CHAPTER III

ABUNDANCE CALCULATION OF CERTAIN INTERSTELLAR MOLECULES

3.1 Introduction

In Chapter II we have considered the formation and destruction processes and rate coefficients of interstellar molecules. In this chapter the calculated abundances of HNO, H₂CS, CH₄, CH₃OH, HCOOH and CH₃NH₂ in the interstellar space are presented. The values thus obtained are compared with the observed values.

In calculating the abundances of interstellar molecules in dark clouds, a model of the cloud is required. It is assumed that

- Mass of the cloud — 300 M☉ (M☉ is the solar mass)
- Optical attenuation coefficient > 1 mag
- Ionization of elements — mainly by cosmic rays
- Average gas temperature — 50°K
- Total number density of molecules — 10⁵ — 10⁶ cm⁻³.

3.2 Calculation of Abundances

a) Nitroxy1 (HNO)

The interstellar nitroxy1 has been detected by Ulich, Hollis and Snyder (1977) and its abundance in Sgr B2 is of the order of 10⁻⁹ n(H), where n(H) is the total number density of hydrogen.
Nitroxyl may be formed by the radiative association of \( \text{NO}^+ \) and \( \text{H}_2 \) (Huntress and Mitchell, 1979). \( \text{NO}^+ \) may be formed by the following reaction

\[
\text{NO} + \text{C}^+ \rightarrow \text{NO}^+ + \text{C}. \quad \text{(3.1)}
\]

It may be lost by recombination with electrons,

\[
\text{NO}^+ + \text{e} \rightarrow \text{N} + \text{O}. \quad \text{(3.2)}
\]

\( \text{NO} \) required for reaction (3.1) has been detected in interstellar clouds and its observed abundance is \( 10^{-8} \text{n(H)} \) (Liszt and Turner, 1978). The rate coefficient of reaction (3.2) is of the order \( 10^{-7} \, \text{cm}^3 \, \text{s}^{-1} \). Assuming the electron number density as \( 3 \times 10^{-7} \text{n(H)} \), the calculated abundance of \( \text{NO}^+ \) is \( 2 \times 10^{-14} \text{n(H)} \). The radiative association reaction of \( \text{NO}^+ \) and \( \text{H}_2 \) gives

\[
\text{NO}^+ + \text{H}_2 \rightarrow \text{H}_2\text{NO}^+ + \text{hv}. \quad \text{(3.3)}
\]

Finally, through dissociative electron recombination \( \text{HNO} \) may be obtained

\[
\text{H}_2\text{NO}^+ + \text{e} \rightarrow \text{HNO} + \text{H}. \quad \text{(3.4)}
\]

The main loss processes of \( \text{HNO} \) are (Ghosh and Ghosh, 1981c)

\[
\text{HNO} + \text{C}^+ \rightarrow \text{HCO}^+ + \text{N} \quad \text{(3.5)}
\]

and

\[
\text{HNO} + \text{hv} (\lambda < 5891.6 \text{Å}) \rightarrow \text{H} + \text{NO}. \quad \text{(3.6)}
\]

Huntress and Mitchell (1979) suggested that the rate coefficient for radiative association is \( 5 \times 10^{-14} \, \text{cm}^3 \, \text{s}^{-1} \). For reaction (3.5)
the rate coefficient may be taken as $1 \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ and the photodissociation cross-section as $10^{-18} \text{ cm}^2$ (Calvert and Pitts, 1966). The attenuated photon flux $F(\lambda)$ at 5891.6 Å in the interior of dark clouds may be calculated using the relation (1.1) and is of the order $2 \times 10^4 \text{ cm}^{-2} \text{s}^{-1}$.

The abundance of $C^+$ is (Mitchell, Ginsburg and Kuntz, 1978),

$$\log \left[ \frac{c^+}{n(H)} \right] \approx -9.67, \text{ for } n(H) = 10^5 \text{cm}^{-3}$$

and

$$\log \left[ \frac{c^+}{n(H)} \right] \approx -10.61, \text{ for } n(H) = 10^6 \text{cm}^{-3}.$$ 

Thus the calculated abundance of HNO is

$$\text{HNO}/n(H) \approx 4 \times 10^{-9}$$

which agrees well with the observed value (Ghosh and Ghosh, 1981c).

Huntress and Mitchell (1979) suggested that HNO can also be produced through the radiative association of NH$_3^+$ and O as

$$\text{NH}_3^+ + O \rightarrow \text{NH}_2O^+ + \text{hv}, \quad \cdots(3.7)$$

followed by recombination with electrons,

$$\text{NH}_2O^+ + e \rightarrow \text{HNO} + \text{H}_2. \quad \cdots(3.8)$$

This process can also produce the required amount of HNO if the rate coefficient of reaction (3.7) is $10^{-13} \text{ cm}^3\text{s}^{-1}$. 
Instead of reaction (3.7) Hartquist and Dalgarno (1978) suggested that the bimolecular reaction for the formation of H$_2$NO$^+$ is

\[ \text{NH}_3^+ + \text{O} \rightarrow \text{H}_2\text{NO}^+ + \text{H}, \quad \text{(3.9)} \]

followed by recombination with electron to yield HNO and H. But, Huntress and Mitchell (1979) showed that the products of the bimolecular reaction between NH$_3^+$ and O are HNO$^+$ and H$_2$ rather than as given in reaction (3.9):

\[ \text{NH}_3^+ + \text{O} \rightarrow \text{HNO}^+ + \text{H}_2. \quad \text{(3.10)} \]

This HNO$^+$ may transfer its charge to a metal atom but is incapable of producing observed amount of HNO.

b) Thioformaldehyde (H$_2$CS)

Thioformaldehyde, the sulphur analogue of formaldehyde (H$_2$CO), is widespread in the galaxy. It was detected through the transitions $J_k = 2_{11} - 2_{12}$ and $4_{13} - 4_{14}$ in the dark clouds (Doherty, MacLeod and Oka, 1974). H$_2$CS may be formed by an ion-molecule reaction. However, a loose cluster ion is formed which is then destroyed by a dissociative recombination process. Oppenheimer and Dalgarno (1974) suggested a radical reaction, viz.

\[ \text{CH}_3 + \text{S} \rightarrow \text{H}_2\text{CS} + \text{H} \quad \text{(3.11)} \]

adopting a rate coefficient $10^{-11}\text{cm}^3\text{s}^{-1}$ which is thought to be fast (Liddy, Freeman and McEwan, 1975).
H₂CS may be formed through the radiative association of H₂ and CS (Ghosh and Ghosh, 1979a) as

\[
H_2 + CS \rightarrow H_2CS + hv. \tag{3.12}
\]

The interstellar chemistry of H₂ is already discussed in detail (Dalgarno and Black, 1976, Lee, 1972, Allen and Robinson, 1975). The formation and destruction mechanisms of CS are discussed by Oppenheimer and Dalgarno (1974). The observed abundance of CS is about \(10^{-7}n(H)\) (Sargent, 1975).

The principal chemical destruction mechanisms of H₂CS include (Ghosh and Ghosh, 1979a)

\[
H_2CS + C^+ \rightarrow H_2CS^+ + C \tag{3.13}
\]

and

\[
H_2CS + O \rightarrow OCS + H_2. \tag{3.14}
\]

The rate coefficient for charge exchange reaction (3.13) may be taken as \(10^{-9}\text{cm}^3\text{s}^{-1}\) (Oppenheimer and Dalgarno, 1974) and that for neutral-neutral reaction (3.14) is of the order \(10^{-13}\text{cm}^3\text{s}^{-1}\) (Nieles, 1974).

The other route for the formation of H₂CS may be the radiative association of CH₂ and S (Ghosh and Ghosh, 1979a),

\[
CH_2 + S \rightarrow H_2CS + hv. \tag{3.15}
\]

Dalgarno and Black (1976) discussed the formation and destruction processes of interstellar CH₂. Its abundance is still uncertain. The observed abundance of S is about \(10^{-5}n(H)\) (Morton and Hu, 1975).
Dalgarno, Oppenheimer and Black (1973) suggested that CH$_3$ may be formed by the following processes,

\[ \text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+_2 + \text{hv} \]  \hspace{1cm} (3.16)
\[ \text{CH}^+_2 + \text{H}_2 \rightarrow \text{CH}^+_3 + \text{H} \]  \hspace{1cm} (3.17)
\[ \text{CH}^+_3 + \text{e} \rightarrow \text{CH}^+_3 + \text{hv} \]  \hspace{1cm} (3.18)

assuming (i) the reaction (3.16) is very fast, (ii) reaction (3.17) is highly probable, and (iii) that the rate coefficient of reaction (3.18) is not smaller than $10^{-3}$ times the dissociative recombination rate. Thus, CH$_3$ formed by this process may not follow the reaction (3.11). But CH$_3$ can be formed through the radiative association of CH and H$_2$ which occurs at an appreciable rate in the flash photolysis of methane (Braun, McNeby and Bass, 1967). The compound CH$_3$ formed by this process may provide another route for H$_2$CS formation, namely

\[ \text{CH}^+_3 + \text{S} \rightarrow \text{H}_2\text{CS} + \text{H} \]  \hspace{1cm} (3.19)

The rate coefficient for this reaction may be taken as $10^{-13}\text{cm}^3\text{s}^{-1}$ (Nieles, 1974).

The radiative association reaction occurs in the following two-step process

\[ \text{X} + \text{Y} \rightarrow (XY)^* \]  \hspace{1cm} \text{Forward rate:} R_1 (\text{in cm}^3\text{s}^{-1})
\[ \text{Backward rate:} R_2 (\text{in s}^{-1}) \]
\[ (XY)^* \rightarrow XY + \text{hv} \]  \hspace{1cm} \text{Rate} R_2 \text{ in (Sec}^{-1})).
This type of association is known as 'inverse vibrational predissociation' (Herzberg, 1966). At first, it is assumed that $R_1$ is equal to the Langvin value and is of the order of $10^{-9}$ cm$^3$s$^{-1}$.

A $N$-atom complex is assumed to possess $S( = 3N - 6)$ harmonic oscillators of identical frequency. If $j$ be the excited quanta of the complex and if dissociation occurs when $m$ ($m < j$) quanta are transferred to a single oscillator, the statistical rate of dissociation is given by

$$R_{-1} = \frac{(j - m + s - 1)! \cdot j!}{(j + s - 1)! \cdot (j - m)!} \text{ sec}^{-1}.$$

The spontaneous emission rate constant ($R_2$) is approximately equal to $10^2$ times the average number of excited infrared active oscillators in the complex.

Hence the radiative association rate coefficient becomes

$$R = \frac{R_1 R_2}{R_{-1} + R_2} \approx \frac{R_1 R_2}{R_{-1}} \text{ cm}^3\text{s}^{-1}.$$

In this case ($\text{H}_2\text{CS}$)* has six normal modes and the value of $R$ is approximately equal to $2 \times 10^{-16}$ cm$^3$s$^{-1}$.

The observed abundance of $\text{H}_2\text{CS}$ in a dark cloud is $10^{-9}n(\text{H})$ (Doherty et al. 1974). Under steady state condition the calculation shows that $\text{H}_2\text{CS}$ formed by reaction (3.12) is
able to supply required amount of $\text{H}_2\text{CS}$ in such a cloud and that by reaction $(3.15), 10^{-1}$ times the observed value. The reaction $(3.19)$ has proved to be of no consequence (Ghosh and Ghosh 1979a).

The radiative association

$$\text{HCS}^+ + \text{H}_2 \rightarrow \text{H}_2\text{CS}^+ + \text{hv} \quad \cdots (3.20)$$

followed by

$$\text{H}_2\text{CS}^+ + \text{e} \rightarrow \text{H}_2\text{CS} + \text{H}, \quad \cdots (3.21)$$

may be another route for $\text{H}_2\text{CS}$ formation, but the calculated abundance does not agree well with the observed value.

$\text{H}_2\text{CS}$ may also be formed through the ion-molecule reactions

$$\text{CH}^+_3 + \text{COS} \rightarrow \text{H}_2\text{CS}^+ + \text{CO} \quad \cdots (3.22)$$

and

$$\text{CH}^+_3 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{CS}^+ + \text{H}, \quad \cdots (3.23)$$

followed by recombination with electrons to yield $\text{H}_2\text{CS}$ and $\text{H}$. The rate coefficients for reactions $(3.22)$ and $(3.23)$ at $300^\circ \text{K}$ are $1.4 \times 10^{-9}$ and $1.2 \times 10^{-9} \text{cm}^3\text{s}^{-1}$ respectively (Smith and Adams, 1978). The calculated abundance by these processes agrees well with the observed value.

c) Methane ($\text{CH}_4$)

Due to the nonthermal excitation of methane, its column density is uncertain in the interstellar medium. It is recently detected in Orion A (Fox and Jennings, 1978). The radiative
association of CH$_3^+$ ion with H$_2$ is

\[
\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + \text{hv} \tag{3.24}
\]

followed by

\[
\text{CH}_5^+ + e \rightarrow \text{CH}_4 + \text{H} \tag{3.25a}
\]

\[
\rightarrow \text{CH}_3 + \text{H}_2 \tag{3.25b}
\]

may yield methane molecule. The rate coefficients for reaction (3.24) at 100°K, 50°K and 20°K are 2.9 x 10$^{-14}$, 4 x 10$^{-13}$ and 1.3 x 10$^{-11}$cm$^{-3}$s$^{-1}$ respectively (Smith and Adams, 1978). Its loss processes may be as follows (Ghosh and Ghosh, 1981c)

\[
\text{CH}_4 + \text{C}^+ \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \tag{3.26a}
\]

\[
\rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2 \tag{3.26b}
\]

and

\[
\text{CH}_4 + \text{hv} \rightarrow \text{CH}_3 + \text{H}. \lambda < 2817 \text{ A} \tag{3.27}
\]

The rate coefficient of reactions (3.26a) and (3.26b) is 1.45 x 10 cm$^{-3}$s$^{-1}$ (Anicich et al., 1976). The abundance of CH$_3^+$ has been presented earlier. The attenuated photon flux at 2817 A is nearly 10$^{2}$-10$^{3}$cm$^{-2}$s$^{-1}$. The calculated abundance of methane under steady state condition at 100°K, 50°K and 20°K are 10$^{-6}$n(H), 2 x 10$^{-5}$n(H) and 6 x 10$^{-4}$n(H)cm$^{-3}$ respectively. These values agree well with the observed values.

d) Methanol (CH$_2$OH)

Gottlieb et al (1979) detected methanol in the dark cloud of interstellar space. Its average abundance is of the order
$10^{-7} n(H)$: It may be formed from the association of $CH^+$ with $H_2O$ (Huntress and Mitchell, 1979)

$$CH^+_3 + H_2O \rightarrow CH_3OH^+ + hv \quad \text{(3.28)}$$

followed by

$$CH_3OH^+ + e \rightarrow CH_3OH + H. \quad \text{(3.29)}$$

The rate coefficients for the reaction (3.28) at 100°K, 50°K and 20°K are $8 \times 10^{-11}$, $2 \times 10^{-9}$ and $2.5 \times 10^{-9}$ cm$^3$ s$^{-1}$ respectively (Smith and Adams, 1978). The observed abundance of $H_2O$ in Orion A is $H_2O/n > 10^{-6}$ (Waters et al., 1979). The loss processes of methanol are (Ghosh and Ghosh, 1980b)

$$C^+ + CH_3OH \rightarrow CH_3OH^+ + C \quad \text{(3.30a)}$$
$$\quad \rightarrow CH_3O^+ + CH \quad \text{(3.30b)}$$
$$\quad \rightarrow HCO^+ + CH_3 \quad \text{(3.30c)}$$
$$\quad \rightarrow CH^+_3 + HCO \quad \text{(3.30d)}$$

and

$$CH_3OH + hv \rightarrow CH_3O + H. \quad \text{(3.31)}$$

The attenuated photon flux at 2809 A in the denser regions of dark clouds is less than $10^3$ cm$^{-2}$ s$^{-1}$. The calculated abundance of methanol at 100°K, 50°K and 20°K are $8 \times 10^{-8}$, $1.5 \times 10^{-7}$ and $2 \times 10^{-7}$ cm$^{-3}$ respectively. These values agree well with the observed value.

An alternate path for the formation of methanol may be the association of $CH_2^+$ and $H_2O$, but this process can supply only $10^{-2}$ times the observed value (Ghosh and Ghosh, 1980b).
e) **Formic Acid (HCOOH)**

Formic acid was detected in the denser regions of dark clouds of interstellar medium and its observed abundance is obtained as \((10^{-10} - 10^{-11})n(H)\) (Winnewisser, et al. 1975). It may be formed through the radiative association of \(\text{CH}_3^+\) ion with \(O_2\) molecule (Huntress and Mitchell, 1979)

\[
\text{CH}_3^+ + O_2 \rightarrow \text{CH}_2^+ + O_2 + hv \tag{3.32}
\]

followed by

\[
\text{CH}_2^+ + O_2 + e \rightarrow \text{HCOOH} + H \tag{3.33}
\]

The abundance of \(O_2\) is \((10^{-3} - 10^{-5})n(H)\). The rate coefficients for reaction (3.32) at 100°K, 50°K and 20°K are \(3 \times 10^{-15}\), \(4.8 \times 10^{-14}\) and \(1.9 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}\) respectively (Smith and Adams, 1978). Smith and Adams (1978) have suggested that the reaction (3.32) may be only a minor channel for the formation of formic acid. Its loss processes may be as follows (Ghosh and Ghosh, 1980b):

\[
\text{C}^+ + \text{HCOOH} \rightarrow \text{HCO} + \text{COH}^+ \tag{3.34a}
\]

\[
\rightarrow \text{HCOOH}^+ + C \tag{3.34b}
\]

and

\[
\text{HCOOH} + hv \rightarrow \text{HCO} + \text{OH} \tag{3.35}
\]

The calculated abundances of formic acid at 100°K, 50°K and 20°K agree well with the observed value.

An alternative mechanism,

\[
\text{HCO}^+ + \text{H}_2\text{O} \rightarrow \text{HCOOH}_2^+ + hv \tag{3.36a}
\]

\[
\rightarrow \text{H}_3\text{O}^+ + \text{CO} \tag{3.36b}
\]

followed by

\[
\text{HCOOH}_2^+ + e \rightarrow \text{HCOOH} + H \tag{3.37}
\]
may give HCOOH (Huntress and Mitchell, 1979). If the rate
coefficient for reaction (3.36a) is $10^{-13}$ cm$^{-3}$ s$^{-1}$ at 50°K,
the calculated abundance agrees well with the observed value.

g) Methylamine (CH$_3$NH$_2$)

From the transitions $5_{15} - 5_{05}$ (73.0 GHz) the presence of
interstellar methylamine was confirmed (Kaifu et al, 1974
and Fourikis et al, 1974). Its observed abundance is obtained
as $10^{-10}$n(H). Smith and Adams (1978) have suggested that the
radiative association

$$\text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_3\cdot \text{NH}_3^+ + \text{hv}$$  \hspace{1cm} (3.38)

followed by

$$\text{CH}_3^+ \cdot \text{NH}_3^+ + e \rightarrow \text{CH}_3\text{NH}_2 + \text{H}$$  \hspace{1cm} (3.39)

may be a possible source of methylamine. The rate coefficients
for reaction (3.38) at 100°K, 50°K and 20°K are $>4 \times 10^{-11}$,
$>4 \times 10^{-10}$ and $5 \times 10^{-10}$ cm$^{-3}$ s$^{-1}$ respectively (Smith
and Adams, 1978). The loss processes of methylamine are (Ghosh
and Ghosh, 1980b) :

$$\text{C}^+ + \text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{NH}^+_2 + \text{C}$$  \hspace{1cm} (3.40a)

$$\rightarrow \text{CH}_3\text{NH}^+_2 + \text{CH}$$  \hspace{1cm} (3.40b)

$$\rightarrow \text{H}_2\text{CN}^+ + \text{CH}_3$$  \hspace{1cm} (3.40c)

$$\rightarrow \text{CH}_3^+ + \text{(HCN + H)}$$  \hspace{1cm} (3.40d)

and

$$\text{CH}_2\text{NH}_2 + \text{hv} \rightarrow \text{CH}_2 + \text{NH}_2\cdot$$  \hspace{1cm} (3.41)

$\lambda < 3536$ A

The calculated abundance at 50°K by reaction (3.38) does not
agree with the observed value (Ghosh and Ghosh, 1980a).
The heat of formation of CH$_3$ is 33°K cal/mole (1.44 ev) which can easily dissociate NH$_4^+$ (NH$_3^+$ - H) and may form CH$_3$.NH$_3^+$ whose ground state binding energy is 4.6 ev. The reaction of CH$_3$ and NH$_4^+$ is

$$\text{CH}_3 + \text{NH}_4^+ \rightarrow \text{CH}_3\cdot\text{NH}_3^+ + \text{H}.$$  (3.42)

The complex CH$_3$·NH$_3^+$ can produce methylamine by electron recombination. The calculated rate coefficient for reaction (3.42) is $7 \times 10^{-10}$ cm$^3$ s$^{-1}$ at 50°K. But this process cannot supply the required amount of methylamine (Ghosh and Ghosh, 1980b).

Huntress and Mitchell (1979) proposed that the radiative association reaction

$$\text{CH}_3^+ + \text{NH}_3 \rightarrow \text{CH}_3\cdot\text{NH}_3^+ + \text{H}_2$$  (3.43)

followed by electron recombination would yield an abundance of methylamine in good agreement with observation provided CH$_3^+/\text{CH}_3^+$≈10 and rate coefficient for reaction (3.43) $\approx 10^{-9}$ cm$^3$ s$^{-1}$.

3.3 Discussion

The reactions presented in the previous sections of this chapter can produce a large variety of molecules observed in dark clouds. In most cases laboratory rate coefficients are used to calculate the abundances of molecules. Even then, more and accurate laboratory data for rate coefficients of
radiative association and bimolecular reactions are needed at low temperatures to explain the observed abundances. Progress in the development of chemistry of the interstellar medium will be accelerated by theoretical and laboratory studies of possible reactions. However the essential requirement is an enlarged observational programme at high spatial resolution over an extended wavelength region which allows a variety of interstellar molecules to be studied. From the above study it may be concluded that ion-neutral collisions play dominant role for the formation and destruction of interstellar molecules.
REFERENCES


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