

PART 1.

**Chemistry in Pre-Stellar Cores and
Low-Mass Star-Forming Regions**

Chemistry and Depletion in Pre-Stellar Cores

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Abstract. The star-formation history of molecular cores is largely determined by gas phase chemical processes that are greatly modified by gas-dust interactions. Substantial elemental depletions may result from the efficient formation of refractory grain material. The depletion of carbon and of refractory elements such as S, Si, Mg, etc. in molecular clouds is well known, but is very poorly constrained. Star forming regions are cold, dark and chemically quiescent, so that in addition to the initial elemental depletions, an ongoing dynamical depletion of molecular material occurs as gas-phase material freezes out onto the surface of dust grains. Observational evidence for anomalous depletions in low mass star forming clumps became apparent in the early 1980s when the narrowness of molecular emission lines (especially those of NH_3) suggested that high velocity infalling material is being depleted from the gas phase. This prompted further studies into the chemical effects of differential depletion and together with radiative transfer models has established molecular diagnostics of infall/depletion sources. Recent observations at high spatial resolution show direct evidence for gas-phase depletions in the central regions of protostellar cores.

In addition to the diagnostic and purely chemical implications for collapsing cores, depletion plays a very active role in the physical evolution of star-forming regions. Most gravitationally unstable low mass cores are believed to be magnetically sub-critical. Recent polarimetric studies of elongated cores are also providing evidence of magnetic alignment, giving strong support to the idea that magnetic fields play a dominant role in core evolution. The relaxation of magnetic pressure (whether through ambipolar diffusion, or by the damping of MHD waves) is critically dependent on the ionization structure which, in turn, is highly sensitive to the elemental and molecular depletions.

1. Introduction

In recent years it has become increasingly appreciated that the star-formation history of molecular cloud cores is largely determined by a combination of gas-phase processes and gas-dust interactions. These interactions fall into three categories:

- i) Depletion (or freeze-out) of atoms and molecules from the gas phase

- ii) Solid-state chemistry in the form of surface reactions occurring on the ice mantles of dust grains, and
- iii) Desorption, or ejection, from ice grain mantles and/or dust grain constituents back into the gas phase

Depletion can itself be further subdivided into (a) the removal of non-volatile elements from the gas, and (b) the depletion of atoms and molecules into icy mantles. The dominant cause of (a) is in the formation of refractory grain cores which are typically believed to be silicates coated in amorphous carbon and/or small particles of carbon, iron, silicon carbide, etc. Such refractory materials are not volatile and the elements that they contain (C, O, Na, Mg, Si, S, Fe, etc.) tend to remain heavily depleted even in relatively diffuse environments which are unshielded from the interstellar ultraviolet radiation field. Of course, some of these elements (e.g. C, O and S) are constituents of both the core and the mantle of the grains and in these cases the level of their depletion is dependent on the physical conditions in their environment.

In the 'standard' dust grain model, a population of large ($\sim 0.1 \mu\text{m}$), mostly refractory, grains is responsible for the visual extinction. The silicates in these grains account for $\sim 10\%$ of the oxygen budget. Typically the oxygen depletion $\delta_{\text{O}} < 20\%$. The ultraviolet extinction is caused by small carbonaceous grains and/or molecules. These, together with the organic mantles on the dust grains, can account for carbon depletions of $\delta_{\text{C}} > 50\%$. The depletions of low ionization potential metals, such as Fe and Mg are close to unity, but sufficiently variable for there to be large variations in the gas-phase abundances. Thus $(1-\delta)$ can be as high as 0.25 or as low as 0.01.

The rate at which a species freezes-out is given by (Rawlings et al. 1992):

$$\dot{n}_i = 4.57 \times 10^4 d_g a^2 T^{1/2} C n_H S_i m_i^{-1/2} n_i \text{ cm}^{-3} \text{ s}^{-1}$$

where d_g is the ratio of the number density of grains to hydrogen nuclei, a is the grain radius in cm, n_H is the hydrogen nucleon density (cm^{-3}), n_i is the number density of species i (cm^{-3}), S_i is the sticking coefficient (in the range 0 to 1), m_i is the molecular mass of species i in amu, and C is a factor which takes into account electrostatic effects. Using

$$\langle d_g a^2 \rangle = 2.2 \times 10^{-22} \text{ cm}^2$$

appropriate for standard dust grain size distribution models (e.g. Mathis, Rumpl, & Nordsieck 1997) and $S \sim 1.0$ we find that that the depletion or 'freeze-out' timescale is typically of the order of 10^5 – 10^6 years in cloud cores. This immediately poses an interesting problem; since this timescale is less than the dynamical evolutionary timescale for molecular clouds in general and star-forming regions in particular, then one might expect that if freeze-out operates with this efficiency then all elements should be fully depleted from the gas-phase. The fact that certain elements (such as Na and S) are depleted by factors of 100–1000 suggest that there is some regulatory mechanism or process in which elements are desorbed from grains. In the case of loosely bound molecular species a variety of desorption mechanisms have been postulated and investigated in some detail, but in the case of tightly bound refractory elements the feedback mechanisms

are currently unclear. Of course, even the material in the refractory cores can be returned to the gas phase in certain extreme situations, such as exist within shocks or HII regions, where grain-grain collisions and sputtering may occur. For this reason, SiO is seen to be a good tracer of shock activity; Si which is sputtered from grains drives a simple silicon chemistry leading to SiO formation. Although the correlation between SiO emission and the shocked boundary layers is sometimes debatable, in most cases the SiO emission accurately delineates regions of shock activity in molecular outflows (e.g. Martín-Pintado et al. 1992).

In addition to the depletion of elements into refractory materials, we must also consider the variable and physical condition-sensitive depletion of elements and molecules into volatile icy and/or organic mantles on the surface of the refractory dust grain cores. These ices (and particularly their surfaces) form the sites for active and apparently highly efficient solid-state chemistry. The products of this surface chemistry can then be returned to the gas-phase and drive an enriched gas-phase chemistry.

Many mechanisms for the return of ice mantle components to the gas-phase ('desorption') have been proposed in the literature. These can broadly be subdivided into three sub-categories; continuous desorption, primarily as a result of interaction with the interstellar radiation field and cosmic ray flux; sudden desorption, brought about by a change in physical conditions, i.e. rapid heating leading to thermal evaporation, and the passage of shocks; and chemical desorption, resulting from the energy released by chemical reactions occurring within the ice mantles. The major uncertainties in all of the desorption processes are the (species-specific) desorption efficiencies, the assumptions about the physics and morphology of the grain substrate, and the ro-vibrational state of the desorbed species.

Due to its high abundance and surface mobility, atomic hydrogen is the most significant reactant on grain surfaces and it is generally assumed that the carbon, nitrogen and oxygen that are frozen out are efficiently hydrogenated to CH₄, NH₃ and H₂O respectively on astrophysically short timescales. The surface chemistry of adsorbed molecules is a somewhat less obvious, but similar hydrogenation reactions can convert species such as CO to H₂CO and eventually CH₃OH. Direct evidence for these processes is provided by the most well-known of all surface reactions; the conversion of H to H₂ in diffuse clouds. Other abundance anomalies in diffuse regions have also been ascribed to surface chemistry. In denser, hotter regions, such as hot cores, the high abundances of complex organics, especially CH₃OH, also requires the presence of an efficient surface chemistry. There are, however, major uncertainties and unresolved issues concerning surface reactions. The theoretical and laboratory bases are limited and it is unclear, for example, why species like NH₃ do not appear to be major ice mantle constituents, whilst CO₂ is highly abundant. The most recent observations by SWAS and Odin (Melnick, this volume) suggest that the spatially averaged gas-phase abundance of H₂O may be much lower than both gas-phase and gas-grain chemical models predict.

There is ample observational and theoretical evidence to suggest that the dust grains retain significant ice mantles in quiescent dark clouds (e.g. Whittet et al. 1996), whilst in dynamically active and more diffuse regions the mantles are desorbed back into the gas phase. However, the absence of retentive ice mantles

does not necessarily imply that surface reactions are inhibited in diffuse clouds. Indeed, the most well known and important of all astrophysical surface reactions, the conversion of H to H₂ occurs in diffuse clouds with high efficiency (e.g. see Duley & Williams 1984). From the correlation between molecular ice absorption bands (such as the water ice feature at 3.1 μm) and the interstellar extinction along the line of sight, it would seem that the onset of ice mantle formation is triggered above a ‘critical’ value of the extinction ($A_v^{crit.}$) which varies from one molecular cloud to another. The physical origin of this criticality and its variation is unclear. Up to now, chemical models have treated this issue in a very simplistic fashion – they merely assume that there are *no* gas-grain interactions at $A_v < A_v^{crit.}$. An equally likely alternative possibility, that molecules freeze-out, hydrogenate and are very rapidly desorbed, has until recently not been considered. Yet, such a process would result in very significant enhancements of the gas-phase abundances of most molecular species in diffuse and translucent clouds.

2. Depletion in Star-forming Regions

In dynamically evolving star-formation regions, and specifically in contracting clouds, depletion plays a number of roles. In the discussion that follows we concentrate on the earliest stages of low mass star-formation when the cloud is largely isothermal and may not even contain a protostar in the form of an infra-red source. In the classification schemes of André et al. (1993) and Ward-Thompson et al. (1994) these objects correspond to “starless cores” and Class 0 objects. We restrict our discussion to low mass ($M \sim 1-3 M_\odot$), rather than high mass, star-forming regions for a number of reasons; as compared to high mass star-forming regions, low mass cores tend to be closer, more likely to occur in isolation with relatively simple geometries, simple dynamics and ordered magnetic fields. The early stages of collapse are approximately isothermal and low mass star-forming regions are relatively long lived and therefore common. By concentrating on the initial stages of gravitational collapse we aim to avoid the complicating factors of large scale molecular outflows (even though these are present from a very early stage of evolution), high velocity jets and HH-objects and the details of the accretion process, including the formation of a protostellar accretion disk. Moreover, thermal desorption of ice mantles, which plays such an important role in high-mass “hot cores”, is not significant in the low temperature cores. Thus, we can limit the uncertainties that are introduced by our very poor understanding of the surface chemistry.

In these early stages of collapse, the most direct implication of depletion is in actively controlling the collapse dynamics. A cloud is supported against gravitational collapse by internal pressures; thermal, magnetic (static), and magnetoturbulent. Thermal pressure is relieved through cooling by dust continuum emission and molecular emission lines (such as CO $J=2 \rightarrow 1$). Static magnetic pressure is relieved (perpendicular to the direction of the field lines) by the process of ambipolar diffusion (the relative drift between ions, which are tied to the magnetic field lines, and neutrals, which are not). Turbulent magnetic pressure is provided by MHD waves. The damping rate for the turbulence is critically sensitive to the ion-neutral coupling efficiency which is, in turn, sensitive to the

Table 1. Characteristic timescales in molecular clouds.

Process	Driving mechanism	Timescale (yrs)	Timescale (yrs) for $n=10^4\text{cm}^{-3}$
Gas-phase chemistry	c-r ionization	$\sim 3 \times 10^5$	$\sim 3 \times 10^5$
Freeze-out	gas/grain collisions	$\sim 3 \times 10^9/n$	$\sim 3 \times 10^5$
Cooling	radiative	$\sim 10^6$	$\sim 10^6$
Collapse	gravity	$\sim 10^8/n^{1/2}$	$\sim 10^6$
Ambipolar diffusion	ion-neutral drift	$\sim 4 \times 10^{13} \cdot X(i)$	$\sim 4 \times 10^5$

ionization level; the damping rate is approximately proportional to $\nu^2/n(e^-)$ where ν is the wave frequency. Thus the thermal pressure can be reduced in molecular-rich regions, whilst magnetic pressures can be relaxed when the ionization level is sufficiently low. The ionization is itself dependent on the degree of molecular depletion: in general, the rate coefficients for the dissociative recombination of molecular ions are very much greater than those for the radiative recombination of elemental ions. Thus, the fractional ionization of regions that have undergone substantial molecular depletion are typically somewhat higher than in regions of low depletion. Ruffle et al. (1998) modelled the dependence of the fractional ionization $[X(e^-)]$ on the extinction (A_v) for a range of physical parameters and found that it is sensitive to the density and metallicity of the gas. In particular they found that $X(e^-)$ falls very sharply for $A_v \sim 2-3$, perhaps providing an explanation for the fact that in the Rosette molecular cloud, clumps with $A_v \leq 3$ appear to be supported against collapse and do not contain embedded stars.

In general, it is clear that depletion inhibits the relaxation of internal pressures and therefore the viability of collapse and star-formation. We may even speculate that in a magnetically sub-critical contracting core, if depletion occurs more rapidly than ambipolar diffusion, the core may be stable against collapse (Hartquist et al. 1993).

The reason why depletion can play such a critical role in determining the stability and evolution of star-forming regions can be seen by comparing the relevant timescales. Table 1 gives the timescales for the various chemical and physical processes that operate in molecular clouds. The final column gives the timescale calculated for a (typical core) density of 10^4cm^{-3} and it is important to note that all of the timescales lie within a fairly narrow range of values.

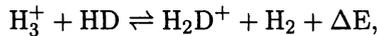
There are several very important consequences of the similarity of these timescales;

- It is hard to distinguish between chemical variations resulting from the non-linearity of gas-phase processes and gas-grain depletion effects
- Small variations in one or more of the parameters (such as, for example, the depletion rate) can propagate into very large variations in the chemical abundances

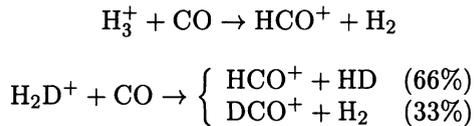
- To characterise the chemical composition of an evolving region it is essential to consider the *complete* history of the cloud. In particular the chemistry will be sensitive to the assumed initial conditions.

3. Chemical Implications of Depletion

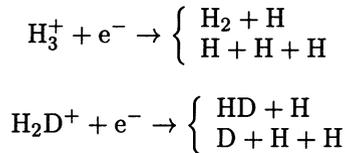
To highlight the significance of the first of the points given above we will look at two examples of situations where depletion effects can affect our interpretation of observations. Firstly, we consider the use of the $\text{DCO}^+ : \text{HCO}^+$ ratio in determining fractional ionizations. In interstellar clouds this ratio is enhanced by factors of $\sim 10^2$ – 10^5 over the cosmic D : H ratio. The ratio is determined by the balance between H_3^+ and H_2D^+ :



where $\Delta E/k \sim 140$ K. The H_3^+ and H_2D^+ ions can react with CO:



so that, if the rate coefficients are similar, $\text{DCO}^+ : \text{HCO}^+ \sim \frac{1}{3} \text{H}_2\text{D}^+ : \text{H}_3^+$. The dissociative recombination channels for H_3^+ and H_2D^+ are:



so that $\text{H}_2\text{D}^+ : \text{H}_3^+$ and hence $\text{DCO}^+ : \text{HCO}^+$ are related to the electron density. However, this picture is complicated by the fact that whilst H_3^+ and H_2D^+ have loss channels involving reactions with molecules such as CO, N_2 and H_2O etc., H_3^+ has an additional (albeit slower) loss path in its reaction with HD, which also acts as a formation pathway for H_2D^+ . Thus in regions of high molecular depletion, this secondary loss channel assumes greater significance and the $\text{H}_2\text{D}^+ : \text{H}_3^+$ and $\text{DCO}^+ : \text{HCO}^+$ ratios will be enhanced (until DCO^+ and HCO^+ freeze out) regardless of the ionization level.

In recent years it has become popular to describe the time-dependent behaviour of certain important molecular tracer species as being “early time” or “late time” depending on when the abundances of the species reach their peaks. Apart from the fact that such qualitative behaviours are dependent on the assumptions concerning the initial conditions, these definitions usually refer to the gas-phase chemistry. Depletion effects can radically modify this picture. This was shown, quite graphically, by Ruffle et al. (1997) who considered the chemistry of HC_3N (typically referred to as an “early-time” species) in a model of TMC-1. The model which chose as its initial conditions a gas that is atomic ($n_{\text{H}} = 2 \times 10^4 \text{ cm}^{-3}$ and $A_v = 10$), with the exception of hydrogen which is all in

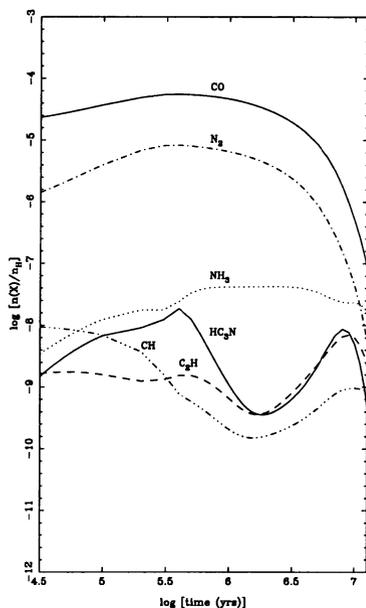


Figure 1. A model of the time-dependence of several species in TMC-1. The abundance curve of HC_3N clearly shows the presence of both an ‘early time’ gas-phase chemical peak and a ‘late time’ peak caused by differential depletion effects. From Ruffle et al. (1997).

the form of H_2 , assumed that material steadily freezes out on to grains. It was found (see Fig. 1) that whilst the characteristic “early-time” peak is seen at $t \sim 4 \times 10^5$ years, a *secondary* “depletion” peak is also seen at $t \sim 8 \times 10^6$ years. Similar behaviours are seen for species like C_2H and C_2S and imply that if depletion effects are ignored then the simple interpretation of abundance peaks in terms of source age are highly ambiguous.

In their model of L1498, Rawlings et al. (1992) used the term ‘depletion enhanced’ to describe the chemical behaviour of those species whose abundance actually *rise* (albeit temporarily) in regions of high depletion. As emphasised in the previous section, the timescales for the depletion, dynamics and chemistry are similar. The precise details of the chemical behaviours (whose origins are the non-linearities in the chemistry brought about by differentials in the timescales) are, in general, critically dependent on the assumptions concerning the initial conditions and the depletion efficiencies. This has implications both for the interpretation of the morphological distributions of molecules and also in the analysis of line profiles in the attempt to determine the collapse kinematics.

3.1. The interpretation of morphologies

In order to interpret the morphological distribution of molecular tracers in star-forming regions we need to have clear ideas of:

- (a) The dynamical evolution and physical structure of the cores
- (b) The time-dependence of the chemistry and how it is influenced by the effects of depletion, and
- (c) The excitation conditions and optical depths of the transitions

Although the details are not clear, it would seem reasonable to assume, for (a), that there is a systemic inflow of material from the outer envelopes of the cores into regions of higher density. Thus, the time-dependence of (b) can be considered in terms of the radial dependence of the chemical abundances. It is often convenient to think in terms of ‘critical’ densities ($n_{crit.}$) for the thermalisation of the excited states of transitions; different transitions, with different values of $n_{crit.}$ effectively trace regions with $n > n_{crit.}$. In the case of the CS ($J=2 \rightarrow 1$), NH₃ (1,1) and C¹⁸O ($J=1 \rightarrow 0$) transitions we find $n_{crit.}(\text{CO}) < n_{crit.}(\text{NH}_3) < n_{crit.}(\text{CS})$. However, surveys (e.g. Myers et al. 1991) consistently show that the NH₃-cores are more compact than the CS-cores – the opposite result to what we might expect. Attempts to interpret the discrepancy in terms of simple gas-phase chemical behaviours (i.e. by postulating that since NH₃ is a ‘late-time’ species it only develops an appreciable abundance well into the collapse, and hence at smaller radii than the CS, which is an ‘early-time’ species) are apparently undermined by the kinematics; the line profiles of NH₃ are generally *narrower* than those of CS. Indeed, the HC₃N ($J=4 \rightarrow 3$) transition, which has similar excitation characteristics to NH₃ (1,1) and exhibits similar spatial distributions has, if anything, even narrower line profiles (Fuller & Myers 1993). These authors suggest that the discrepancies may be at least partially accounted for by optical depth/line of sight effects, noting that observations sample both the dense core and the low density envelope that surrounds it. Taylor et al. (1996) postulated a combination of differential ageing and the presence of unresolved clumps as the cause. In their model, unresolved CS clumps may be transient, unbound entities with large random motions, that dissipate on timescales that are shorter than the NH₃ formation timescale. The NH₃ clumps are more massive, survive longer, and go on to form stars.

Nevertheless, the question still remains as to why NH₃ and related species have such narrow line profiles in what should be infalling regions of the cores. Indeed, in the starless core L1498, Myers & Benson (1983) found the intrinsic line width of the NH₃ (1,1) profiles to be only very marginally greater than that expected for thermal broadening at 10 K. This suggests that the NH₃ emission is not sampling the inflowing gas and that it is essentially *depleted* from the high density central regions of the core. Bearing in mind the high densities and low temperatures, this is an entirely feasible suggestion, which has since been confirmed by high resolution observations of other molecular tracers.

3.2. Models of dynamically evolving regions

This hypothesis has been developed and expanded to form the basis of chemical models which are capable of diagnosing the dynamical and chemical status of candidate infall sources. Major uncertainties in the chemical modelling derive from the assumptions concerning: (1) The chemical and physical ‘initial’ conditions, (2) The consequences of depletion and gas-grain interactions in general, and (3) The dynamical behaviour of the earliest stages of the collapse. We shall not discuss (3); suffice to say that the collapse dynamics, even of isolated low-mass cores, is a poorly understood and hotly debated topic. This is exemplified by the case of the starless core L1544: significant and spatially varying line asymmetries, perhaps indicative of infall, are detected along numerous lines of sight towards this source (Tafalla et al. 1998). The absence of a protostellar

accretion source combined with the observed large extent of apparent infall is hard to reconcile with the hydrodynamic models, whilst the implied infall velocities and the observed absence of any systematic velocity shifts between ions and neutrals does not agree with the MHD/ambipolar diffusion models either.

By identifying molecular species whose abundances (temporarily) rise in regions of high depletion, Rawlings et al. (1992) postulated that appropriate transitions of these species would provide better tracers of the dynamics of the innermost, denser regions of collapsing clouds than species like NH_3 and CO which are known to be depleted. The ‘depletion enhanced’ species (such as HCO^+ and OH) effectively probe the dynamically active parts of a core and are expected to exhibit significant line profile broadening. The precise appearance of the lines will depend strongly on the details of the chemical and dynamical behaviour. Several papers have addressed the issue of how molecular abundances vary throughout a collapsing cloud core (e.g. Bergin & Langer 1997; Charnley 1997) and these models are discussed elsewhere in this volume. However, the point to note here is that the discrepancies in the predictions of these various models are essentially consequences of the different assumptions concerning the initial conditions and the depletion characteristics.

To illustrate this, let us consider the chemical behaviours in the model of the starless core L1498 that was developed by Rawlings et al. (1992). This was formulated as a multipoint model, incorporating a simple “inside out” (Shu 1977) dynamics. The gas-grain interaction was limited to simple freeze-out (with no return mechanism) and, most importantly, the chemical initial conditions were defined by a separate model of the dynamical cycling of material between stellar winds and star-forming clumps (Nejad et al. 1990). This model, which was invoked so as to explain the high $\text{C}:\text{CO}$ ratios and NH_3 abundances that are observed in collapsing cores, predicted a large gas-phase abundance of H_2O (formed on grains, subsequent to the freeze-out of atomic oxygen). When the H_2O abundance is very high, the dominant destruction mechanism for many molecular ions is reaction with H_2O , rather than dissociative recombination. Thus, as H_2O depletes, the destruction rate for these ions falls and their abundances rise. The ‘depletion enhancement’ of these species can therefore be at least partially attributed to the initial conditions which, in turn, depend on the efficiency of the depletion and surface reactions in the cyclic model.

4. Case Studies

With the advent of high sensitivity detectors and improved spatial resolution, the direct detection of molecular depletions in star-forming regions is becoming commonplace although the trends of depletion with source characteristics, such as age, mass etc. have yet to be established. We discuss here a few examples of some recent results. Gibb & Little (1998) have observed HH 24-26, a string of dense star-forming cores in L1630, in HCO^+ ($J=4-3$), C^{18}O ($J=2-1$) and the dust continuum. They find that whilst the distribution of HCO^+ correlates well with the dust emission, the C^{18}O does not. The implication is that although HCO^+ does not deplete at high densities, the C^{18}O abundances are depleted by factors of between 9 and 46. This would seem to be at least consistent with the predictions of the models described in the previous section. The isolated

core L1498 apparently has a very complex chemical structure. This flattened, pre-collapse core has been observed in several transitions at high resolution by Kuiper et al. (1996). The NH_3 core has the smallest spatial extent, C_3H_2 has a more extended and lopsided distribution, but CS and C_2S are almost completely absent from the central peak of the NH_3 emission (which correlates well with the dust emission). The CS and C_2S emission peaks are, instead, located on either side (perhaps limb-brightened) of the nominal core centre. A comparison of the $200\ \mu\text{m}$ continuum with the C^{18}O distribution (Willacy et al. 1998) shows that the C^{18}O is depleted by a factor of > 8 . The CO ‘hole’ is also aligned with the NH_3 peak. The distribution of HC_7N is similar to that of the C^{18}O , but is stronger at one of the offset peaks. The core is cold ($T < 10\ \text{K}$) but shows evidence for widespread systemic motions. The linewidths are very small and L1498 does not possess a central IRAS source. Kuiper et al. interpret this in terms of a clumpy ellipsoid or “onion skin” model, noting that since the density, temperature and implied radiation field strength do not vary significantly across the source, the chemical variations are probably a combination of chemical and clumping effects. In this model it is postulated that the core is undergoing a period of quasi-static contraction, prior to collapse, and that it is being ‘fed’ by an envelope that is still growing. As yet, an adequate chemical model for this source has not been developed, but it would seem highly likely that much of the observed chemical differentiation is caused by differential depletion effects.

The Class 0 source B335 is a well-studied test-bed of dynamical and chemical models of star-forming regions. It is a relatively close ($\sim 250\ \text{pc}$), nearly circularly symmetric, isolated, approximately isothermal core whose outflow lobes are approximately in the plane of the sky. It was the first source to demonstrate the infall ‘fingerprint’ in line profiles (Zhou et al. 1993): a deeply self-reversed line profile with the blue emission wing brighter than the red. Following recent observations of the dust continuum with SCUBA (Shirley et al. 2000) the density and temperature profiles have been accurately constrained. The observed line profiles for species like H_2CO , CS and HCO^+ are found to be *consistent* with the velocity profiles given by the simple “inside out” collapse model of Shu (1977) with a collapse age of 1.5×10^5 years but are based on the (unrealistic) *assumption* that the fractional abundances of the species are spatially invariant. By considering off-centre observations, Choi et al. (1995) deduced that the CS fractional abundance within the ‘infall radius’ is 5.5×10^{-9} , nearly half that in the outer (static) envelope (9×10^{-9}). However, other than this simple refinement, no other models of the line profiles from this or any other infall source which take into account the radial variation of molecular abundances have yet been published.

Rawlings & Evans (2000) have addressed this problem and have developed complex models of B335 which combine chemical kinetics, dynamics and radiative transfer. A variety of different initial conditions have been considered and various possibilities are investigated in connection with the gas-grain interaction, including the implementation of a net freeze-out rate that is sensitive to the extinction (A_v). The (preliminary) results from the modelling suggest that in order to explain the chemical composition, the interstellar radiation field must be suppressed in the vicinity of B335 by an amount corresponding to a visual extinction of 3–5 magnitudes. This result is apparently in good agreement with the models of the thermal (dust) emission from B335 and confirms the hy-

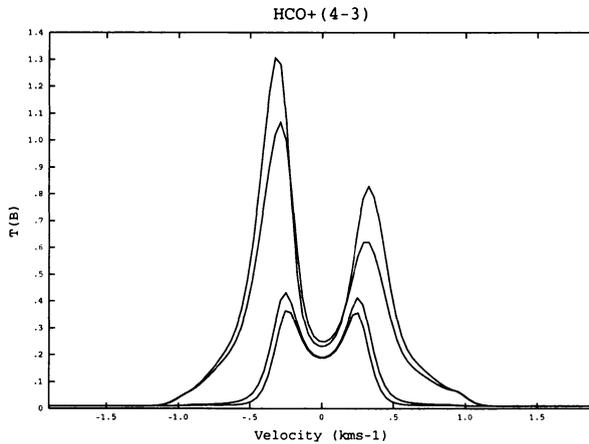


Figure 2. HCO^+ line profiles in an infalling cloud produced by a combined model of chemistry, dynamics and radiative transfer. The top profile is the standard result, the second shows the effect of increasing the cosmic ray ionization rate from 1 to $5 \times 10^{-17} \text{ s}^{-1}$, the third shows the effect of changing the nominal sticking efficiency of atoms and molecules on to grains from 0.3 to 0.5, and the lowest shows the effect of introducing a hydrodynamical ‘pause’ of 2×10^5 years into the dynamical model.

pothesis that both the beam-averaged chemical abundances and the individual line profile shapes are strongly determined by depletion and surface chemistry effects.

Most recently, Rawlings & Yates (2000) have investigated the sensitivity of the line profiles of common infall tracers, such as HCO^+ , to the poorly-constrained parameters in the models. An example of the results obtained is shown in Figure 2 which depicts the HCO^+ $J=4 \rightarrow 3$ emission line profile generated in a model similar to that used to study B335; Simple ‘inside out’ collapse dynamics are adopted and the gas-grain interaction is limited to freeze-out and thermal desorption. The initial conditions are similar to those used in the L1498 model of Rawlings et al. (1992) – in which chemical enrichment is achieved by dynamical cycling, and the radiative transfer is performed with the SMMOL code which utilises accelerated lambda iteration techniques.

The results demonstrate the extreme sensitivity of the emission line profiles to the various free parameters – most notably the sticking coefficient (S_i). A variation of S_i between 0.3 and 0.5 is certainly well within the error bounds for this parameter which is, in any case, strongly dependent on the dust properties, such as the dust to gas ratio and the mean surface area per grain. Consequently, we note that infall characteristics *cannot* be determined from simple observations of individual ‘infall fingerprint’ line profiles. However, the degeneracy can be overcome and a determination of the infall characteristics *can* be made by making observations of multiple transitions along a number of lines of sight.

5. Conclusions and Prospects

It is now possible to combine self-consistently dynamical, chemical and radiative transfer models to make direct predictions about the observed line strengths and shapes for molecular transitions that can be used to trace protostellar infall. Until very recently, the approaches that have been used have made major assumptions concerning one or more of these aspects. In particular, attempts to model the observed line profiles have assumed that the abundance of the molecular tracer is uniform throughout the infall region. Moreover, attempts to match chemical models with observations have tended to ignore the wide range of physical and chemical conditions that are sampled in a single-dish telescope beam. Such approximations take no account either of the gas-phase chemistry, or of the pivotal role that gas-grain interactions in general and depletion in particular play in determining both the spatially averaged abundances (through the definition of the chemical initial conditions) and the temporal and, by inference, spatial variation in the molecular abundances.

In conclusion it should be emphasised that we *can* understand the physics and chemistry of the pre-stellar cores in their earliest stages of collapse. However, to do so requires the interpretation of multi-transition, multi-line-of-sight maps, realistic radiative transfer models and, above all, models which take into account the uncertainties, especially in the assumptions concerning the initial conditions and the gas-grain interactions. It cannot be stressed too strongly that the chemical and physical conditions within molecular clouds, and particularly collapsing cores, cannot be assessed correctly without an accurate understanding of the depletion characteristics of the region. Provided a sufficiently comprehensive observational dataset is available for a source, then with the appropriate suite of chemical, dynamical and radiative transfer models it is possible to establish the depletion, dynamics and chemical history of the source.

References

- André, P., Ward-Thompson, D., & Barsony, M. 1993, *ApJ*, 406, 122
Bergin, E.A. & Langer, W.D. 1997, *ApJ*, 486, 316
Charnley, S.B. 1997, *MNRAS*, 291, 455
Choi, M., Evans II, N.J., Gregersen, E.M., & Wang, Y. 1995, *ApJ*, 448, 742
Duley, W.W. & Williams D.A. 1984, *Interstellar Chemistry*, Academic Press, London
Fuller, G.A. & Myers, P.C. 1993, *ApJ*, 418, 273
Gibb, A.G. & Little, L.T. 1998, *MNRAS*, 295, 299
Hartquist, T.W., Rawlings, J.M.C., Williams, D.A., & Dalgarno, A. 1993, *QJ RAS*, 34, 213
Kuiper, T.B.H., Langer, W.D., & Velusamy, T. 1996, *ApJ*, 468, 761
Martín-Pintado, J., et al. 1992, *A&A*, 254, 315
Mathis, J.S., Ruml, W., & Nordsieck, K.H. 1977, *ApJ*, 217, 425
Myers, P.C. & Benson, P.J. 1983, *ApJ*, 266, 309
Myers, P.C., Fuller, G.A., Goodman, A.A., & Benson, P.J. 1991, *ApJ*, 376, 561
Nejad, L.A.M., Williams, D.A., & Charnley, S.B. 1990, *MNRAS*, 246, 183
Rawlings, J.M.C., Hartquist, T.W., Menten, K.M., & Williams, D.A. 1992, *MNRAS*, 255, 471

- Rawlings, J.M.C. & Evans II, N.J. 2000, MNRAS, in preparation
Rawlings, J.M.C. & Yates, J.A. 2000, MNRAS, in preparation
Ruffle, D.P., Hartquist, T.W., Taylor, S.D., & Williams, D.A. 1997, MNRAS, 291, 235
Ruffle, D.P., Hartquist, T.W., Rawlings, J.M.C., & Williams, D.A. 1998, A&A, 334, 678
Shirley, Y., Evans II, N.J., Rawlings, J.M.C., & Gregersen, E. 2000, ApJ, submitted
Shu, F.H. 1977, ApJ, 214, 488
Tafalla, M., Mardones, D., Myers, P.C., Caselli, P., Bachiller, R., & Benson, P.J. 1998, ApJ, 504, 900
Taylor, S.D., Morata, O., & Williams, D.A. 1996, A&A, 313, 269
Ward-Thompson, D., Scott, P.F., Hills, R.E., & André, P. 1994, MNRAS, 268, 276
Whittet, D.C.B., et al. 1996, ApJ, 458, 363
Willacy, K., Langer, W.D., & Velusamy, T. 1998, ApJ, 507, L171
Zhou, S., Evans II, N.J., Kömpe, C., & Walmsley, C.M. 1993, ApJ, 404, 232

Discussion

C. W. Lee: You mentioned that L1498 shows depletion in HCO^+ and N_2H^+ . However my recent data do not show any depletion in HCO^+ and N_2H^+ . Do you have any data which show different results from my data, or do you have any other explanation on my question?

J. Rawlings: The earlier model of L1498 assumed (incorrectly) that this source was quite well evolved. More recent studies suggest that it has quite a different structure to the simple 'inside-out' collapse that we had originally assumed. Near the center, in a region of moderate depletion we would expect the N_2H^+ to be enhanced (and nearly co-incident with the NH_3 core). The HCO^+ is more sensitive to the H_2O abundance in the core.

T. Velusamy: L1498 is in a pre-collapse stage. The mass in its dense core is not high enough to initiate collapse. It is likely in a quasi-static phase in which its outer envelope is still growing in mass by accretion of new material from an extended low density core. NH_3 in the center has the narrowest line width because it is not yet in collapse. Slightly larger line widths for the other species come from the outer regions where they are more abundant.

J. Rawlings: It is hard to understand how L1498 can be accreting material if it is not gravitationally bound. A likely scenario is that L1498 is gravitationally super-critical but magnetically sub-critical and is therefore undergoing quasi-static contraction on the ambipolar diffusion timescale.

M. Guélin: I would like to stress that the abundance of HCO^+ is very difficult to measure in dense clouds. The mm lines of the main isotopes are optically thick and the H^{13}CO^+ abundance depends on ^{13}C fractionation. To my knowledge, the only clean measurements are the absorption measurements by Lucas & Liszt on the line of sight to quasars. Comparisons between computed and observed abundances are thus not easy.

J. Rawlings: There are all sorts of problems in assigning abundances to species by single dish observations which sample regions of very different physical characteristics. We use a variety of observed abundances (HCO^+ , H_2CO , NH_3 , CS , etc.) to constrain the models. The radiative transfer codes predict line strengths and shapes for higher transitions which can provide some security for the abundance determinations.

M. Walmsley: The 'ammonia problem' might be explained if N_2 survives (is not depleted) in high density regions where depletion of other species takes place. Thus if sticking coefficients are indeed smaller than 1, one might understand the concentration, e.g., of NH_3 to the 'core of cores' like L1498.

J. Rawlings: The over-abundance of NH_3 was originally seen as a problem in gas-phase (only) chemical models. A variety of gas-grain interactions may result in NH_3 enhancement. The absence of NH_3 in ice mantles suggests that there is not a significant nitrogen abundance in dust grain mantles. The very high N_2H^+ abundances in star-forming regions (Benson et al. 1998, ApJ, 506, 743) suggests that $X(\text{N}_2) \sim 7 \times 10^{-5}$.

G. J. Melnick: In your models, an enhanced abundance of HCO^+ can result from the depletion of H_2O – a proposed loss mechanism of HCO^+ . What residual gas-phase abundance of H_2O do your models predict?

J. Rawlings: As H_2O freezes-out, the HCO^+ ion route is inhibited and the $\text{HCO}^+ : \text{CO}$ ratio rises, as is observed in regions of high depletion. The 'initial' H_2O abundance is given by the model which is used to define the initial conditions. To obtain the required selective depletion a significant fraction of all oxygen is in the form of H_2O .

J. M. Greenberg: What reason do you suggest for varying the sticking coefficient? I would expect that at $T_d < 10$ K it should be very close to 1, yet you find $S \simeq 0.3$ gives the most acceptable result. Is it possible that using $S < 1$ is equivalent to including some desorption mechanism?

J. Rawlings: Laboratory studies indicate that $S \sim 1$ but there is some uncertainty in this value. More importantly, there are significant uncertainties in the grain size distribution and the effective 'surface area per unit volume'. The effective sticking coefficient takes account of these uncertainties. $S < 1$ could be partially equivalent to including desorption, but that would assume that there is no chemical processing on the surface of grains.

H. Fraser: With regards to the sticking coefficient of 0.3–0.5 that you used for HCO^+ in your model: since the value of this sticking coefficient will depend on the type of chemical surface the HCO^+ freezes-out onto, what kind of chemical surface do you use in your model? Furthermore, the nature of this chemical surface will change depending on the $\text{H} : \text{H}_2$ ratio, so how is your chemical surface linked to your initial conditions in the model such as the $\text{H} : \text{H}_2$ ratio?

J. Rawlings: The models that I have described simply assume that dust grains form a 'sink' for molecules freezing out, there is no desorption mechanism and a 'sticking coefficient' (of 0.3–0.5) is adopted for all species heavier than He (enhanced by Coulombic effects where appropriate). There is no parameterization of the grain surface. However, this issue is being addressed by a new equipment

at UCL (see poster) which aims to characterise (in the laboratory) H₂ formation on dust analogues.

E. Herbst: How do you handle the sticking probability of molecular ions? In our models, we find that results are very sensitive to this highly uncertain parameter. What is probably most likely is that dissociative recombination followed by desorption occurs; e.g., $\text{HCO}^+ + \text{grain-e} \rightarrow \text{CO} + \text{H} + \text{grain}$.

J. Rawlings: This is a very good question, and one that I have not had time to comment upon in my talk. In my early models I simply assumed that molecular ions stick with the same sticking probability as neutrals (but enhanced by a Coulombic factor). In my more recent papers, I include the effects that you mention, together with the possibility that a long range interaction may occur, i.e., dissociative recombination may occur 'before' the HCO⁺ sticks to the grains.

E. van Dishoeck: You mentioned several times in your talk the crucial importance of the initial conditions in your models. Can you elaborate on what you think reasonable initial conditions are?

J. Rawlings: We should be guided by the observations. In our early models we invoked a dynamic cycling model (between stellar winds, clumps and the next generation of stars) to explain the perceived overabundance of NH₃, CH and the C:CO ratio. In general, a sensible approximation might be to start the chemistry with abundances appropriate to a diffuse/translucent cloud in equilibrium. In any case there is very little justification for using the *traditional* initial conditions of H₂ and atomic gas.

J. Black: The assumption of fully molecular hydrogen as an initial condition may be a problem. Even a small enhancement of H/H₂ over its steady-state value might affect the future chemical evolution, especially since the amount of atomic H can alter the ionization balance. Moreover, the depletion of molecules alters the cover of surfaces and affects (potentially) the formation of H₂ on those surfaces, thus possibly preserving an excess of H in the gas.

J. Rawlings: The *initial* conditions are extremely important in *all* models of star-forming regions. The 'traditional' assumption of starting from H₂ and atomic C, N, O, ... is without justification and the H/H₂ ratio is an important free parameter. In all cases the results of chemical models should be checked for 'robustness' to variations in the initial abundances. The efficiencies of H₂ formation has always been taken as fixed.

