction 6, are the same regardless of the length of each cyanopolyyne but vary with temperature. A reduction in
temperature to 100K, increases the reaction rate by 1.6 and therefore increases the abundances. This is shown in figure 14. The sulphur bearing species SO and SO$_2$ also show similarities with temperature up to $10^5$ years since the rate coefficients for reactions (28) and (30) are independent of temperature. The abundances vary after $10^5$ years since SO is mainly formed by reaction (29) which has a rate coefficient that is enhanced by a factor of 24 for a temperature of 200K. In figure 15 we consider the effect of a change in density. The increase by a factor of 10 to $n_{\text{H}_2} = 8 \times 10^4 \text{cm}^{-3}$ also enhances the species abundances, but does not greatly effect the time dependent features.

5 SUMMARY
In the core chemical model presented here, with density $n_{\text{H}_2} = 8 \times 10^4 \text{cm}^{-3}$ and a temperature of 200K, the car-
Figure 14. Comparing the time dependent chemistry for model with $n_{H_2} = 8 \times 10^4 \text{cm}^{-3}$ and temperatures of 100 and 200K.

Figure 15. Comparing the time dependent chemistry for model with a temperature of 200K and densities of $n_{H_2} = 8 \times 10^4 \text{cm}^{-3}$ and $n_{H_2} = 8 \times 10^5 \text{cm}^{-3}$.

carbon and sulphur bearing species show highly time dependent chemistry between $10^2$ and $10^6$ years. The grain mantle species OCS and H$_2$S are processed and a rapid sulphur chemistry follows. Although the larger cyanopolyynes HC$_n$N ($n > 3$) are usually not observed and have not been considered in theoretical models in the past, we have shown that they can be produced under hot core conditions. Their abundance is directly linked to acetylene, which is highly abundant in the earlier stages of the core evolution when it is evaporated from grain mantles. The reactions responsible for processing acetylene into the daughter species cyanopolyynes are efficient under hot core conditions. The abundance of the larger cyanopolyynes increase and decrease over a short period of the order of $10^5$ years, and are relatively short lived compared with other more commonly observed species. This may explain why they have been observed in so few sources. Since they are only present in the gas phase for a relatively short time, they make useful species as chemical clocks, if the source age lies within this window. HC$_3$N, however, is produced in large abundances much earlier on than the larger cyanopolyynes which may explain why it has been detected in several sources.

Through the use of a molecular excitation model, we presented a series of line intensity and line ratio plots, useful for the interpretation of spectral line data. Given a series of line intensities measured from a source, these and the associated line ratios can be used to look up the column density of a species. If only limited line data is available, limits may still be placed on the column density. Using both temperature and density dependent plots, the physical parameters may also be determined.

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