Modeling the chemistry of early universe

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Resumen / La química del Universo primitivo consistía principalmente en especies atómicas simples y moléculas compuestas de hidrógeno y helio. Por lo tanto, para comprender la química del Universo primitivo es necesario conocer los procesos químicos que sufrieron estas especies. Además, la interacción con el fondo cósmico de microondas (CMB) es la mejor prueba para determinar la evolución y abundancia de las especies primordiales. Modelizamos la química del Universo primigenio en función del corrimiento al rojo utilizando el paquete astroquímico KROME. Nos centramos en la molécula HeH^+ porque esta molécula tiene un alto momento dipolar y se forma a partir de las especies más abundantes, H y He. Además, su contribución a la opacidad óptica afecta al CMB. En particular, exploraremos el impacto en la abundancia de HeH^+ de nuevas tasas para procesos como la recombinación disociativa y la fotodisociación. La determinación precisa de la composición química del gas primordial es importante para comprender la formación de las primeras estrellas del universo.

Abstract / The chemical composition of the early universe consisted mainly of simple atomic species and molecules made of hydrogen and helium. Therefore, to understand the chemistry of the early universe it is necessary to know the chemical processes that these species underwent. Also, the interaction with the Cosmic Microwave Background (CMB) is the best test to determine the evolution and abundance of the primordial species. We model the chemistry of the early universe as a function of redshift using the astrochemistry package KROME. We focus on the HeH^+ molecule because this molecule has a high dipole moment and is formed from the most abundant species, H and He. Also, its contribution to the optical opacity affects the CMB. In particular, we explore the impact of new rates for processes such as dissociative recombination and photodissociation on the abundance of HeH^+. An accurate determination of the chemical composition of the primordial gas is important to understand the formation of the first stars in the universe.

Keywords / early universe — dark ages, reionization, first stars — primordial nucleosynthesis

1. Introduction

It is important to know the processes that primordial molecules and atoms underwent, and their interactions with the cosmic microwave background to understand the evolution of the early universe. Maoli et al. (1994) suggested that primordial molecules are important for the CMB because they can smear the primary fluctuations of the CMB, and create second anisotropies. Primordial molecules can produce low-frequency photons (rotational lines). For the interaction of molecules and photons, it is important to consider two important physical quantities, the cross section for scattering, and the concentration, which depends on the abundance of the chemical elements and the rate of their reactions Dubrovich (1997). The early universe was extremely hot and dense. Density perturbations first expanded adiabatically, then began to cool, forming the first bound structures Lepp et al. (2002). To understand all this, it is important to know the chemical processes, which first appeared in the recombination era Dalgarno (2005). At redshift ≈ 1100 the universe was controlled by the net 2s-1s two-photon decay. At redshift $< 800 - 900$, free electrons and protons are available, which allows the rate of recombination to be of importance, thus the fractional abundance of protons and free electrons starts to decrease Chluba et al. (2010). Approximately 250 reactions of 30 species have been studied so far. In this way, they compute the abundances of the first molecules Gay et al. (2011). To understand the primordial chemistry of the universe one must consider the Friedmann-Robertson-Walker model, this model considers a homogeneous, flat and isotropic universe. According to this model, the formation of the first elements occurred in a low-density, high-temperature plasma environment Galli & Palla (2013). To model the early chemistry we estimate the abundance of these species as a function of redshift using the astrochemistry package KROME. The main objective is to explore new rates of destruction of the HeH^+ molecule and the impact it has on the abundance of this molecular ion.

2. Chemical network

Considering the network of chemical reactions for hydrogen and helium in the early universe, we compute the abundance of this species, so it is important to know the reactions that occurred to this species. First, we consider the most abundant molecular, which is molecular hydrogen. This molecule can be formed by two

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channels.

The first is via the H_2^+ channel:

$$H_2^+ + H \longrightarrow H_2 + H^+. \quad (1)$$

The second reaction is via associative detachment,

$$H^- + H \longrightarrow H_2 + e. \quad (2)$$

The early universe was dominated mainly by H and He. The main interaction between these species is via HeH^+ molecule (helium hydride ion), one of the first molecular ions. The formation process of this species is the radiative association. In this process two gas phase species collide to form a new species while emitting a photon Bates & Herbst (1988):

$$He + H^+ \longrightarrow HeH^+ + h\nu. \quad (3)$$

On the other hand, another process that contributes to determine HeH^+ abundance is the charge-exchange destruction process via:

$$HeH^+ + H \longrightarrow He + H_2^+. \quad (4)$$

For the destruction process, photodissociation is dominated by two processes Coppola et al. (2017):

$$HeH^+ + h\nu \longrightarrow He^+ + H, \quad (5)$$

$$HeH^+ + h\nu \longrightarrow He + H^+. \quad (6)$$

Another destruction process is dissociative recombination, in which the ion captures a free electron while its internal degrees of freedom undergo excitation Novotný et al. (2019):

$$HeH^+ + e \longrightarrow He + H. \quad (7)$$

The chemical network is completed by the equation for the redshift:

$$\frac{dt}{dz} = \frac{1}{H_0(1+z)^2\sqrt{1+\Omega_0 z}}, \quad (8)$$

where H_0 is the Hubble constant and Ω_0 is the closure parameter.

3. Numerical algorithm

To obtain the abundances of the species i we use the following differential equation:

$$\frac{dn_i}{dt} = -D_i n_i + C_i, \quad (9)$$

where D_i represents the destruction coefficient and C_i represents the creation coefficient, both for species i.

To model the early chemistry we will compute the abundance of these species as a function of redshift (Fig. 1 and Fig. 2) using the astrochemistry package KROME Grassi et al. (2014). To reproduce the evolution of the primordial gas, the test is based on the rate coefficient for the different reactions for the species from Galli & Palla (1998).

4. Chemical rate coefficients

To compute the abundances of primordial molecules, it is important to know the rate coefficients of the different reactions, we will focus on the molecule HeH^+ and we will use different rate coefficients from the literature.

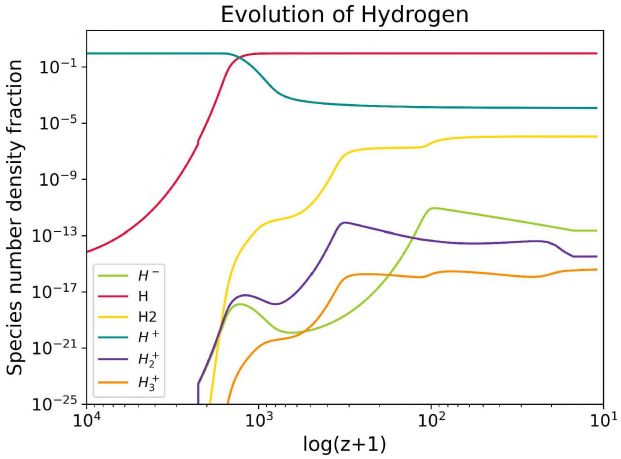

Fig. 1. Hydrogen chemistry considered in the standard model as a function of redshift.

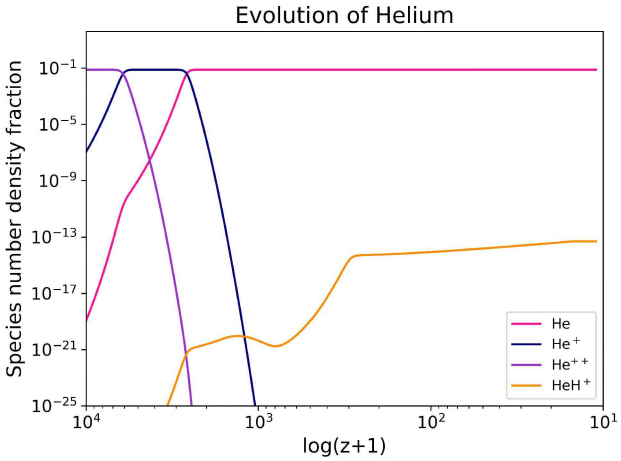

Fig. 2. Helium chemistry considered in the standard model as a function of redshift.

4.1. Rate coefficients of HeH^+

The reactions used to compute the HeH^+ abundance are the same as those used by Schleicher et al. (2008), and a comparison will be made with Galli & Palla (1998) (Fig. 3). However for some of the reactions new rate coefficients that have been calculated will be used, such as Coppola et al. (2017) for the reaction Eq. 5 and Eq. 6, Novotný et al. (2019) for Eq. 7.

Table 1 collects the reactions used and the reaction number. Table 2, next to the reaction number, compares the rate coefficients of Galli & Palla (1998) with those used by Schleicher et al. (2008).

We will also use the rate coefficient calculated from Coppola et al. (2017) they presented a new calculation for direct photoionization, they use Eq. 10 to the processes Eq. 5, and for Eq. 6:

$$\alpha(T_r) = aT_r^b \exp(-c/T_r), \quad (10)$$

the parameter values for Eq. 10 are given in Table 3.

Table 1. Reactions considered in this paper for HeH^+.

	Reaction
He8)	$He + H^+ \longrightarrow HeH^+ + h\nu$
He9)	$He + H_2^+ \longrightarrow HeH^+ + H$
He10)	$He^+ + H \longrightarrow HeH^+ + h\nu$
He11)	$HeH^+ + H \longrightarrow He + H_2^+$
He12)	$HeH^+ + e \longrightarrow He + H$
He13)	$HeH^+ + H_2 \longrightarrow H_3^+ + He$
He14)	$HeH^+ + h\nu \longrightarrow He + H^+$
He15)	$HeH^+ + h\nu \longrightarrow He^+ + H$

4.2. Dissociative recombination of HeH^+

Using ion storage, Novotný et al. (2019) performed measurements of the rate coefficient of dissociative recombination. This is a process in which the ion captures a free electron while its internal freedom undergoes excitation. They found a decrease in the recombined electrons for low rotational states of HeH^+.

To determine the rate coefficient, they use the Eq. 11:

$$\alpha(T) = A\left(\frac{300}{T}\right)^n + T^{-1.5}\sum_{i=1}^{3} c_i \exp(-T_i/T). \quad (11)$$

The units for Eq. 11 are $cm^3\ s^{-1}$, assuming thermal level populations, the parameters are, $A = 2.0 \times 10^{-10}\ cm^3\,s^{-1}$, $n = 0.68$ (dimensionless) , c_1 =$2.8 \times 10^{-7}\ K^{3/2}\,cm^3\,s^{-1}$, $c_2 = 1.3 \times 10^{-6}\ K^{3/2}\,cm^3\,s^{-1}$, $c_3 = 8.6 \times 10^{-5}\ K^{3/2}\,cm^3\,s^{-1}$, $T_1 = 20$ K, $T_2 = 140$ K and $T_3 = 420$ K.

5. Results

In the following we report our results and compare the new HeH^+ abundances, using rate coefficients calculated in previous works.

5.1. Fit coefficients

Considering the rate from Galli & Palla (1998), Stancil et al. (1998) and from Novotný et al. (2019) for dissociative recombination, we obtained the results shown in Fig. 3, which presents the rate of this reaction as a function of the temperature.

5.2. Evolution of HeH^+

To calculate the evolution of HeH^+ we use the value used by Schleicher et al. (2008), but we also use the rate calculated in different works. In particular for the reaction Eq. 7, we use the rate calculated from Novotný et al. (2019), for photodissociation Eq. 5 and Eq. 6 we use the value calculated from Coppola et al. (2017). In addition for Eq. 4 we use the value calculated from Bovino et al. (2011) is:

$$\alpha(T) = 4.3489 \times 10^{-10} T^{10.110373} e^{-315396/T}. \quad (12)$$

The units for Eq. 12 are $cm^3\ s^{-1}$ valid for T $\leq$ 1000 K.

First considering the values used in Schleicher et al. (2008), we compute the abundance of the species in function of redshift. Figure 4 shows the evolution of HeH^+ with the values of Galli & Palla (1998) and from Schleicher et al. (2008).

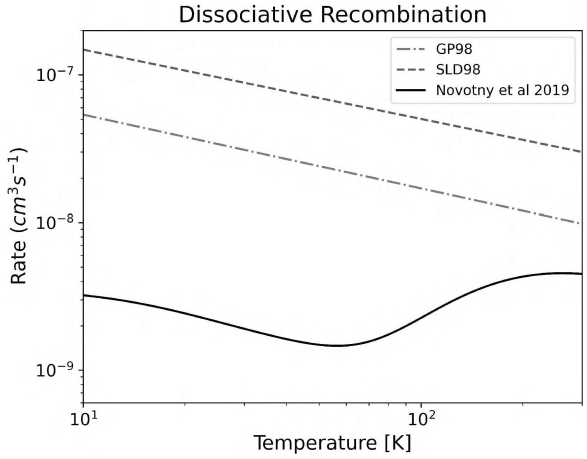

Fig. 3. Rate coefficients as a function of temperature for the destruction reaction dissociative recombination of HeH^+.

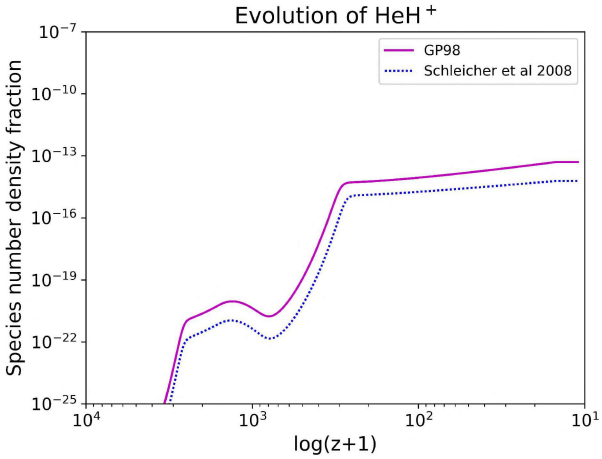

Fig. 4. Fractional abundance of HeH^+ using the rate coefficients from Galli & Palla (1998)(magenta) and from Schleicher et al. (2008)(blue)

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In Fig. 5 it can be seen how the evolution of HeH^+ changes as the rate coefficients from Bovino et al. (2011), Coppola et al. (2017) and Novotný et al. (2019) are considered.

6. Discussion and conclusion

To understand the chemistry of the early universe it is necessary to know about the atomic and molecular processes presented in this epoch Bovino et al. (2011). One of the primordial molecules that we focus on is HeH^+, this is because this molecule presents a large dipole moment, which is important to radiative cooling and coupling to the CMB Novotný et al. (2019). The cooling of primordial gas is crucial to the formation of the first

Table 2. Rate coefficients in $cm^3\ s^{-1}$for each reaction of the molecule HeH^+. The gas temperature T is in K, and T_r is the temperature of the radiation in K. The first column shows the reactions of HeH^+, the second shows the value from Galli & Palla (1998), and the last column shows the value from Schleicher et al. (2008) that recompile the value from; GP98: Galli and Palla (1998), JSK95:Juřek, Špirko, Kraemer (1995), LJB95: Linder, Janev, Botero (1995), SLD98: Stancil, Lepp, Dalgarno (1998) and ZSD98: Zygelman, Stancil, Dalgarno (1998).

	Rate from GP98	Rate from Schleicher et. al (2008)
He8)	$7.6 \times 10^{-18} T_g^{-0.5}$, $T_g \leq 10^3$	$8.0 \times 10{-}20 \left(\frac{T}{300}\right)^{-0.24} \exp\left(\frac{-T}{4000}\right)$ (SLD98)
He9)	$3.0 \times^{-10} \exp\left(-\frac{6717}{T}\right)$	GP98
He10)	$1.6 \times 10^{-14} T^{-0.33}$, $T \leq 4000$,fit 1.0×10^{-15}, $T > 4000$	$4.16 \times 10^{-16} T^{-0.37} \exp\left(\frac{-T}{87600}\right)$ (SLD98)
He11)	9.1×10^{-10}	$0.69 \times 10^{-9} \left(\frac{T}{300}\right)^{0.13} \exp\left(\frac{-T}{33100}\right)$ (LJB95)
He12)	$1.7 \times 10^{-7} T^{-0.5}$	$3.0 \times 10^{-8} \left(\frac{T}{300}\right)^{-0.47}$ (SLD98)
He13)	1.3×10^{-9}	–
He14)	$6.8 \times 10^{-1} T_r^{1.5} \exp\left(\frac{-22750}{T_r}\right)$	$220 T_r^{0.9} \exp\left(\frac{-22740}{T_r}\right)$ (JSK95)
He15)	$7.8 \times 10^3 T_r^{1.2} \exp\left(-\frac{240000}{T_r}\right)$	GP98

Table 3. Fits for the thermal contribution as a function of T_r for HeH^+ direct photodissociation.

	Thermal
$HeH^+ + h\nu \longrightarrow He^+ + H$	a = 273518 b = 0.623525 c = 1444044 K
$HeH^+ + h\nu \longrightarrow He + H^+$	a = 2.03097×10^8 b = −1.20281 c = 24735 K

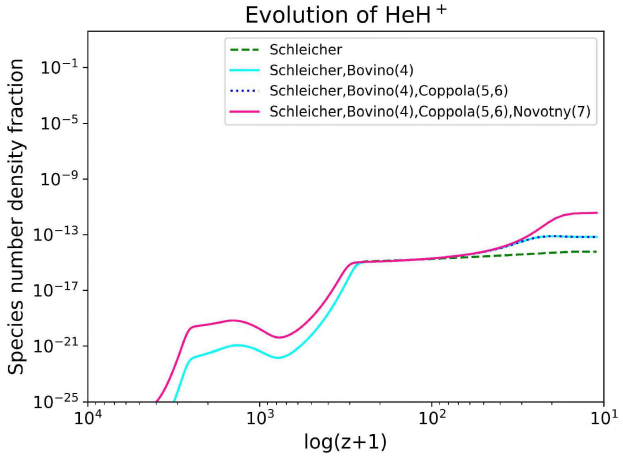

Fig. 5. Fractional abundance of HeH^+ in function of redshift. The green curve represents the evolution of HeH^+ using the rate coefficients of Schleicher et al. (2008). The cyan curve is the evolution of HeH^+ but changing the reaction 4 of Bovino et al. (2011). The blue curve is the evolution of HeH^+ but changing the rate coefficient for the reaction 5 and 6 of Coppola et al. (2017), and the magenta curve is changing the rate coefficient for the reaction 7 of Novotný et al. (2019).

stars Coppola et al. (2011). Implementing new values of the rate coefficients for HeH^+ we have been able to compute the abundance of this molecule using KROME, we reproduced the results obtained by Schleicher et al. (2008) and also added the new value of rate coefficient from Bovino et al. (2011), Coppola et al. (2017) and Novotný et al. (2019). In particular, we obtained an increase in the abundance of HeH^+, which means that at low z, the detection of HeH^+ may become more feasible. Also, the increase of this abundance can affect the formation of the first stars as it contributes to the formation of molecular hydrogen.

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