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Laboratory Measurements of Primordial Chemistry

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Abstract. Molecular hydrogen plays a key role in structure formation during the early Universe, sometimes cooling the gas and at other times heating it. We discuss three of the key chemical reactions controling the formation of H_2 during the epoch of primordial galaxy and first star formation. These are the associative detachment (AD) reaction $H^- + H \rightarrow H_2 + e^-$, the mutual neutral (MN) reaction $H^- + H^+ \rightarrow H + H$, and the three body association (TBA) process $H + H + H \rightarrow H_2 + H$. For each reaction we discuss the cosmological implications due to uncertainties in the relevant rate coefficients. In the case of AD we also present our recent experimental work to remove these uncertainties. For MN we discuss our ongoing experimental work. Lastly, for TBA we discuss the theoretical and experimental challenges facing attempts to improve the required reaction data.

Keywords: Early Universe Chemistry, Population III Star Formation
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INTRODUCTION

During the epoch of first star formation, H_2 was the dominant coolant for primordial clouds undergoing collapse at temperatures below 8,000 K. These clouds are initially composed almost entirely of atomic hydrogen and helium, although ion-neutral reactions involving the H^- and H_2^+ ions are able to produce a small amount of molecular hydrogen. The cooling provided by this small H_2 fraction removes pressure support from the gas and allows it to undergo gravitational collapse. Thus, a reliable chemical model of the H_2 formation and abundance during this epoch is critical for our understanding of structure formation in the early Universe. Recent reviews of this chemistry have shown how uncertainties in several key reactions can limit our ability to the formation of protogalaxies and metal-free stars in the early Universe [1, 2, 3, 4, 5].

Here we update the community on progress in our understanding for three of the most important reactions in the chemical network forming H_2. Our focus is on the relevant chemistry in metal-free gas between the redshifts of $z \sim 100$ and that of reionization at $z \sim 10$. Additionally we briefly discuss a few of the cosmological implications of the currently available chemical data.

ASSOCIATIVE DETACHMENT

During the epoch of interest, the dominant H_2 formation mechanism in a collapsing cloud is initially the associative detachment (AD) reaction

$$H^- + H \rightarrow H_2 + e^-. \quad (1)$$

FIRST STARS IV -From Hayashi to the Future-
AIP Conf. Proc. 1480, 81-86 (2012); doi: 10.1063/1.4754333

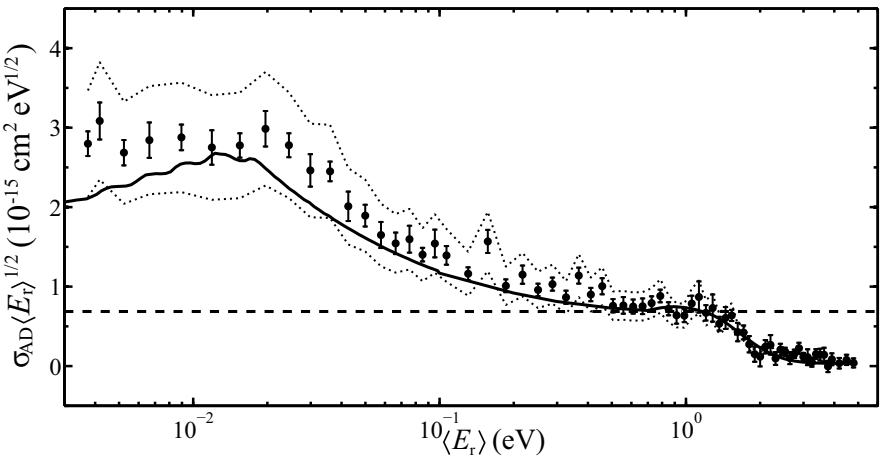

FIGURE 1. The cross section σ_{AD} versus mean relative collision energy $\langle E_r \rangle$ for the AD reaction (1). The cross section has been multiplied by $\langle E_r \rangle^{1/2}$ to remove any Langevin-like behavior. The filled circles give the measured results, the error bars the 1σ statical uncertainty on each point and the dotted curve the total systematic uncertainty of $\pm 24\%$ at an estimated 1σ statistical confidence level. The solid curves plots the theoretical results of [4, 7, 9] and the dashed curve the Langevin value. Adapted from [7].

Until recently, despite over 40 years of research, theory and experiment had failed to converge in either the magnitude or the temperature dependence for this reaction. However, in the past couple of years the situation has dramatically improved. Experiment and theory have finally converged as the result of a series of merged-beams measurements [4, 6, 7] as is shown in Figure 1. What was a previous order-of-magnitude spread in the published values for the rate coefficient [1] has now been reduced to an only $\pm 25\%$ uncertainty in the recommended rate coefficient for this reaction [4].

One implication of these results for structure formation by ionized gas in the early Universe can be seen in Figure 2a. The Jeans mass at which a gas cloud can collapse under the force of gravity is proportional to $T^{3/2}n^{-1/2}$, where T is the gas temperature and n the number density. The mass scale of a collapsing object is thought to be set by the density of the gas at the minimum temperature $T_{\rm min}$ reached [8]. Figure 2a shows the predicted T and n of the gas. Taking the values of $T_{\rm min}$ and n corresponding to the previous lower and upper limits for the AD rate coefficient yields a factor of 20 difference in the predicted Jeans mass. Using the newly benchmarked AD rate coefficient, the resulting spread in predicted Jeans mass is only a factory of 2. This represents a significant improvement in our ability to model structure formation [4].

MUTUAL NEUTRALIZATION

There are a number of reactions which limit the H^- abundance available to form H_2. One of the most important of these is the mutual neutralization (MN) reaction

$$H^- + H^+ \rightarrow H + H. \qquad (2)$$

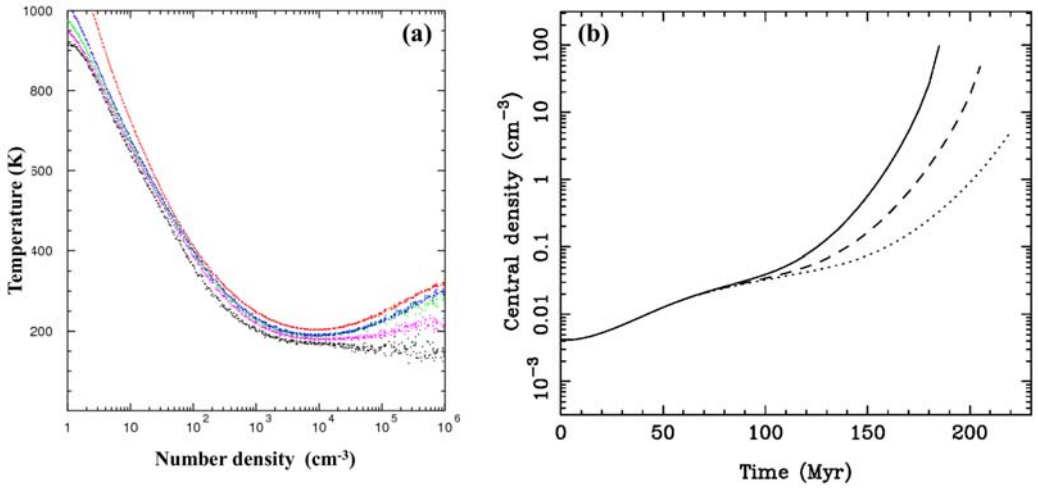

FIGURE 2. Two different simulations of primordial gas evolving in an initially ionized protogalactic halo. See text for details. (a) Gas temperature versus number density. Each point corresponds to a spherical shell of material surrounding the center of the cloud. The top red and bottom black data show the predicted T and n using, respectively, the previous lower and upper limits for the AD rate coefficient. The middle green data use the newly benchmarked AD rate coefficient while the second from the top blue and second from the bottom magenta show the results for $\mp 25\%$ of this value, respectively. Adapted from [4]. (b) Central H_2 density versus time. The solid curve corresponds to the slowest published rate coefficient for reaction (2), the dashed curve to a moderate value, and the dotted curve to the fastest published value. Adapted from [1]. (A color version of Figure 2a is available in the online edition of this proceedings.)

The published rate coefficients for this reaction vary by about an order-of-magnitude. This has significant implications for our ability to predict whether an initially ionized halo can cool and condense to form a protogalaxy on a sufficiently short time scale before it is gravitationally disrupted by a collision with another halo [1]. The model results displayed in Figure 2b are for $z \sim 20$ where the mean collision time between halos corresponds to about 220 Myr. As can be seen in the figure, for a slow to moderate rate coeffient for reaction (2), the cloud begins to collapse exponentially fast on a sufficiently short time scale to form a protogalaxy. That is not the case for a fast rate coefficient and the cloud is more likely to be gravitationally disrupted before collapse.

In order to remove the uncertainty in reaction (2), Prof. X. Urbain at the Université catholique de Louvain has recently modified his merged beams apparatus to be able to access the low energy collision regime relevant to early Universe chemistry [10]. Work is currently under way to measure this reaction and results should be reported shortly.

THREE BODY ASSOCIATION

Whether the primordial cloud begins from a neutral or ionized initial state, as the gas cools and collapses, its density increases. Eventually the density becomes high enough that almost all of the atomic H is converted into H_2 via three body association (TBA)

$$H + H + H \rightarrow H_2 + H. \tag{3}$$

The binding energy released by this reaction is a major source of energy input into the gas and can thereby affect the dynamical evolution of the clouds. However, the published rate coefficients for this reaction vary by two orders of magnitude at any given temperature within the $\sim 200-2000$ K range relevant during this epoch [2, 11]. This range of possible values introduces a significant uncertainty into models of the final stages of gravitational collapse in primordial clouds and limits our ability to predict how primordial clouds fragment and the resulting mass distribution for the first generation of stars [5]. As the mass of a star determines which elements it will form via nucleosynthesis during its lifetime, this uncertainty has important consequences for our ability to reliably predict the chemical (i.e., elemental) evolution of the Universe.

The various published rate coefficients for reaction (3) have been reviewed by [11]. We are unaware of any published quantum mechanical calculations for this reaction. Such calculations are theoretically and computationally challenging due, in part, to the six-body nature of the problem and to the existence of many possible exchange reaction channels resulting from the identical nature of the three H atoms. Additionally, at the temperatures we are interested in, simple *s*-wave scattering is not sufficient and a large number of partial waves need to be included. In discussions with various theoretical atomic physicists who specialize in these types of calculations for gases of $\lesssim 100$ mK, they say that it would require at least a year to develop the required theoretical and computational framework for studying this reaction at the relevant temperatures and at least another year to perform and analyze the results.

Researchers have tried to use laboratory measurements of the time reverse reaction of collisional destruction (CD) via

$$H_2 + H \rightarrow H + H + H \tag{4}$$

combined with detailed balance to produce the desired TBA rate coefficient [e.g., 12]. However the available laboratory data are for H_2 initially in low ro-vibrational levels, whereas reaction (3) populates primarily high ro-vibrational levels where experimental CD data are lacking. Thus one cannot use existing CD data coupled with detailed balance to generate the desired TBA rate coefficient. Given the experimental challenges of generating sufficient quantities of excited H_2, it is unlikely that the necessary CD measurements will be performed in the foreseeable future.

In fact, some experimental studies of TBA do exist, but they have been carried out under conditions not relevant to primordial chemistry. Measurements have been carried out for spin-polarized atomic hydrogen, but at temperatures of $130-600$ mK and magnetic fields of $3-9$ T [13]. TBA measurements have also been performed with ultracold atoms at $\sim 10-500$ nK, though not yet with atomic H [14]. In any case, all these measurements are essentially suitable only for testing *s*-wave calculations and cannot be extrapolated to the higher temperatures relevant for first star formation.

Thus we find ourselves in the situation of trying to determine if one can experimentally study reaction (3) at the desired temperatures. A rough estimate for the required atomic H number density can be given by

$$n_H \sim \left(\frac{S}{\alpha V}\right)^{1/3}, \tag{5}$$

where S is the signal rate, α is the TBA rate coefficient, and V is the detected interaction volume. In the $200-2000$ K temperature range of interest, the lowest published value for the rate coefficient is $\alpha \sim 10^{-33}$ cm^6 s^{-1}. Using this value will give an upper limit for the required H density. While one can hope that α is larger and the required density lower, it is safer to design an experiment assuming the least promising conditions.

A major challenge in studying this reaction is how to separate the neutral daughter H_2 product from the parent H atoms in the reaction. One possibility would be to use a Resonant Excitation MultiPhoton Ionization (REMPI) method [e.g., 15, 16]. This could be used to convert the product H_2 into a far more readily detectable H_2^+. In that case the detection volume would be on the order of 10^{-3} cm^3. The REMPI method has a duty cycle of $f \sim 10^{-7}$ as determined by the ~ 10 ns width of the laser pulses and the ~ 10 Hz repetition rate. Additionally, the REMPI method can detect only one individual ro-vibrational level of H_2 at a time, though with an efficiency per pulse approaching 100%. There are on the order of~ 500 such levels in the ground electonic state of H_2. Here we make the crude assumption that these are all equally populated in the TBA reaction. Putting all the above together, eq. (5) becomes

$$n_{\rm H} \sim \left(\frac{500S}{f\alpha V}\right)^{1/3}. \tag{6}$$

A healthy experimental signal rate would be 1 s^{-1}. Plugging in this and the relevant numbers given above, yields a required density of $n_{\rm H} \sim 2 \times 10^{15}$ cm^{-3}.

These $n_{\rm H}$ densities could perhaps be achieved in a hydrogen discharge, but the plasma chemistry involving neutrals, electrons and ions, as well as surface reactions, is likely to preclude being able to derive a reliable TBA rate coefficient. Other methods appear unable to reach the desired densities. With photodetachment of H^-, as was done in [4, 6], one can achieve densities of only $\sim 10^4$ cm^{-3}, but with no H_2 contamination. Neutral beam injectors [e.g., 17] and comercially available cracked atom sources [e.g., 18] are each expected to reach densities of only $\lesssim 10^{10}$ cm^{-3}. Gas jets can reach denisities of $\sim 10^{12}$ cm^{-3} [19]. None of these appear to be sufficiently dense. Plus, these last three approaches are contaminated with $\sim 0.1\% - 30\%$ H_2, a background level which could potentially swamp the desired signal H_2 molecules and prevent meaningful TBA studies.

From the perspective of an atomic physicist, the situation does not look promising in the short term. Quantum theory is still at least several years away from being able to calculate the cosmologically important TBA rate coefficient. Experimentally, more thought is required to find a way to measure reaction (3). Perhaps we have overlooked or are unaware of recent experimental or technological advances. Perhaps one could develop a different detection method which collects signal from more than one ro-vibrational level at a time and/or has a larger detection volume. Perhaps the final ro-vibrational distribution is sufficiently non-uniform that the rate coefficient into certain individual levels is large enough to measure. Or perhaps something else may come along which would also result in reducing the required H density needed to perform this measurement. This is a tough nut to crack, of critical importance for advancing our understanding of structure formation in the early Universe, and a great challenge to work towards solving.

SUMMARY

We have discussed three key reactions controlling the H_2 abundance during the epoch of protogalaxy and first star formation and reviewed how uncertainties in the rate coefficients for each affect our ability to model structure formation during this epoch. Our recent AD work greatly reduces the former uncertainties due to the previously available chemical data. We are in the process of measuring MN to put those data on a more solid footing. Lastly, it appears that neither theoretical nor experimental atomic physics will be capable of generating a reliable TBA rate coefficients any time in the near future.

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