

The Chemistry of the Early Universe

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Abstract. The chemistry of the early Universe is a fascinating field of study. Even in the absence of any elements heavier than lithium, a surprising degree of chemical complexity proves to be possible, giving the topic considerable interest in its own right. In addition, the fact that molecular hydrogen plays a key role in the formation of the first stars and galaxies means that if we want to understand the formation of these objects, we must first develop a good understanding of the chemical evolution of the gas. In this review, I first give a brief introduction to the chemistry occurring in the gas prior to the formation of the first stars and galaxies, and then go on to discuss in more detail the main chemical processes occurring during the gravitational collapse of gas from intergalactic to protostellar densities, and how these processes influence the final outcome of the collapse.

Keywords. stars: formation – galaxies: formation – cosmology: theory

1. Introduction

Chemistry in the early Universe has proved to be an interesting topic of study for several reasons. Before the first stars and galaxies formed, the elemental composition of the gas was very simple – it consisted only of hydrogen and helium (and their isotopes) plus a tiny trace of lithium – and yet this is sufficient to give rise to a surprising degree of chemical complexity. In addition, the interaction between the gas and the cosmic microwave background (CMB) plays an important role in regulating the chemistry of the gas, and moreover one which may lead to observable changes in the CMB (see e.g. Maoli, Melchiorri & Tosti 1994; Dubrovich, Bajkova & Khaikin 2008; Schleicher *et al.* 2008). Furthermore, understanding the chemical evolution of the gas at these early epochs is vital if one wants to understand the formation of the first stars and galaxies, given the crucial role played by molecular hydrogen (H_2) in this process.

There is a wide range of topics that one could discuss in a review of the chemistry of the early universe, ranging from the physics and chemistry of the recombination epoch at redshift $z > 800$ to the reionization of the Universe at $z < 15$. However, to keep this review to a manageable length, I will focus on only a few key issues, and will not discuss either the recombination epoch or the process of cosmological reionization. Both of these topics are treated in detail elsewhere (see e.g. Fendt *et al.* (2009) and references therein for a lengthy discussion of the physics of the recombination epoch, or the recent review by Morales & Wyithe (2010) for a discussion of the epoch of reionization).

In the next Section, I review what we know about the chemical evolution of the IGM from the end of the recombination epoch until the time at which the earliest protogalaxies form. I follow this up in Section 3 by discussing the chemical evolution of the gas within these early protogalaxies. I show how an understanding of the gas chemistry can allow us to determine the mass scale of the first star-forming minihalos, outline the main chemical changes that occur in the gas during its collapse to protostellar densities, and highlight the important role played by molecular hydrogen throughout this process.

2. Pregalactic chemistry

2.1. *The chemical composition of the gas at the end of the recombination epoch*

At the end of the recombination epoch, at a redshift $z \sim 800$, the chemical makeup of the gas in the Universe – what we might refer to as pregalactic gas – was very simple. The main constituent of the gas was neutral atomic hydrogen, accounting for roughly 75% of the total mass. A small amount of hydrogen remained ionized, with the ratio by number of ionized to neutral hydrogen being roughly $H^+/H \simeq 2.5 \times 10^{-3}$ (Wong, Moss & Scott 2008; note that this value continues to decline at lower redshift, decreasing by about an order of magnitude by the time we reach $z = 100$). Neutral atomic helium (primarily ^4He , but also including a small fraction of ^3He) accounted for most of the remaining mass, but in this case the abundance of singly or doubly ionized helium was very close to zero, as helium recombination comes to an end at a significantly higher redshift than hydrogen recombination (Wong, Moss & Scott 2008). Deuterium was also present, with a fractional abundance relative to hydrogen $D/H \simeq 2.5 \times 10^{-5}$ (Cyburt, Fields & Olive 2008), and a ratio of D^+ to D that was essentially the same as the ratio of ionized to neutral hydrogen. Finally, there was a trace amount of lithium ($\text{Li}/H \simeq 5 \times 10^{-10}$; Cyburt, Fields & Olive 2008), the majority of which was in the form of Li^+ . The fractional abundances of all other ionized or molecular species were smaller than 10^{-12} at this point (Alizadeh & Hirata 2010).

2.2. *The chemical evolution of the IGM*

Starting from this simple beginning, many other chemical species were produced as the Universe evolved. Detailed chemical models for the evolution of pregalactic gas have been constructed by a number of authors (see e.g. Stancil, Lepp & Dalgarno 1996, 1998; Galli & Palla 1998; Lepp, Stancil, & Dalgarno 2002; Puy & Signore 2002; Schleicher *et al.* 2008), but in this discussion I will focus on a few general principles that can help us to understand the chemical evolution of the gas at these early times.

As a starting point, it is useful to draw a distinction between what I will call “primary” species, i.e. species that are formed directly from chemical reactions amongst the main chemical constituents of the gas (H , H^+ , D , D^+ , He and Li^+), and “secondary” species that are formed mainly from reactions involving one or more of the primary species. Good examples of primary species are H^- , formed via the reaction



or H_2^+ , formed via the reaction



The prime example of a secondary species is H_2 , as direct formation of H_2 via the reaction



occurs at a negligible rate (Gould & Salpeter 1963), and most H_2 in metal-free gas forms via the reactions



and



The evolution of the fractional abundance of a primary species X is largely governed by the relative sizes of three important timescales: the formation time, defined as

$$t_{\text{form},X} = \frac{n_X}{R_{\text{form},X}} \quad (2.6)$$

where n_X is the number density of species X and $R_{\text{form},X}$ is the formation rate per unit volume of X; the photodissociation time,

$$t_{\text{pd},X} = \frac{1}{R_{\text{pd},X}}, \quad (2.7)$$

where $R_{\text{pd},X}$ is the photodissociation rate of species X; and the Hubble time

$$t_H = \frac{1}{H(z)}, \quad (2.8)$$

where $H(z)$ is the Hubble constant.

At high redshift, photodissociation of most molecules and molecular ions by the CMB occurs rapidly, and the photodissociation time is small. Similarly, the high gas density means that the formation timescale of most species is also small. In this regime, both timescales are typically much shorter than the Hubble time, and hence the abundance of species X evolves until it reaches an equilibrium value set by the balance between formation and photodissociation (in which case $t_{\text{form},X} = t_{\text{pd},X}$). Since photodissociation is very effective at high redshift, this equilibrium value is generally very small.

As we move to lower redshifts, the cosmological background density decreases, since $\rho(z) \propto (1+z)^3$, and hence the formation time of any given primary species tends to increase. However, the energy density of the CMB decreases even more rapidly, $\rho_{\text{rad}} \propto (1+z)^4$, and the CMB temperature decreases as $T_{\text{CMB}} \propto (1+z)$. What this means is that we eventually reach a redshift at which the number density of photons capable of photodissociating species X starts to fall off exponentially, as the threshold energy for photodissociation starts to fall within the Wien tail of the CMB spectrum.† Once we reach this point, t_{pd} rapidly increases, and we are left with a situation in which t_{form} is by far the shortest of the three timescales. The abundance of species X therefore increases rapidly until $t_{\text{form},X} \simeq t_H$. Beyond this point, the abundance of X does not increase significantly, as the time required would be longer than the age of the Universe, and we speak of the abundance of the species “freezing out” at some asymptotic value.

The evolution with redshift of secondary species such as H_2 is harder to generalize in this way, as it often depends on the behaviour of more than one primary species, each of which passes through the three stages noted above at a different redshift. For example, H_2 formation via the H_2^+ ion becomes possible at a redshift $z \sim 400$, but H_2 formation via the H^- ion is suppressed until $z \sim 100$, owing to the fact that H^- has a much lower binding energy than H_2^+ (0.755 eV for the former, 2.65 eV for the latter), and hence can be destroyed by photons with significantly smaller energies. The H_2 abundance in the pregalactic gas therefore passes through two periods of relatively rapid growth, one occurring around $z \sim 400$ and the second around $z \sim 100$. Following this second period of growth, the fractional abundance of H_2 is of the order of 10^{-6} , and H_2 is the most abundant molecule in the gas. However, this is still far smaller than the typical amount

† This simple picture is complicated somewhat by the presence of non-thermal photons produced during hydrogen recombination that slightly distort the spectral shape of the CMB (Switzer & Hirata 2005; Hirata & Padmanabhan 2006), but even in this case the general principle is the same.

of H_2 produced within the earliest star-forming protogalaxies, and hence although the chemical evolution of the pregalactic gas is interesting, it is of limited influence: almost all of the chemistry affecting the formation of the first stars and galaxies occurs within the protogalaxies themselves, as I explore in more detail in the next section.

3. Protogalactic chemistry

As we move to lower redshifts, the distribution of matter in the Universe becomes increasingly inhomogeneous. The small perturbations in the dark matter distribution that were present during the recombination epoch grow with time, evolving initially as $\delta \propto t^{2/3}$, but eventually entering the regime in which their evolution becomes non-linear. These perturbations undergo runaway gravitational collapse and virialization, forming dense, gravitationally bound structures that are often referred to as dark matter halos. In the Λ CDM model, the earliest halos to form do so on the smallest scales, with larger, more massive halos forming at later times.

Very little gas accumulates within the earliest halos, as it is prevented from undergoing gravitational collapse by its own thermal pressure, and also by the significant relative velocity that exists between the gas and the dark matter (Tselikhovich & Hirata 2010). However, once the dark matter halos become sufficiently massive, their gravitational attraction dominates over these effects and substantial quantities of gas flow into them, being heated by adiabatic compression and shocks in the process. In regions where the relative velocity between gas and dark matter is very small, this occurs once the mass of the dark matter halo exceeds $M_{\text{min}} \sim 2 \times 10^4 M_{\odot}$ (Naoz & Barkana 2007), but in more typical regions where there is a relative velocity between gas and dark matter of several kilometers per second, the minimum halo mass is higher, $M_{\text{min}} \sim 10^5 M_{\odot}$ (Tselikhovich, Barkana & Hirata 2010). Low-mass halos with masses close to M_{min} – often referred to as “minihalos” to distinguish them from their considerably more massive, low-redshift brethren – are therefore the first objects that have the potential to form stars. Whether or not the gas within them can actually form stars depends on how rapidly it can cool. This in turn depends on the chemical evolution of the gas within the minihalos, a subject that I address below.

3.1. H_2 formation and the onset of cooling

As gas falls into a typical minihalo, it is heated up to a temperature close to the virial temperature of the minihalo

$$T_{\text{vir}} \simeq 1200 \left(\frac{M}{10^6 h^{-1} M_{\odot}} \right)^{2/3} \left(\frac{1+z}{10} \right) \text{ K}, \quad (3.1)$$

(where this expression assumes that the gas is predominantly atomic hydrogen, and that $z \geq 10$; see Barkana & Loeb 2001 for a more general expression). In the post-shock gas, the electron fraction decreases due to radiative recombination, but at the same time H_2 forms, primarily via reactions 2.1 and 2.4. The amount of H_2 that forms in the gas can be estimated using a simple toy model for the chemistry first introduced by Tegmark *et al.* (1997). We start by assuming that radiative recombination is the only process affecting the electron abundance, and writing the rate of change of the electron number density as

$$\frac{dn_e}{dt} = -k_{\text{rec}} n_e n_{\text{H}^+}, \quad (3.2)$$

where n_e is the number density of electrons, n_{H^+} is the number density of protons, and k_{rec} is the recombination coefficient. If we assume that ionized hydrogen is the only source

of free electrons, implying that $n_e = n_{H^+}$, and that the temperature remains roughly constant during the evolution of the gas, then we can solve for the time evolution of the electron fraction:

$$x = \frac{x_0}{1 + k_{\text{rec}} n t x_0}, \tag{3.3}$$

where $x \equiv n_e/n$, n is the number density of hydrogen nuclei, and x_0 is the initial value of x . If we now assume that all of the H_2 forms via the pair of reactions given above, and that the only process competing with reaction 2.4 for the H^- is mutual neutralization



then we can write the time evolution of the H_2 fraction, $x_{H_2} \equiv n_{H_2}/n$, as

$$\frac{dx_{H_2}}{dt} = k_{\text{ra}} x n_H p_{\text{ad}}, \tag{3.5}$$

where k_{ra} is the rate coefficient of reaction 2.1, and p_{ad} is the probability that any given H^- ion will be destroyed by associative detachment (reaction 2.4) rather than by mutual neutralization. Given our assumptions above, this can be written as

$$p_{\text{ad}} = \frac{k_{\text{ad}} n_H}{k_{\text{ad}} n_H + k_{\text{mn}} n_{H^+}}, \tag{3.6}$$

where k_{ad} is the rate coefficient for reaction 2.4 and k_{mn} is the rate coefficient for reaction 3.4. If we again assume that $n_e = n_{H^+}$, and in addition assume that the H_2 fraction and the fractional ionization are small, so that $n_H \simeq n$, then the expression for p_{ad} can be simplified to

$$p_{\text{ad}} = \left(1 + \frac{k_{\text{mn}}}{k_{\text{ad}}} x \right)^{-1}. \tag{3.7}$$

Substituting this into Equation 3.5, we obtain

$$\frac{dx_{H_2}}{dt} = k_{\text{ra}} x n_H \left(1 + \frac{k_{\text{mn}}}{k_{\text{ad}}} x \right)^{-1}. \tag{3.8}$$

We can solve for the time evolution of the H_2 fraction

$$x_{H_2} = \frac{k_{\text{ra}}}{k_{\text{rec}}} \ln \left(\frac{1 + x_0 k_{\text{mn}}/k_{\text{ad}} + t/t_{\text{rec}}}{1 + x_0 k_{\text{mn}}/k_{\text{ad}}} \right), \tag{3.9}$$

where $t_{\text{rec}} = (k_{\text{rec}} n x_0)^{-1}$ is the recombination time, and where we have once again assumed that $n_H \sim n$. If the initial fraction ionization is small, so that $x_0 \ll k_{\text{ad}}/k_{\text{mn}}$, then we can write this expression in the simpler form

$$x_{H_2} = \frac{k_{\text{ra}}}{k_{\text{rec}}} \ln (1 + t/t_{\text{rec}}). \tag{3.10}$$

This analysis tells us two important things. First, it shows us that the H_2 fraction evolves only logarithmically with time: most of the H_2 forms within the first few recombination times, with H_2 formation at later times being strongly suppressed owing to the loss of the free electrons from the gas due to recombination. Second, it shows us that the amount of H_2 that forms depends on the ratio of the rate coefficients for H^- formation (reaction 2.1) and H^+ recombination, $k_{\text{ra}}/k_{\text{rec}}$. The value of this ratio is strongly temperature dependent, and can be written approximately as

$$\frac{k_{\text{ra}}}{k_{\text{rec}}} \simeq 10^{-8} T^{1.5}. \tag{3.11}$$

The amount of H_2 that forms in the gas therefore increases significantly with increasing temperature. As the H_2 cooling rate is also a strongly increasing function of temperature (see e.g. Flower *et al.* 2000), one finds that there is a reasonably sharp divide occurring at a critical virial temperature $T_{\text{crit}} \sim 1000$ K between minihalos that contain gas that can cool rapidly and form stars, and minihalos that contain gas that barely cools over a Hubble time (see e.g. Tegmark *et al.* 1997; Yoshida *et al.* 2003). If we convert this critical virial temperature into a corresponding critical minihalo mass using Equation 3.1, we find that

$$M_{\text{crit}} \simeq 7.6 \times 10^5 h^{-1} \left(\frac{1+z}{10} \right)^{-3/2} M_{\odot}. \quad (3.12)$$

At $z > 40$, this value is smaller than the minimum mass $M_{\text{min}} \sim 10^5 M_{\odot}$ required to overcome the effects of the streaming of the gas relative to the dark matter, which therefore sets the minimum mass scale for a star-forming minihalo. At $z < 40$, however, $M_{\text{crit}} > M_{\text{min}}$, and it is the amount of H_2 that can form within the gas that is responsible for setting the minimum mass scale. One implication of this result is that there will be a population of small minihalos that forming at $z < 40$ that contain significant gas fractions, but that do not form stars, because their gas is unable to cool in less than a Hubble time. These small starless minihalos may be important sinks for ionizing photons during the epoch of reionization (Haiman, Abel & Madau 2001).

3.2. The initial collapse phase

In minihalos where H_2 cooling is efficient, the gas cools and collapses under its own self-gravity, collecting at the centre of the minihalo. The evolution of the gas at this stage depends on the amount of H_2 it is able to form, which in turn depends upon the initial ionization state of the gas.

During the formation of the very first Population III stars, the initial fractional ionization of the gas is the same as the residual ionization in the intergalactic medium, i.e. $x_0 \sim 2 \times 10^{-4}$ at $z \sim 30$. In this case, the amount of H_2 that forms in the gas is typically enough to cool it to a temperature of $T \sim 200$ K but not below. At this temperature, deuterated hydrogen, HD, forms easily from H_2 via



but its destruction via the inverse reaction



is starting to become ineffective, owing to the fact that this reaction is endothermic by around 0.04 eV. At $T = 200$ K, chemical fractionation therefore boosts the HD/ H_2 ratio by a factor of 20 compared to the cosmic deuterium-to-hydrogen ratio. This boost to the HD abundance, together with the fact that HD is a much more effective coolant than H_2 at low temperatures (see e.g. Flower *et al.* 2000), allows HD to become an important coolant at 200 K, but detailed studies have shown that the extra cooling provided by HD is not enough to reduce the temperature significantly below 200 K (Bromm, Coppi & Larson 2002). Therefore, H_2 continues to dominate the cooling and control the further evolution of the gas. In this scenario, the collapse of the gas is greatly slowed once its density reaches a value of around 10^4 cm^{-3} , corresponding to the critical density n_{crit} , at which the rotational and vibrational level populations of H_2 approach their local thermodynamic equilibrium (LTE) values. At densities higher than this critical density, the H_2 cooling rate per unit volume scales only linearly with n (compared to a quadratic dependence, $\Lambda_{\text{H}_2} \propto n^2$ at lower densities), while processes such as compressional heating

continue to increase more rapidly with n . As a result, the gas temperature begins to increase once the density exceeds n_{crit} .

Gas reaching this point in the collapse enters what Bromm, Coppi & Larson (2002) term a “loitering” phase, during which cold gas accumulates in the centre of the halo but only slowly increases its density. This loitering phase ends once the mass of cold gas that has accumulated exceeds the local value of the Bonnor-Ebert mass (Bonnor 1956; Ebert 1955), given in this case by (Abel, Bryan, & Norman 2002)

$$M_{\text{BE}} \simeq 40T^{3/2}n^{-1/2} M_{\odot}, \quad (3.15)$$

which for $n \sim 10^4 \text{ cm}^{-3}$ and $T \sim 200 \text{ K}$ yields $M_{\text{BE}} \sim 1000 M_{\odot}$. Once the mass of cold gas exceeds M_{BE} , its collapse speeds up again, and becomes largely decoupled from the larger-scale behaviour of the gas. The next notable event to occur in the gas is the onset of three-body H_2 formation, which is discussed in Section 3.3 below.

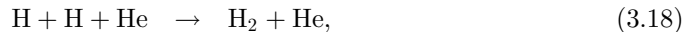
If the initial fractional ionization of the gas is significantly higher than the residual fraction in the IGM, then a slightly different chain of events occurs. A larger initial fractional ionization implies that t_{rec} is shorter and hence leads to a logarithmic increase in the amount of H_2 formed after a given physical time. The higher H_2 fraction produced in this way allows the gas to cool to a slightly lower temperature, thereby boosting the HD abundance to a significantly higher level than is reached in the low ionization case. This allows HD to take over as the dominant coolant, driving the temperature down further. A number of studies have examined this HD-dominated regime (see e.g. Nakamura & Umemura 2002; Nagakura & Omukai 2005; Johnson & Bromm 2006; Yoshida *et al.* 2007; McGreer & Bryan 2008; Kreckel *et al.* 2010), and have shown that the minimum temperature reached in this case can be as low as the CMB temperature, and that the higher critical density of HD, $n_{\text{crit,HD}} \sim 10^6 \text{ cm}^{-3}$, means that the gas does not reach the loitering phase until much later in its collapse. Once the gas does reach this phase, however, its subsequent evolution is very similar to that in the low-ionization case discussed above. Cold gas accumulates at $n \sim n_{\text{crit}}$ until its mass exceeds the Bonnor-Ebert mass, which in this case is $M_{\text{BE}} \sim 40 M_{\odot}$ if $T = 100 \text{ K}$ and $n = 10^6 \text{ cm}^{-3}$. Once the gas mass exceeds M_{BE} , the collapse speeds up again, and the gas begins to heat up. Aside from the substantial difference in the size of M_{BE} , the main difference between the evolution of the gas in this case and in the low ionization case lies in the fact that in the high ionization case, the gas reheats from $T \sim 200 \text{ K}$ or below to $T \sim 1000 \text{ K}$ much more rapidly than in the low ionization case. As we shall see later, this period of rapid heating may exert an important influence on the ability of the gas to fragment.

Several different scenarios have been identified that lead to an enhanced fractional ionization in the gas, and that potentially allow the gas to reach the HD-dominated regime. Gas within minihalos with $T_{\text{vir}} > 9000 \text{ K}$ will become hot enough for collisional ionization of hydrogen to supply the necessary electrons, but halos of this size will typically have at least one star-forming progenitor (Johnson, Greif & Bromm 2008; Greif *et al.* 2010), and hence typically will have already been enriched with metals. Other possibilities include the formation of protogalaxies in “fossil” HII regions, i.e. regions that are recombining after having been ionized by a previous Population III protostar (Oh & Haiman 2003; Nagakura & Omukai 2005; Yoshida *et al.* 2007), or that are irradiated with a significant flux of X-rays (e.g. Glover & Brand 2003) or cosmic rays (Stacy & Bromm 2007; Jasche, Ciardi & Ensslin 2007). However, recent work by Wolcott-Green & Haiman (2011) has shown that the HD forming within a primordial minihalo is very susceptible to photodissociation by even a weak extragalactic UV background (see also Yoshida, Omukai

& Hernquist 2007), and so it is possible that gas will reach the HD-dominated regime in only a few minihalos.

3.3. Three-body H_2 formation

Once the collapsing gas reaches a density of around 10^8 – 10^9 cm^{-3} , its chemical makeup starts to change significantly. The reason for this is that at these densities, the formation of H_2 via the three-body reactions (Palla, Salpeter, & Stahler 1983)



starts to become significant. These reactions quickly convert most of the hydrogen in the gas into H_2 . At the same time, however, they generate a substantial amount of thermal energy: every time an H_2 molecule forms via one of these three-body reactions, its binding energy of 4.48 eV is converted into heat, and so at these densities, three-body H_2 formation heating can become the main process responsible for heating the gas. For this reason, even though the abundance of H_2 , the dominant coolant during this phase of the collapse, increases by more than two orders of magnitude, the gas typically does not cool significantly. Indeed, the temperature often increases.

One major uncertainty in current treatments of the gas chemistry at this point in the collapse is exactly how quickly the gas becomes molecular. Although reaction 3.16 is the dominant source of H_2 at these densities, the rate coefficient for this reaction is poorly known, with published values differing by almost two orders of magnitude at 1000 K, and by an even larger factor at lower temperatures (Glover 2008; Turk *et al.* 2011). The effects of this uncertainty have recently been studied by Turk *et al.* (2011). They show that it has little effect on the density profile of the gas, and only a limited effect on the temperature profile. However, it has far more significant effects on the morphology of the gas and on its velocity structure. Simulations in which a high value was used for the three-body rate coefficient find that gravitational collapse occurs more rapidly, and show that the molecular gas develops a much more flattened, filamentary structure. Significant differences are also apparent in the infall velocities and the degree of rotational support. The effect that this has on the ability of the gas to fragment (see Section 3.5 below) is not yet understood.

3.4. The final stages of collapse

As the gas collapses to even higher densities, several important events occur which affect its ability to cool. The first of these occurs at a density of around 10^{10} cm^{-3} , where the main rotational and vibrational lines of H_2 start to become optically thick. This reduces the effectiveness of H_2 cooling, leading to an ongoing rise in the gas temperature. In one-dimensional simulations (e.g. Omukai & Nishi 1998; Omukai *et al.* 1998; Ripamonti *et al.* 2002; Ripamonti & Abel 2004), it is possible to treat optically thick H_2 cooling accurately by solving the full radiative transfer problem. These models show that although the optical depth of the gas becomes large at frequencies corresponding to the centers of the main H_2 emission lines, the low continuum opacity of the gas allows photons to continue to escape through the wings of the lines, with the result that the H_2 cooling rate is suppressed far less rapidly as the collapse proceeds than one might at first expect (see Omukai *et al.* 1998 for a detailed discussion of this point). In three-dimensional simulations, more approximate treatments of the cooling are necessary (see e.g. Yoshida *et al.* 2006; Turk, Abel & O'Shea 2009; Clark *et al.* 2011a), but the general

findings are the same – H₂ cooling is suppressed to some extent, but still provides enough dissipation of energy to allow the collapse to continue without a large increase in the temperature.

A second important event occurs once the number density reaches $n \sim 10^{14} \text{ cm}^{-3}$. At this density, collision-induced emission from H₂ (the inverse of the more familiar collision-induced absorption; see e.g. Frommhold 1993) becomes important. An isolated H₂ molecule has no dipole moment, but the activated complex formed during the collision of two H₂ molecules can have a dipole moment, and hence can emit radiation via dipole transitions. In principle, this can occur in gas of any density, but the probability of a photon being emitted in any given collision is very small, owing to the short lifetime of the collision state ($\Delta t < 10^{-12} \text{ s}$ at the temperatures relevant for Pop. III star formation; see Ripamonti & Abel 2004). For this reason, collision-induced emission (CIE) becomes an important process only at very high gas densities. Another consequence of the short lifetime of the collision state is that the individual lines associated with the dipole transitions become so broadened that they actually merge into a continuum. This is important, as it means that the high opacity of the gas in the rovibrational lines of H₂ does not significantly reduce the amount of energy that can be radiated away by CIE. Therefore, once the gas reaches a sufficiently high density, CIE becomes the dominant form of cooling, as pointed out by several authors (Omukai & Nishi 1998; Ripamonti *et al.* 2002; Ripamonti & Abel 2004).

The most detailed study of the effects of CIE cooling on the collapse of primordial gas was carried out by Ripamonti & Abel (2004). They showed that CIE cooling could actually become strong enough to trigger a thermal instability. However, the growth rate of this instability is longer than the gravitational free-fall time, meaning that it is unlikely that this process can drive fragmentation during the initial collapse of the gas.

The phase of the collapse dominated by CIE cooling lasts for only a relatively short period of time. The gas becomes optically thick in the continuum once it reaches a density $n \sim 10^{16} \text{ cm}^{-3}$ (Omukai & Nishi 1998; Ripamonti & Abel 2004), which strongly suppresses any further radiative cooling. Once this occurs, the gas temperature rises until it reaches a point at which the H₂ begins to dissociate. At these densities, this occurs at a temperature $T \sim 3000 \text{ K}$. The dissociation of H₂ slows the temperature rise for a while, as most of the energy released during the collapse goes into dissociating the H₂ rather than raising the temperature. However, once the H₂ is exhausted, the temperature once again begins to climb steeply. The thermal pressure in the interior of the collapsing core rises rapidly and eventually becomes strong enough to halt the collapse. At the point at which this occurs, the size of the dense core is around 0.1 AU, its mass is around 0.01 M_⊙ and its mean density is of order 10^{20} cm^{-3} (Yoshida, Omukai & Hernquist 2008). It is bounded by a strong accretion shock. This pressure-supported, shock-bounded core is the structure that we identify as a Population III protostar.

3.5. Formation and fragmentation of the protostellar accretion disk

Most numerical simulations of the formation of Population III stars stop at or before the point at which the protostar forms, owing to the increasingly small timesteps that need to be taken to follow the evolution of the gas. As significant fragmentation of the gas during the initial collapse is uncommon (see e.g. Turk, Abel & O’Shea 2009, who find that fragmentation into a binary system occurs in only one out of five cases), most studies have assumed that the gas surrounding the protostar does not fragment at later times either, but instead is simply accreted by the existing protostar, either directly or via a protostellar accretion disk. A good overview of the results of these studies can be found in Bromm & Yoshida (2011).

However, in the past few years, a number of simulations have been performed that attempt to directly model the evolution of the gas after the formation of the first Population III protostar using a technique developed for studies of contemporary star formation (see e.g. Clark *et al.* 2008; Stacy, Greif & Bromm 2010; Clark *et al.* 2011a,b; Greif *et al.* 2011; Smith *et al.* 2011). Gravitationally bound regions of gas that become smaller than some pre-selected size scale are replaced by what are usually termed sink particles (in an SPH code; see e.g. Bate, Bonnell & Price 1995) or sink cells (in a grid code; see e.g. Federrath *et al.* 2010). These sinks can accrete gas from their surroundings and continue to interact gravitationally with the surrounding gas, but allow one to neglect the very small-scale hydrodynamical flows that would otherwise force one to take very small numerical timesteps owing to the Courant condition.

One of the main results of these simulations is the demonstration that the first protostar to form does not simply accrete all of the available gas. The infalling gas forms an accretion disk around the protostar, but this disk is unable to transfer gas inwards, onto the protostar, rapidly enough to balance the rate at which new material is falling onto the disk. The disk therefore grows in mass until it becomes gravitationally unstable, at which point it begins to fragment, forming multiple protostars (Clark *et al.* 2011b). The gravitational interaction between these protostars and the surrounding gas can trigger further fragmentation, and close encounters between protostars may lead to mergers, or in some cases to protostars being ejected from the center of the minihalo (Greif *et al.* 2011).

Molecular hydrogen plays a crucial role in this process. The midplane temperature of the protostellar accretion disk is typically 1500–2000 K, and the disk is maintained at this temperature primarily by a combination of H₂ line cooling and CIE cooling (Clark *et al.* 2011b). If the molecular hydrogen were not present, the main disk coolant would be bound-free emission from H⁻, which becomes effective only at a temperature $T \sim 6000$ K. The disk would therefore be considerably hotter, allowing it to transfer gas more rapidly onto the central protostar, and making it less susceptible to gravitational instability. In this case, previous studies have shown that the disk would probably remain stable and would not fragment (Tan & McKee 2004; Tan & Blackman 2004; Mayer & Duschl 2005a).

As well as regulating the disk temperature, molecular hydrogen also provides the cooling necessary to allow the fragments forming in the disk to survive as distinct, gravitationally-bound objects. Studies of the fragmentation of self-gravitating accretion disks have shown that in order for fragments to survive, they must be able to cool within roughly half of an orbital period (Gammie 2001). Fragments that cannot cool this quickly undergo a thermal bounce and are then sheared apart by disk rotation, rather than continuing to collapse. In the case of the fragments forming in a Pop. III accretion disk, two key processes provide the necessary cooling: CIE cooling at $n < 10^{16}$ cm⁻³ and the collisional dissociation of H₂ at $n > 10^{16}$ cm⁻³ (Clark *et al.* 2011b).

Finally, there are some indications that the chemical state of the gas at early times during its collapse exerts a substantial influence on the degree of fragmentation that occurs at much later times. As we have already seen, if HD cooling becomes efficient during the collapse of the gas, then the gas can cool to a significantly lower temperature than in the standard H₂-dominated case. However, a consequence of this is that the gas undergoes a more rapid period of reheating once the HD molecules reach LTE, during which it has a very stiff effective equation of state. This leads to a pronounced loss of small-scale structure from the gas, which appears to reduce the amount of fragmentation that occurs at later times in the evolution of the minihalo (Clark *et al.* 2011a; Greif *et al.* 2011).

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