

MODELS OF HOT MOLECULAR CORES

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Abstract. We review the properties of hot molecular cores with specific reference to chemical modelling. While most theoretical modelling has been generic, we discuss models for two specific sources, G34.3+0.15 and W3 (H₂O). We show that the hot core gas in both these regions has an age of $5 \times 10^3 - 10^4$ yrs and that the abundances of many molecules are consistent with formation in the gas-phase following evaporation of simple molecular ices from the grains. We end with a discussion of current problems and future directions.

1. Introduction

Interstellar molecular clouds represent a wide spectrum of physical conditions and chemical compositions. Complex molecules have been observed in two types of cloud. Cold, dense clouds, such as Taurus Molecular Cloud 1 (TMC-1), have $n(\text{H}_2) \sim 10^4 \text{ cm}^{-3}$, $T \sim 10 \text{ K}$ and $A_V \sim 10 \text{ mag}$. They are observed to be rich in large, linear unsaturated molecules such as the cyanopolyynes, HC₃N, HC₅N, HC₇N, HC₉N, C_nH (n=2-8), organo-sulphur species, C₂S, C₃S, and C₂O, C₃O and the carbenes H₂CCC and H₂CCCC. In addition, there are a large number of D-bearing molecules observed with D/H ratios enhanced by factors of $10^3 - 10^4$ over the cosmic D/H ratio of $\sim 1.5 \times 10^{-5}$ (Table 1). The fractional ionisation in these clouds is derived from measurements of molecular ions and is fairly small, $\sim 10^{-8}$, consistent with ionisation by low-energy cosmic-rays at a rate $\sim 10^{-17}$ ionisations per s per H-atom. Molecules of intermediate size, such as CH₃OH and CH₃CN, have fractional abundances $\sim 10^{-9}$. Essentially all of the observational evidence to date can be interpreted in terms of purely gas-phase chemical processes at low temperature – the latter being essential to account for the deuterium fractionation observed (see Millar et al. 1987, 1989, Millar &

Herbst 1990, Millar 1992, Hasagawa & Herbst 1993, Herbst et al. 1994). Molecular hydrogen, on the other hand, needs to be produced on grain surfaces while the detection of infrared ice bands implies that some fraction, but not all, of the gas phase molecules freeze onto dust particles at low temperatures.

Hot molecular cores (HMCs) are small ($\lesssim 0.1$ pc), dense ($n(\text{H}_2) \sim 10^6 - 10^8 \text{ cm}^{-3}$), hot ($T \sim 100 - 300$ K) and dark ($A_V \sim 10^3$ mag) clumps of gas in regions of massive star formation. Physically they appear to have been affected by nearby or internal star formation, either through direct heating or shock interaction. Chemically, they are known to be very different from cold clouds. They contain very large abundances of saturated molecules, including small species such as H_2O , NH_3 , H_2S and CH_4 , and large species such as CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{CN}$ and $(\text{CH}_3)_2\text{O}$, with abundances larger by a factor of at least 10^3 over those in cold clouds. Very few unsaturated hydrocarbon molecules are detected. Cyanoacetylene, HC_3N , is detected, often in vibrationally excited states, but larger cyanopolyynes are not. C_2H has been detected but no larger C_nH molecule. It may be that C_2H occupies a skin layer around a hot core and may not trace the hot dense gas in the volume of the core. Additionally, D fractionation is seen in many molecules, including HDO , NH_2D , DCN and HDCO with enhancements similar to those in cold clouds (Table 1). Indeed the fractional abundance of NH_2D in the Orion Hot Core is larger than that of NH_3 in TMC-1. Since fractionation is a very temperature-sensitive process (see Millar 1993, Millar et al. 1989), the chemical synthesis of deuterium must be occurring at cold temperatures, *not* at the gas kinetic temperature of the hot gas. Taken together with the abundance enhancements of saturated molecules, the implication is that significant processing has taken place on grain surfaces. In this sense, HMCs can be placed in an evolutionary picture of star formation. Cold, dense cores are at an early, or pre-collapse phase. The time-scale for accretion of gas onto grain surfaces is $\sim 3 \times 10^9/n \text{ (cm}^{-3}\text{) yr}$ at 10 K, so that on a timescale of $\sim 10^6$ yr, the cold, unsaturated, but D-rich molecules freeze onto grains to form molecular rich ices and can be detected by IR observations of protostellar sources. Once star formation occurs, heating or shock-induced processes liberate the mantle molecules into a hot, dense and essentially neutral gas – the latter is a result of cosmic-ray ionisation being less efficient at high density. Since the grain surface chemistry tends to form chemically stable molecules, the hot gas is stable for time-scales of at least $10^3 - 10^4$ yr. Eventually however, these parent species are destroyed to produce daughter molecules, some of which may also be very complex.

TABLE 1. Abundance ratios of D-bearing molecules to their H-bearing parents.

Molecule	TMC-1 ¹	OMC-1 ²	Hot Core ³
HDO			> 0.002
DCO ⁺	0.015	0.002	
N ₂ D ⁺	<0.045		
DCN	0.023	0.02	0.005
DNC	0.015	0.01	
C ₂ D	0.01	0.045	
NH ₂ D	<0.02		0.003
HDCO	0.015	0.02	0.14
c-C ₃ HD	0.08		
C ₄ D	0.004		
DC ₃ N	0.06		
DC ₅ N	0.013		
CH ₃ OD			0.03
CH ₂ DOH			0.04
CH ₂ DCCH	0.054	<0.05	
D ₂ CO			0.02

¹ TMC-1: Taurus Molecular Cloud 1, T = 10 K

² OMC-1: Orion Molecular Cloud 1, T ~ 60 K

³ Hot Core: Orion Hot Core, T ~ 150-200 K

2. Chemical models – recent work

The first models of HMCs were developed by Brown et al. (1988) who considered a three phase scenario. In phase (1), they followed the chemistry and accretion of an initially atomic gas (with the exception of H₂) as it underwent collapse to high density. Since the accretion time-scale ($\sim 10^6$ yr) was shorter than the timescale to reach a chemical steady-state, the accreted grain mantle was rich in atoms such as C, N and O. Phase (2) followed the hydrogenation of these atoms on the grain surface. Hydrogenation is always rapid, providing that there are sufficient H-atoms to collide with the dust. This requires a fractional abundance $\sim 10^{-3}$ which is met at low density and at early times. In this case all accreted C, N and O atoms are converted to CH₄, NH₃ and H₂O with abundances which agree well with observations of many hot cores. At higher density and later times, the H-atom abundance is less whilst the atoms are processed in the gas into stable molecules such as CO, N₂ and O₂. In this case these molecules accrete on

to the grains, along with heavier species. In phase (3), Brown et al. followed the chemistry of the evaporated molecules in the hot gas and found that, with a rather limited chemistry, the molecules survived for at least 10^4 yr. Brown & Millar (1989 a,b) extended this work to include deuterium with essentially the same conclusions, and showed also that multiply deuterated molecules would be formed on the surface. Brown and colleagues concluded that observations of gas phase molecules in hot cores would give direct information on the composition of ice mantles in the cold phase. Since infrared observations cannot detect molecules whose abundances are $\lesssim 1\text{--}5\%$ of the total number of molecules in the ice, whereas submillimeter observations of gas phase molecules are sensitive to abundances 10^6 times smaller, one can hope to use these observations to trace species in grain ices, and thus to constrain grain surface chemistry to a significant degree. This early hope has not yet clearly been achieved partly because more recent models of phase (3) have shown that chemical processing in the hot gas can be efficient for some species. On the other hand, such processing offers one the hope to develop a 'chemical clock' for HMCs – that is, to find molecules whose abundances are sensitive to the time-scale following mantle evaporation. Millar (1993) has given a review of the early theoretical models of hot molecular cores.

Observations of HMCs have concentrated on two sources in Orion – the Orion Hot Core (OHC), and the Compact Ridge (CR) – see Blake et al. (1987) for a summary. The former contains large abundances of N-bearing species, the latter large abundances of O-bearing species. This is surprising since both sources lie close together in the sky and close to a very luminous ($\sim 10^5 L_{\odot}$) source IRc2. The Compact Ridge cloud lies on the edge of the southern molecular ridge cloud in Orion, a cloud of much lower density and temperature. Theoretical arguments for the differing compositions were suggested by Charnley et al. (1992) in terms of differences in evaporated mantle compositions, although they did not attempt to answer the fundamental question – why do grain mantles differ in two clumps of gas which are relatively close in the Orion molecular cloud?

Caselli, Hasagawa & Herbst (1993) produced a theoretical model to provide an answer. They modelled the collapse of a molecular cloud onto a central protostellar object and included a radial temperature distribution in the collapse. Since the ability of molecules to remain on grains is a sensitive function of grain temperature, the mantle composition becomes a function of temperature and therefore radial distance from the central source. In their picture the OHC represents denser material closer to the central object. The higher temperatures during the collapse of the OHC lead to the loss of volatile molecules, in particular CO which, when accreted, can form H_2CO and CH_3OH through surface addition of H-atoms (Hiraoka et

al. 1994). Thus in this source O-bearing molecules are relatively unaffected by the grain chemistry. However at the lower initial temperature of the CR cloud, CO can stick to dust grains and be converted to H₂CO and CH₃OH. The evaporation of these molecules then drives the formation of more complex O-bearing molecules in the gas phase.

The model of Caselli et al. (1993) represents one of the few calculations which have attempted to follow both the gas phase and solid-state chemistry in a collapsing object. Although this was treated also by Brown et al. (1988), Caselli et al. included a much more extensive grain chemistry. However, it should be noted that such a calculation is computationally very expensive and also subject to much uncertainty as rates of evaporation, following accretion, and surface mobilities are exponentially dependent on grain temperatures. For this reason, many recent models of hot core chemistry have ignored the collapse phase and simply followed the chemistry of material evaporated from mantles. Since reaction with H-atoms likely dominates the surface chemistry, Charnley & Millar (1994) investigated the hot core chemistry of phosphorus assuming that PH₃ is evaporated from mantles, while Charnley (1996) has investigated sulphur chemistry following evaporation of H₂S and MacKay (1995) the chemistry of silicon following the release of SiH₄.

Charnley & Millar (1994) showed that PH₃ is rapidly destroyed in hot gas – the activation energy for destruction by H-atoms is small – and that phosphorus could be rapidly converted to PN with some PO and P also produced. The activation energy barrier for reaction of H₂S with H is also small, < 400 K, and the S atoms released are extremely reactive. Because of the small activation energy, Charnley (1996) found that the timescale for H₂S destruction can vary widely depending on the gas temperature, with a timescale of about 1000 yr found for T ~ 300 K. Because sulphur is an abundant and reactive element, the hot gas chemistry produces CS initially which is then converted through SO into SO₂. Charnley (1996) proposed that detailed observations of S-bearing molecules in hot cores might be used as a ‘chemical clock’ to measure the time from when the mantles were liberated by star formation.

MacKay (1995) studied the evaporation of ices containing SiH₄. Because most silicon is heavily depleted in interstellar clouds, with much of it being incorporated into refractory grain cores, only relatively little SiH₄ may evaporate. This is quickly processed into SiO which, even if it has an abundance only 0.01% of the cosmic silicon abundance, is readily observable in hot molecular clouds. Measured fractional abundances of SiO approaching 10⁻⁶ have been determined in some sources and indicate violent shock interactions rather than the thermal liberation of icy mantles.

Finally, we note that Charnley et al. (1995), motivated by the ethanol

TABLE 2. Physical parameters adopted in the G34.3 model. The radial distance, r , is measured in pc.

Component	$n(\text{H}_2)$ (cm^{-3})	T (K)	Outer radius (pc)	$N(\text{H}_2)$ (cm^{-2})	A_V (mag)
Ultracompact core	$2 \cdot 10^7$	300	0.01	$6 \cdot 10^{23}$	640
Compact core	10^6	$30r^{-0.4}$	0.1	$2.7 \cdot 10^{23}$	288
Halo	$10^4 r^{-2}$	$30r^{-0.4}$	3.5	$2.9 \cdot 10^{23}$	310

measurements of Millar et al. (1995), have investigated the hot gas-phase chemistry which results when alcohols are released from grain mantles. They find that large esters and ethers, such as $\text{CH}_3\text{OC}_2\text{H}_5$ (methyl ethyl ether) can form on timescales of 10^4 – 10^5 yr. Because of their large size, partition function arguments show that emission from such species should be very weak but may be detectable with current instrumentation.

3. Detailed source modelling

With the exception of the models discussed for the Orion hot cores by Charnley et al. (1992) and Caselli et al. (1993), there has been, until recently, no attempts to model more distant sources. In this section we discuss models developed for two other hot cores, that associated with the ultracompact HII region, G34.3+0.15, and that describing W 3(H₂O).

3.1. G34.3+0.15

This molecular cloud has been studied through a 330–360 GHz spectral scan at the JCMT (Macdonald et al. 1996) and via multitransitional studies of CS (Hauschildt et al. 1995), NH_3 (Heaton et al. 1989), HCO^+ (Heaton et al. 1993) and Cl/CO (Little et al. 1994) and, as a result, its chemical and physical parameters are relatively well determined. The molecular cloud has a three component structure, outlined in Table 2, with the densest and hottest component sitting at the head of a cometary HII region. The interaction between the HII region and the cloud appears to be liberating molecules to the gas. The JCMT spectral scan detected 338 lines from 35 species and rotation diagrams were used to obtain estimates of column density, N , and rotational temperature, T_{rot} , for 13 species. The observations clearly show evidence of emission from all three components.

A detailed time- and depth-dependent chemical kinetic model has been constructed to investigate chemical evolution within the G34.3 cloud. Phys-

ical parameters for this three component model are given in Table 2. Our chemical network is chosen so that we can follow the formation of molecules from atomic gas in the halo, and the breakdown of parent molecules liberated from grains in the hot cores of G34.3. The network contains 225 species and 2184 reactions. Models have been calculated at each of 22 radial positions over a period of 10^8 yr. In the cores, the initial state of the gas is molecular with abundances based on the observed and likely components of interstellar grain mantles. For the halo, all elements are atomic (with the exception of H_2) with total abundances given by summing the relevant abundances of species in the core. Thus for OI we set the initial fractional abundance in the halo as

$$f(\text{OI}) = f(\text{CO}) + f(\text{H}_2\text{O}) + f(\text{CH}_3\text{OH}) + f(\text{H}_2\text{CO}) + 2f(\text{O}_2)$$

where the abundance on the right hand side of this equation refer to the initial fractional abundances in the core. This procedure ensures that the total elemental abundances are equal at every point in the cloud, and are consistent with a picture in which all heavy elements in the gas accrete onto grains in high density cores where they are synthesised to molecular form before evaporation into hot gas.

In order to compare with observations we combine abundances calculated for a specific time, t_{halo} , in the halo gas and those calculated for a different time, t_{core} , in the two inner hot cores, with the restriction that $t_{\text{halo}} > t_{\text{core}}$, since the cloud must be older than the age of the hot gas. Figure 1 gives an example of the output and shows the fractional abundances of selected species with respect to H_2 as a function of radial distance at a time $t_{\text{core}} = 10^4$ yr, $t_{\text{halo}} = 10^5$ yr. Since observations detect column density and not number density, we have integrated to calculate N .

Parent molecules, that is those liberated from grains, get destroyed on timescales which are sensitive to the activation energy barrier for reaction with H atoms. For species with large barriers, for example H_2O , it takes much longer than 10^4 yr to destroy them while H_2S , which has $E_A = 350$ K, is destroyed within 1000 yr after release in the hot, 300 K gas in the ultracompact core. By comparing observed and calculated column densities we derive ages, $t_{\text{core}} \sim 3 \cdot 10^3 - 10^4$ yr and $t_{\text{halo}} \sim 10^5$ yr.

Some molecules can be clearly explained as daughter products. An example is HC_3N which is formed in abundance in the ultracompact core through reaction of parent C_2H_2 with CN and is consistent with the detection of vibrationally excited HC_3N in many hot core sources. Note that HC_3N has traditionally been associated as a tracer of *cold* molecular gas in interstellar clouds, but we find it to be produced easily in hot gas provided C_2H_2 is released from grain mantles. The larger cyanopolyynes are formed

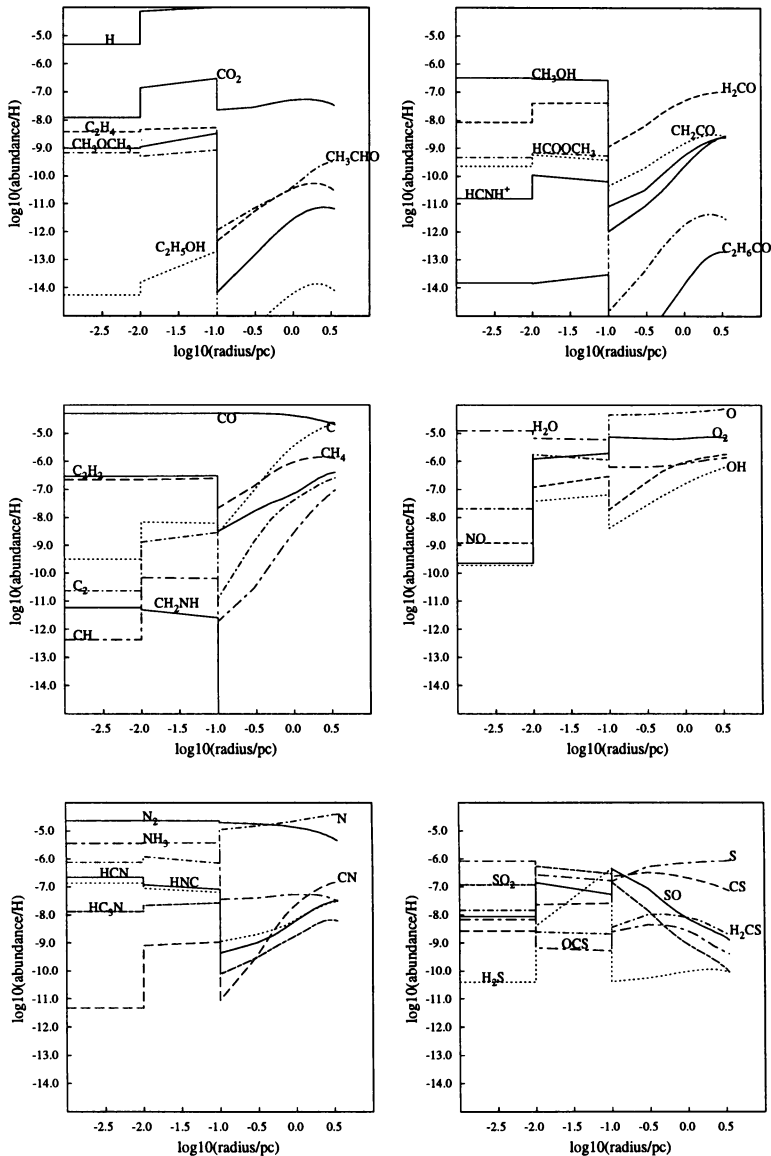


Figure 1. A model for the G34.3 molecular cloud. We plot radial distributions of fractional abundances at 10^4 years in the ultracompact and compact core components, and at 10^5 years in the halo.

inefficiently since we do not consider that grain mantles can contain large unsaturated molecules such as diacetylene, C_4H_2 .

Not all complex molecules appear to be daughter species. While $(CH_3)_2O$ probably is a daughter, the large observed abundances of C_2H_5OH (Millar

TABLE 3. Physical conditions in W 3.

Parameter	W 3 IRS4	W 3 IRS5	W 3(H ₂ O)
T_{kin} (K)	55_{-10}^{+20}	100_{-20}^{+40}	220 ± 40
$n(\text{H}_2)$ (10^6 cm^{-3})	$1.0_{-0.3}^{+1}$	$1.0_{-0.3}^{+1}$	2.0_{-1}^{+4}
$N(\text{H}_2)$ (10^{22} cm^{-2})	$7.0_{-3.5}^{+7}$	12_{-6}^{+12}	9.6_{-5}^{+9}

et al. 1995) and CH₃CN (Olmi et al. 1996a,b; Hatchell et al. 1996) indicate that these may have formed on grain mantles. An observational test for parent/daughter species would be to investigate molecular abundance variations in a wide variety of hot cores. On timescales approaching 10⁴ yr, parents abundances, with the exception of H₂S, are fairly insensitive to time compared to those of daughters. Full details of this model can be found in Millar, Macdonald & Gibb (1996).

3.2. W 3 (H₂O)

Helmich and co-workers have performed a JCMT submillimeter spectral scan at three positions in the W 3 molecular cloud, including W 3 (H₂O) which is a hot molecular core (Helmich et al. 1994, Helmich & van Dishoeck 1997, Helmich, van Dishoeck & Jansen 1996). The physical conditions at these three positions are given in Table 3. The three objects show differing chemical compositions: W 3(H₂O) is rich in saturated and large molecules including CH₃OH, (CH₃)₂O and HCOOCH₃; W 3 IRS4 has large abundances of radicals such as CN and C₂H, small abundances of SO and SO₂ and contains most HCO⁺; W 3 IRS5 has few saturated molecules, but large abundances of SO and SO₂. Helmich & van Dishoeck (1997) suggest that the three sources, which originate from the same parent cloud but have different chemical compositions, are at different evolutionary stages. Toward W 3(H₂O), the large abundance of saturated molecules suggests a hot core chemistry, while toward IRS4 which contains simple molecules, a quiescent chemistry is observed suggesting that, since star formation has already occurred in this region, it is old. IRS5 is the youngest source. It contains a weak, unresolved radio continuum source and has a young outflow which may drive SO and SO₂ formation via shocks, but which is too young to have evaporated molecular mantles to any significant degree.

Helmich, Millar & van Dishoeck (1997) have developed chemical models for each of these three sources, with W 3(H₂O) being modelled as a hot molecular core. They find a best fit to the observations at $t \sim 6000$ yr and

TABLE 4. Model and observed abundances for W 3(H₂O) at $t = 6.3 \cdot 10^3$ yr

Species	x_{mod}	$x_{\text{obs}}/x_{\text{mod}}$	Species	x_{mod}	$x_{\text{obs}}/x_{\text{mod}}$
CO	1.3(-4)	-	CS	8.0(-11)	6.5(1)
CN	6.6(-12)	8.6(1)	SO	6.3(-9)	1.1(0)
HCN	7.9(-9)	8.0(-1)	SO ₂	1.6(-8)	3.3(-1)
HNC	2.1(-9)	2.2(-1)	H ₂ CS	7.2(-11)	1.1(1)
HC ₃ N	1.1(-10)	7.1(-1)	H ₂ S	1.0(-10)	5.2(1)
CCH	2.7(-11)	2.5(1)	OCS	3.1(-11)	3.9(1)
CH ₃ C ₂ H	7.3(-11)	4.4(1)	HCO ⁺	2.5(-10)	4.8(0)
H ₂ CO	5.8(-7)	3.6(-3)	HCS ⁺	7.5(-14)	<1.2(3)
CH ₃ OH	4.1(-6)	1.1(-2)	H ₂ O ¹	7.0(-6)	1.0(0)
CH ₃ CN	3.4(-10)	4.1(-1)	H ₃ O ⁺ ²	1.0(-10)	4(0)
CH ₃ OCH ₃	6.0(-9)	1.7(0)	NH ₃ ³	3.3(-8)	2.0(-1)
CH ₃ OCHO	1.8(-9)	1.9(0)			

a(b) denotes $a \cdot 10^b$.

¹ See Helmich et al (1996a).

² Based on the uncertain column density of Phillips et al. (1992).

³ From Mauersberger et al. (1988).

a comparison of observation and theory is shown in Table 4. The complex molecules (CH₃)₂O and HCOOCH₃ are well fit but only at the expense of predicting abundances for H₂CO and CH₃OH much larger than observed. This may indicate that additional destruction routes for CH₃OH and H₂CO are missing, or that their derived abundances are incorrect, possibly due to optical depth and source size effects. Helmich, Millar & van Dishoeck (1997) have shown that detailed models confirm the evolutionary state of the three sources in W 3 — we refer the interested reader to that paper for further information.

4. Discussion and conclusions

The chemical composition of hot molecular cores appears to be dominated, directly or indirectly, by the evaporation of molecular material from the ice mantles on interstellar dust grains. From a comparison of observations and theoretical models, one can conclude that the ices are not simply a repository for material accreted from cold gas — that is, their composition does not mirror the composition of cold gas in dark clouds. Instead, the mantles undergo a significant degree of chemical processing, principally hydrogenation but also deuteration and the formation of large molecules such

as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$. The details of this processing are still uncertain. It may involve radical production through ultraviolet processing and subsequent reaction, or quantum tunnelling of H and H_2 through activation energy barriers. Whatever the process, the detection of deuterium fractionation in hot cores implies that much of the processing takes place in a cold ice phase. Indeed it is probable that understanding the origin and interrelationship between deuterated species such as HDCO , D_2CO , CH_3OD and CH_2DOH will be the key to describing the chemistry of the molecular ice mantles. In the laboratory, it is already known that H_2CO and CH_3OH can be synthesised from CO through the addition of H atoms at 10 K (Hiraoka et al. 1994).

Since infrared studies of molecular ices, even those with ISO, are not sensitive to mantle components less than 1–5% that of the dominant molecule, H_2O , submillimeter observations of gas-phase molecules in hot cores allow one to probe the trace constituents of the ices, and thus can provide sensitive tests of models for surface chemistry. Such observations are also of importance in studying the star formation process. At high densities, one expects that cold gas, including CO, freezes onto grains and becomes unobservable through radio spectroscopy. In many instances the grain mantles are also unobservable because of the lack of a background continuum source. Although dust continuum emission can be detected from such ‘protostars’, this only gives information on the total mass of dust and gas, via a dust-to-gas ratio. One might therefore expect that there will be a phase in the formation of a star, which may last $10^5 - 10^6$ yr, in which the star formation process becomes ‘invisible’ through the lack of a good observational diagnostic probe. Observational studies of hot molecular cores can help probe this hidden phase of star formation.

Despite our advances in understanding hot molecular cores, much still remains to be done. We need to study the molecular composition of a wide variety of hot cores to look for systematic trends in abundances and excitation. The structure of the molecular cloud associated with G34.3+0.15 is complex and the same may be true in general of hot cores. We need multitransitional studies of several molecules to determine physical structure and studies at offset positions to separate out core/halo contributions.

On the theoretical side, we need to investigate depth-dependent models in which the grain mantle composition may vary radially. Such effects may be expected if sublimation controls the nature of the molecules accreted, as argued by Caselli et al. (1993). There is already some evidence that the mantle compositions differ radially. De Graauw et al. (1996) have studied the ice band features along the line-of-sight to several protostars and find that they can be fitted best by models in which some ices appear to be relatively pure while other ices are mixed. The picture is complicated because

the ices could, in fact, be different layers on the same grain core. The ISO observations of CO₂ have already thrown up one major problem for the hot core models (van Dishoeck et al. 1996). The CO₂ ice band is very prominent, at a level $\sim 15\%$ that of water ice, yet gas-phase absorption due to hot CO₂ has not been observed. Toward young embedded protostars, van Dishoeck et al. (1996) find that the fractional abundance of gas phase CO₂ is at most 2×10^{-7} , less than 5% of that in the solid state, and in marked contrast to CO which is a factor 10–100 times more abundant in the gas than in the ice, and H₂O which has, to within a factor of two, roughly equal abundances in the gas and in the dust. Since the high gas-phase abundances are thought to be produced by evaporation of mantles, it is surprising that gas-phase CO₂ has not been detected since its sublimation temperature is less than that of H₂O. This means that if H₂O has evaporated from grains then CO₂ should also have done so, particularly if, as suggested by the shape of the CO₂ infrared ice band, it is embedded in a H₂O matrix. The band also shows some evidence of a pure CO₂ ice component which might be due to a separate component along the line of sight and may be far enough from the central source to remain frozen. However, it appears that the pure CO₂ ice is much less abundant than the CO₂/H₂O mixture. A final possibility is that CO₂ is destroyed rapidly upon evaporation. CO₂ is a very stable molecule and reactions with abundant species (H,C,N,O,...) have large activation energies and are inefficient. However, Si atoms do react with CO₂ with a rate coefficient of $1.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 300 K (Husain & Norris 1978) and would destroy CO₂ rapidly if Si atoms are present in sufficient abundance.

Although we have a lot of room-temperature laboratory data on which to base our models of hot gas phase chemistry (Mallard et al. 1994), the above discussion on CO₂ shows that we have important gaps in our knowledge. Based on modelling we have asserted that certain molecules, for example C₂H₅OH and CH₃CN, are formed through surface chemistry. However, it is still very possible that we have not correctly identified the gas phase routes to these molecules and that solid state chemistry is a much simpler process than we envisage. In addition to experimental measurements of the rate coefficients of neutral-neutral reactions, we need to build more detailed physical models of grain mantles and cloud structures. We need also to investigate the removal of mantles by shock waves. In shocked regions the neutral gas will reach much higher temperatures than are possible due to thermal evaporation and the subsequent gas-phase chemistry may be qualitatively and quantitatively different from that described in this article. Hot molecular cores promise to be a fascinating laboratory into the study of the star formation process, as well as an astronomical example of fundamental low-temperature solid-state chemistry for many years to come.

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Discussion

Black: How far does the disruption of grains go? Do you see evidence of the break up of refractory grain cores in the hot cores recently surveyed? For example, are there excessive amounts of silicon-bearing species?

Millar: In most hot cores associated with ultracompact H II regions, there appears to be SiO present in the gas with abundances more representative of those expected from thermal evaporation of icy mantles than the much larger abundances expected when refractory cores are broken up.

Glassgold: What is the effect of the large cosmic ray ionisation rate, expected on the basis of the Comptel observations by Bloemen et al. (e.g., 1994, *A&A* 281, L5), on the durability of the molecules released from grain surfaces?

Millar: Large ionisation rates lead to a more rapid destruction of parent molecules and a more rapid gas phase chemistry. In my model for the molecular cloud G34.3 + 0.15 I need an ionisation rate ten times larger than the standard interstellar value in order to reproduce the column density of HCO⁺ observed in the molecular cloud envelope. Much larger enhancements of the cosmic ray ionisation rates can probably be ruled out because HCO⁺ and other ions have not been detected in the dense hot cores of the clouds.

Mauersberger: What is your notion about the physical process of evaporation: is it a single event or can it be maintained over thousands of years? Do all different molecules evaporate simultaneously? Would it make a difference for the models?

Millar: We have, in general, modelled evaporation as a single instantaneous event but have checked that the results are insensitive to evaporation over a time-scale of a few hundred years. If the evaporation occurs over thousands of years, which is the time-scale for appreciable gas-phase processing, then one might expect a significant effect on the model predictions. It is also important to point out that all models have assumed that the ices are well mixed. Evaporation of layered ices or of pure ices, which may have condensed in different regions of the molecular cloud and which may therefore evaporate at different temperatures and different times, have not yet been studied. Recent observational results indicate that such calculations need to be made.

Greenberg: The bottom line to my question is: How can you ignore UV processing in all your discussions of grain evolution? After all, CO₂ is an obvious example of dust photoprocessing. Incidentally even in high temperature and high density regions the UV may be important on relevant (10³ yr) time scales.

Millar: UV processing is, of course, important in the ice mantle evolution. In my models, which only consider what happens after the evaporation of the ices, the UV plays a negligible role, because the UV extinction is around 3000 magnitudes. However, as input, I adopt molecular abundances consistent with those observed in the infrared spectra of ices, i.e., abundances which depend on the chemical and physical history of the ices in the interstellar medium.