The first molecules in the intergalactic medium and halos of the Dark Ages and Cosmic Dawn

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ABSTRACT

We study the formation and destruction of the first molecules at the epochs of the Dark Ages and Cosmic Dawn to evaluate the luminosity of the protogalaxy clumps (halos) in the molecular lines. The cosmological recombination is described using the RecFast model of an effective three-level atom, while the chemistry of the molecules is examined using the relevant basic kinetic equations. We then studied the effect of collisional and radiative excitation of molecules on the intensity of molecular emission in both warm and hot halos. Using the Planck data on the reionization of the intergalactic medium at $z \sim 6 - 8$, we evaluated the upper limits of the light energy density for four models of thermal light from the first sources that appeared in the Cosmic Dawn epoch. Assuming that in the halos, the light energy density may essentially be even higher, we estimated the impact of the light from the first sources (the first light) on the formation and destruction of the first molecules in them as well as between them. We show that the molecules H$_2$ and HD are destroyed by photodissociation processes shortly before the full reionization in the inter-halo medium, in the medium of both types of halos and for all models of the first light. At the same time, the number density of helium hydride ions, HeH\textsuperscript{+}, shows essentially more complicated dependences on the kinetic temperature of halos and the models of the first light. These features characterizing the abundance of molecules also determine the intensity of the halos luminescence during their evolution. Furthermore, we calculated the evolution of the brightness temperature of the individual halo in the rotational lines of H$_2$, HD and HeH\textsuperscript{+} molecules relative to the temperature of the cosmic microwave background at redshifts corresponding to the Dark Ages and Cosmic Dawn epochs. It does not exceed the microkelvin, but its detection may be an important source of information about the physical processes taking place at the beginning of the formation of the first stars and galaxies at the epochs of the Dark Ages and Cosmic Dawn.

Key words. cosmology: theory — Dark Ages and Cosmic Dawn: formation — galaxies: high-redshift — stars: intergalactic medium — reionization

1. Introduction

The upcoming decade promises to be a time of significant breakthroughs in the observational investigation exploring the epochs of the Dark Ages and Cosmic Dawn. These studies are expected to fill the gap in our understanding of how the first stars and galaxies formed. A few teams of cosmologists and observers are competing to detect the signal in the hyperfine 21 cm line of atomic hydrogen that is redshifted according to these epochs. The first detection of the absorption in this line at $z = 15 - 20$ was announced by the EDGES\textsuperscript{1} team a few years ago (Bowman et al. 2018; Hills et al. 2018). Other sources of important information about the formation of the first stars and galaxies are the first molecules, which absorb the cosmic microwave background radiation (CMBR) in their ro-vibrational transitions in cold baryonic matter clouds, while emitting additional radiation in hot ones or resonantly scattering it in moving clouds (Dubrovich 1977; Maoli et al. 1994, 1996; Kamaya & Silk 2002; Ripamonti et al. 2002; Kamaya & Silk 2003; Omukai & Kitayama 2003; Mizusawa et al. 2004, 2005; Liu et al. 2019; Novosyadlyj et al. 2020; Maio et al. 2022) and a marginal possibility has been predicted for modern and projected telescopes such as ALMA\textsuperscript{2}, JWST\textsuperscript{3}, SAFIR Observery, SPICA\textsuperscript{4}, and OST\textsuperscript{6}.

In our previous papers (Novosyadlyj et al. 2017, 2018, 2020; Kulinich et al. 2020) we studied the formation and destruction of the first molecules, H$_2$, HD, and HeH\textsuperscript{+}, in the halos of the Dark Ages and their luminescence in the rotational lines of these molecules. Here, we elucidate the matter of how the radiation of the first sources, arising at Cosmic Dawn, influences the abundances of the first molecules and their luminescence in the same rotational lines. For simplicity, we suppose the thermal energy distribution of the first sources and consider the different evolution of its spectral density and radiation temperature at the moment of cosmological reionization, $z_{rei}$. The latter we assume to be between $6 \leq z \leq 8$, according to the observational data coming from the measurements of the polarization of CMBR at low spherical harmonics (Planck Collaboration 2020a,b), Gunn-Peterson trough in the spectra of high-redshift quasars (Bouwens et al. 2015; Banados et al. 2018; Davies et al. 2018), and the Lyman Break galaxies (Mason et al. 2018).

2 https://www.almaobservatory.org/en/home/
3 https://www.jwst.nasa.gov/
4 https://safir.jpl.nasa.gov/
5 https://www.ir.isas.jaxa.jp/SPICA/
6 https://asd.gsfc.nasa.gov/firs/
All computations in the paper were performed for consistent values of the main parameters of the cosmological model following the final data release of the Planck Space Observatory (Planck Collaboration 2020b): the Hubble constant $H_0 = 67.4$ km/s/Mpc, the mean density of baryonic matter in the units of critical one $\Omega_m = 0.0493$, the mean density of dark matter $\Omega_{dm} = 0.2657$, the mean density of dark energy $\Omega_{\Lambda} = 0.685$, its equation of state parameter $w_{de} = -1.03$, the spectral index of the scalar mode of cosmological perturbations $n_s = 0.965$ and the matter fluctuation amplitude $\sigma_8 = 0.811$, and the current temperature of cosmic microwave radiation $T_{00} = 2.7255$ K. We use also the primordial helium abundance $Y_e = 0.2446$ (Peimbert et al. 2016) and deuteron fraction $x_D = 2.527 \cdot 10^{-5}$ (Cooke et al. 2018), which are in good agreement with the posterior means from Planck Collaboration (2020b).

The outline of this paper is as follows. In Section 2, we present the network of chemical reactions leading to the formation and destruction of molecules and the recombination and photoionization of atoms as well as the corresponding kinetics equations and energy balance. In Section 3, we describe the models of the energy distribution for the first sources of light (the first light) and estimate the value of the dilution coefficient for each from them. In Section 4, we compute the kinetics of chemical reactions in the inter-halo medium and analyze the influence of the first light on the number density of the first molecules $H_2$, HD, and HeH$. The intra-halo chemistry and luminosity of halos in the ro-vibrational molecular lines are analyzed in Section 5. To do this, together with the equations of the kinetics of chemical reactions and the kinetics of excitations and de-excitations of the ro-vibrational energy levels of the first molecules, we solve the equations for the evolution of the density and temperature of matter. The top-hat halos with hot and warm baryonic gas inside and with masses that are typical for $\Lambda$CDM/AWDM models of the Universe are considered. As a result, we obtain the evolution of the number density of molecules $H_2$, HD, and HeH$ at different stages of halo formation up to the reionization epoch for different models of the first light. Our conclusions are given in Section 6. Useful approximations for the rates of photorecombination and photoionization for HII and DI are presented in Appendix A, while the rates of photodissociation for molecules $H_2$ and HD are presented in Appendix B.

### 2. Chemical network

We analyze the formation and destruction of the most abundant molecules in the inter-proto-galaxy medium of the Dark Ages and Cosmic Dawn epochs: $H_2$, HD, and HeH$. The minimal set of reactions important for epochs starting from cosmological recombination, Dark Ages, Cosmic Dawn, and reionization is presented in Table 1. The rates and fitting formulas for them are taken from the sources cited in the last column. Most of fitting formulas are collected in Tables 1-3 of Abel et al. (1997), Tables 1-3 of Galli & Palla (1998), and Table B.1 of Schleicher et al. (2008). We also keep here the notations of reactions (in parentheses) introduced there. In comparison with a minimal set of reactions important for the Dark Ages epoch (Galli & Palla 1998; Novosyadlyj et al. 2018), we have added the important reactions for the Cosmic Dawn epoch, when the first light would ionize atoms and molecules and then photodissociate the molecules. These are: H6, H11, H12, H18, H23, D25, He10, He12, and He15. Since the ionization of hydrogen is important for the formation and destruction of molecules, we propose the more accurate analytical approximation of effective cross-sections of hydrogen photoionization from the base level (case A) and the first metastable 2s one (case B) in Appendix A. The direct reaction of photodissociation H23, as well as that of D25, becomes crucial for the destruction of hydrogen and hydrogen deuteride molecules by first light before reionization (Glover & Jappsen 2007; Schleicher et al. 2008). We propose the new approximation of the rate of photodissociation of H2 (HD) using recent and accurate computations of effective cross-section for this purpose from Heyas et al. (2017), presented in Appendix B.

We computed the evolution of fractions, $x_i$, of neutral atoms, molecules, and ions from the cosmological recombination up to hydrogen reionization at $z_{rei}$. The index “i” notes any atom, molecule, or ion presented in Table 1. The kinetic equations for chemical reactions in the general form are as follows (Puy et al. 1993; Galli & Palla 1998; Vonlanthen et al. 2009; Novosyadlyj et al. 2018):

$$-(1+z)H_0\frac{dx_i}{dz} = \sum_{mn} C_{i,mn} x_m n_n + \sum_{ij} R_{ij} x_i n_j - \sum_j C_{i,j} f_j x_j - \alpha_i x_i,$$

where $z$ is redshift; $C_{i,ij}^{(m)}$ is the rate of collision reaction with reactants, $m$ and $n$, which leads to the formation of the atom, molecule, ion, $i$; $R_{ij}^{(m)}$ is the rate of radiative reaction for reactant, $m$, which leads to the formation of an atom, molecule, ion, $i$; $C_{i,m}$ is the rate of destruction of i-reactant by collision with an n-reactant; and $\alpha_i$ is the photorecombination rate of the reactant, $i$. The total fraction of the main chemical elements in the unit number density of hydrogen, denoted as $f_{\odot}$, namely, $f_{\odot} = n_{\odot}/n_H$ for a reactant, $m$, containing helium; $f_{\odot} = n_{\odot}/n_D$ for a reactant, $m$, containing deuterium; and $f_{\odot} = 1$ for reactant, $m$, containing hydrogen only. For chemical species containing only hydrogen, the fraction, $m$, is $x_m = n_m/n_H$, where $n_m$ is the number of species, $m$, and $n_H$ is the total number density of hydrogen; for species containing deuterium and helium, $x_m = n_m/n_{D+H}$ and $x_m = n_m/n_{D+H_2}$, respectively.
where $n_2$ and $n_{He}$ are the total number densities of deuterium and helium.

Equations (1) for the reactions presented in Table 1 together with equations of cosmological recombinations for hydrogen, deuterium, and helium (Seager et al. 1999, 2000; Novosyadlyj et al. 2017) compose a system of kinetic equations which we solve numerically together with the equations of expansion of the Universe and energy balance for the baryonic component:

$$H = \sqrt{\Omega_0(1+z)^3 + \Omega_m(1+z)^3 + \Omega_r(1+z)^3} \; (1+z),$$

$$\frac{dt_f}{dz} = \frac{2T_f}{1+z} + \frac{8\sigma_T n_H A_f}{3m_c c (1+z)} \left( f_{D} + f_{He} + x_e \right) \left( T_f - T_e \right),$$

$$+ \frac{8\sigma_T n_H A_f}{3m_c c (1+z)} \left( f_{D} + f_{He} + x_e \right) \left( T_f - T_e \right).$$

where $\sigma_T$ is the Thomson scattering cross-section, $a_i$ is the radiative constant, and $m_e$ is the mass of an electron. We set the initial conditions for these reactions at the early epoch before the cosmological recombination when all ingredients were completely ionized and a Saha approximation was applicable (see details in Appendix A in Novosyadlyj et al. (2017)). The publicly available codes RecFast7 and DDRIV8 have been used in the general code CDhalo.f, which was designed for integrating the system of equations (1) in the expanding Universe over cosmological recombination.

Dark Ages, Cosmic Dawn, and the first light becomes important for the ionization and dissociation of atoms and molecules. The last equation (3) is used at $z \leq 850$, at higher $z$ $T_e(1+z)$. It takes into account the main mechanisms of cooling or heating of diluted gas in the Dark Ages and Cosmic Dawn: adiabatic cooling and heating by CMBR at the early epoch and by the first light in the late ones.

3. Models of the first light

In the epoch of Cosmic Dawn, the radiation of the first sources (warm or hot halos, the first dwarf galaxies with Pop III stars, and shock waves), referred to here as the first light, starts to impact the kinetics of the chemical reactions, exciting the ro-vibrational levels of molecules; and at the end of Cosmic Dawn, it starts to ionize the hydrogen, marking the beginning of the epoch of reionization. To indicate the moment of reionization, we assume that this happens when the fraction of ionized hydrogen reaches a value of 0.5. According to the Planck 2018 results on the CMBR anisotropy, this takes place at $6 \leq z \leq 8$ (see Fig. 45 in Planck Collaboration (2020b)). Other observations, such as the Gunn-Peterson trough in the spectra of high-redshift quasars (Bouwens et al. 2015; Banados et al. 2018; Davies et al. 2018) and Lyman Break galaxies (Mason et al. 2018), support this value. Thus, here we analyze models of the first light that satisfy the following condition: $x_{HI} = x_{HI,f} = 0.5$ at $6 \leq z \leq 8$.

To analyze the allowable levels of illumination in the inter-protogalaxy medium of the Cosmic Dawn epoch, we assume that sources of the first light are thermal. We consider here the thermal models of the first light described by the Planck function with temperature, $T_f$, which is some smooth function of redshift and dilution coefficient $a_f$:

$I_f(\nu) = a_f B_\nu (T_f).$

So, in each moment of the Dark Ages and Cosmic Dawn, the total spectral energy density of radiation is the sum of the CMBR energy density and the first light one:

$$J_\nu = \frac{4\pi}{c} \left[ B_\nu (T_{CMB}) + a_f B_\nu (T_f) \right].$$

Since the rates of ionization or dissociation of atoms and molecules are computed by integration over the energy of product of cross-section and intensity per photon energy (see eq. (A11) in Appendix), they can be presented as the following sum:

$$R_{ii} = R_{ii}(T_{CMB}) + a_f R_{ii}(T_f).$$

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7 http://www.astro.ubc.ca/people/scott/recfast.html
8 http://www.netlib.org/slatec/src/ddriv1.f
lines at $z > 200$, and those by the first light are shown by color lines at $z < 30$.

We consider here the simple evolution model of the radiation temperature of the first light:

$$T_{fl} = T_\ast \left( \frac{1 + z_{rei}}{1 + z} \right)^p, \quad \text{with} \quad p = n \left( \frac{1 + z}{1 + z_{rei}} \right)^{1/3},$$

with such values of parameters: a) $T_\ast = 5000$ K, $n = 2$ (Ia), b) $T_\ast = 10000$ K, $n = 2$, (Ib), c) $T_\ast = 5000$ K, $n = 1$ (Ic), and d) $T_\ast = 10000$ K, $n = 1$ (Id). So, at the moment of reionization, $z_{rei}$, the radiation temperature of the first light is 5000 K or 10000 K. For the dilution factor, $\alpha_{fl}$, we set the constant and estimate its value using the condition of reionization. The condition $x_{fl} = x_{HII} = 0.5$ at $6 \leq z_{rei} \leq 8$, which we suppose here, gives $3.3 \cdot 10^{-10} \leq \alpha_{fl} \leq 4.85 \cdot 10^{-10}$ for model Ia, $6.0 \cdot 10^{-17} \leq \alpha_{fl} \leq 8.6 \cdot 10^{-17}$ for model Ib, $1.9 \cdot 10^{-10} \leq \alpha_{fl} \leq 3.0 \cdot 10^{-10}$ for Ic, and $4.5 \cdot 10^{-17} \leq \alpha_{fl} \leq 6.3 \cdot 10^{-17}$ for Id. So, for the same $T_\ast$, the range of values of $\alpha_{fl}$ is narrow for such a range of redshift of reionization, but the value strongly depends on $T_\ast$.

The spectral energy densities for all these models are shown in Fig. 2. The potential of ionization of hydrogen atoms is in the Wien range of the Planck distribution. Thus, the higher the radiation temperature at the moment when $x_{HII} \approx 0.5$, the lower the dilution coefficient should be. For comparison, we present in this figure the spectral energy density of CMBR at the same redshifts as well as at the current epoch ($z = 0$). The observable cosmic infrared background (CIB) (Kogut et al. 2019) is shown as well. Such a comparison shows that at frequencies below $2.5 \cdot 10^4$ GHz ($\lambda > 0.1 \mu m$), the intensity of such a first light is essentially lower than CMBR and CIB. However, it can excite the ro-vibrational levels of the most abundant molecules to produce the spectral distortions of the CMBR in the shortwave range.

In the left panel of Fig. 3, we present the evolution of the hydrogen ionized fraction $x_{HII}$ for the models of the first light Ia-Id. The helium atoms are represented by the neutral fraction. The values of dilution coefficients, $\alpha_\ast$, are adjusted so that $x_{HII} \approx 0.5$ on $z = 8$ and 6. We can see that the data in this figure well match the data in Fig. 4 of Planck Collaboration (2020b). It means that these models of the first light are in agreement with the observational data on the optical depth of reionization.

In the right panel of Fig. 3, we present the ranges of dilution coefficients against the temperature of thermal radiation for two evolution models of the first light, which provide $x_{HII} \approx 0.5$ at $z_{rei} = 8$ (solid line) and $z_{rei} = 6$ (dashed line).

4. Molecules in the inter-proto-galactic medium

The evolution of the number density H, D, and He and the temperature of CMBR and baryonic matter through the Dark Ages and Cosmic Dawn up to reionization are shown in Fig. 4 (top panel and bottom one
Evolution of the number densities of atoms, ions, neutral, and ionized molecules \( n_i(z) \) from cosmological recombination through the Dark Ages and Cosmic Dawn up to reionization for the models of the first light Ia and Ib: the red lines for \( z_{rei} = 6 \), the blue lines for \( z_{rei} = 8 \). The black lines are the number density of species for the case without the first light, \( n_0^i(z) \). In the bottom panel, we also show the evolution of radiation temperature of the first light. The correspondence of the lines of the radiation temperature to the models of the first light is the same as in Fig. 2. The heating of the baryonic gas by the first light is noticeable. We can see that the dilution factor is important in the heating of gas by radiation: the thermal radiation with lower \( T_{fl} \) but higher \( \alpha_{fl} \) (model Ia and Ic) heats more than the thermal radiation with higher \( T_{fl} \) but lower \( \alpha_{fl} \) (models Ic and Id). The temperature of baryonic matter is approximately the same (~ 2000 K) in the cases of models Ia and Ic at the moment of reionization \( z = 8 \) and 6, as it is shown in Fig. 4 (solid red lines of \( T_b \)). At the same time, the temperature of the first light is 5000 K. For the model of the first light with radiation temperature \( T_{fl} = 10000 \) K at the moment of reionization, the dilution factor is \( \sim 10^{-17} \) and the baryonic matter is heated by radiation only by a few degrees (solid blue lines of \( T_b \)).

We computed the evolution of the number densities of atoms and molecules, \( n_i \), starting from the early epoch before the cosmological recombination \( (z = 10000) \) up to the beginning of the epoch of reionization \( (z = 6) \) for different models of the first light. In Figs. 5 and 6, we present the results for the Ia – Id models of the first light. The black lines show the evolution of the number densities of atoms, ions, neutral and ionized molecules without the first light, \( n_0^i(z) \), which well agree with results by Galli & Palla (1998); Schleicher et al. (2008); and Vonlanthen et al. (2009). Recent studies by Maio et al. (2022) of \( \text{H}_2 \) gas evolution over cosmic time \( (2 \leq z \leq 17) \) in the cosmological simulation ColdSIM do not contradict the semi-analytical ones presented here. The fact that the \( \text{H}_2 \) molecules at \( z \leq 8 - 9 \) do not disappear due to photodissociation can be explained by the effect of self-shielding of dense or extended regions of molecular hydrogen, which is taken into account in those studies. The lines of the same atoms and molecules in the epochs preceding the Cosmic Dawn are superimposed and black. The color lines show the influence of the first light on the number density of the first molecules.

We can see that negative hydrogen ions \( \text{H}^- \) are most sensitive to the first light. This is expected since its threshold of dissociation is low, namely, 0.75 eV. The photodissociation reaction \( \text{H}^- + \gamma \rightarrow \text{H} + \text{e}^- \) effectively decreases the number density of \( \text{H}^- \) up to the moment when the ionization of hydrogen starts to increase. Increasing the number density of free electrons makes raises the importance of the reaction \( \text{H} + \text{e}^- \rightarrow \text{H}^- + \gamma \), which leads to the growth in the number density of \( \text{H}^- \). This is not for long, however, as the rapid increase of the number density of photons subsequently makes the process of photodissociation dominant.
The evolution of the number densities of the molecular ions $\mathrm{H}_2^+$ and $\mathrm{HeH}^+$ is similar for the high energy density of the first light because their photodissociation thresholds (2.77 eV and 1.85 eV accordingly) are essentially lower than the photoionization potential of atomic hydrogen (13.6 eV). In both cases, an increase in the value of $n_{\mathrm{HII}}$ causes a brief increase in the number density of these molecular ions, as well as a subsequent decrease due to the growth of the photodissociation. For the low energy density of the first light (bottom panels in the right columns of Figs. 5 and 6), the number density of hydride helium ions $\mathrm{HeH}^+$ increases when the ionization of atomic hydrogen increases because the reaction $\mathrm{He}^+ + \mathrm{H} \rightarrow \mathrm{HeH}^+ + \gamma$ prevails over the reaction $\mathrm{HeH}^+ + \gamma \rightarrow \mathrm{He} + \mathrm{H}^+$.

The number density of the most abundant molecules $\mathrm{H}_2$ (threshold of dissociation is 4.53 eV) drastically decreases when the number density of photons with energy above the threshold becomes larger than a specific value when the rate of direct dissociation of $\mathrm{H}_2$ becomes $\sim 10^{-18} - 10^{-19} \, \text{cm}^3 \, \text{s}^{-1}$. Thus, the spectral energy distribution of the first light and its time dependence crucially impact the formation and dissociation of molecules during the Cosmic Dawn. To demonstrate this impact more clearly, we present in Fig. 7 the ratios of the number densities of molecules in the models with the first light, $n_i(z)$, to the number density of molecules without it, $n_i^0(z)$.

In this study, we supposed the primordial chemical content of hydrogen, helium, and deuterium. Taking into account the PopII stellar nucleosynthesis, metal enrichment will change the relationship between them, which will somewhat affect the number densities of the first molecules in the halos. Obviously, these changes will not be decisive at $z \geq 10$.

5. Molecules in the intra-proto-galactic medium and their luminescence

We went on to repeat the same computations for the intra-proto-galactic medium. We supposed that the proto-galaxies are spherical top-hat halos in the multicomponent Universe, which are filled with dynamical dark energy, dark matter, baryon matter, and two “sorts” of thermal radiation, namely, the CMBR and the first light, which appeared in the Cosmic Dawn epoch. Since the time dependence of the density and temperature of the baryonic matter in the halos at stages before, during, and after virialization differ from the background ones, the number densities of the first molecules are different too. Moreover, the warm and hot halos can slightly shine at the cosmic microwave background (Novosyadlyj et al. 2020; Kulinich et al. 2020). To analyze the impact of
the first light on the abundance of the first molecules and their luminescence in the halos, we use the theory of cosmological perturbations and the halo model to produce accurate computations of physical conditions and integrations of the corresponding kinetics equations.

5.1. Dynamical model of halo

We computed the physical conditions and chemistry of the halo by modeling the evolution of a single spherical perturbation in the four-component Universe (cold dark matter, baryon matter, dark energy, and thermal relic radiation) starting from the linear stage at the early epoch, long before the cosmological recombination, through the quasi-linear stage at the early epoch, and integrations of the corresponding kinetics equations.

\[ \frac{M_b}{M_0} \approx 1160 \Delta_b (1 + z_{\text{vir}})^3 \Omega_m h^3 r_h^3 \approx 4.5 \cdot 10^{12} \Omega_m h^2 k^{-3}, \]

where \( \Omega_m = \frac{8\pi G \rho_m(0)}{3H_0^2} = \Omega_m + \Omega_k \) and \( h = H_0 / 100 \text{ km/s/Mpc} \). In the cosmological model with \( \Omega_m = 0.315 \) and \( h = 0.674 \) for \( k = 80 \text{ Mpc}^{-1} \), we obtain the value \( M_b \approx 1.26 \cdot 10^6 M_\odot \) and \( r_h \approx 0.15 \text{ kpc} \). The angular size of such halo at \( z_{\text{vir}} \) is in the range of 0.07 \( - 0.03 \) arcsec. We suppose that a halo is spherical and homogeneous (top-hat) with values of matter density and kinetic temperature unchanged after virialization.

The kinetic temperature of baryon gas in the halo during the epochs of the Dark Ages and Cosmic Dawn is determined by its interaction with thermal relic radiation and the first light and the adiabatic heating over compression. The bremsstrahlung, molecular cooling and other cooling mechanisms are not effective due to the low gas density (top panels of Fig. 4 and 8). So, the evolution of baryon gas temperature \( T_b \) at \( 6 \leq z \leq 850 \) can be obtained by the integration of the energy balance equation for the intra-halo baryon matter:

\[ \frac{dT_b}{dz} = \text{r.h.s.} (3) + \frac{2}{3} \frac{T_b}{1 + z} \cdot d\delta_b / dz. \]  

The kinetic temperature of gas in such halo after virialization is about 280 K and does not depend on halo mass. The halo with such temperature we call the "warm" halo.

The gas in the halo can also be heated by shocks in the processes of violent relaxation to the virial temperature (Barkana et al. 2001; Bromm & Yoshida 2011):

\[ T_b^{(\text{vir})} = 2 \cdot 10^4 \left( \frac{M_b}{10^8 M_\odot} \right)^{2/3} \left( \frac{\Delta_b}{178} \right)^{1/3} \left( \frac{z_{\text{vir}} + 1}{10} \right) \text{ K}. \]
where \( \mu_H \) is the mass per H atom. In our case, the temperature of such halo is 2280 K and we call it the "hot" halo.

In the bottom panel of Fig. 8, the temperature of the gas in the virialized halo is shown for two cases: when it is heated by adiabatic compression only (dark solid line) and when it is heated in the processes of violent relaxation to virial temperature (8; red line). In the first case, the final temperature is a result of the integration of Eq. (7), in the second one, we set it equal to \( T_{\text{vir}} \) by hand at \( z \geq z_e \).

### 5.2. Number density of molecules

In the halo model described above, the number density of baryon (and lepton) particles is unchanged after virialization, while the number densities of molecules, protons (\( n_p \)) and electrons (\( n_e \)) are changed via recombination and photoionization processes of atoms and molecules as well as the formation and destruction reactions of molecules.

In Fig. 9, we show how the number densities of molecules \( H_2 \), HD, and HeH+ are changed in the warm and hot halos in comparison with the background ones (inter-proto-galaxy medium) without the first light. We can see that increasing of density and temperature of baryon gas leads to the increasing of the number density of molecules \( H_2 \) and HD even after virialization essentially more than \( \Delta t \) times. Moreover, in the hot halos, the number density of these molecules is higher than in the warm ones. The number density of HeH+ molecular ions behaves differently. In the warm halo, the \( n_{\text{HeH}^+} \) decreases so that the ratio \( n_{\text{HeH}^+}/n_{\text{HeH}^+}^{\text{background}} \) is almost constant. In the hot halo, the number density of these molecules sharply decreases since destruction reactions \( \text{He}11 \) and \( \text{He}12 \) (Table 1) dominate.

To estimate the impact of the first light on the chemistry of the intra-halo medium, it is necessary to note that the spectral density of radiation in the halo is larger than the background one and this excess increases over time quickly during the Cosmic Dawn epoch. We analyzed the impact of the first light with different values of dilution coefficients on the halo chemistry: i) \( \alpha_{\text{II}} \), estimated in Section 3; ii) \( 10^2 \alpha_{\text{III}} \); and iii) \( 10^3 \alpha_{\text{III}} \).

We computed the ratios of the number densities of molecules in the halo with the first light to the number densities of molecules in the halo without it. The results for the first light models Ia and Ib are presented in Fig. 10. In the top panels the models of the first light in the halo are the same, which reionize the inter-halo medium at \( z=6 \) (dotted lines) and \( z=8 \) (solid lines). In the left panel, the radiation temperature at the moment of reionization is 5000 K, with dilution coefficients \( \alpha_{\text{III-6}} = 3.3 \cdot 10^{-10} \) and \( \alpha_{\text{III-8}} = 4.85 \cdot 10^{-10} \) for \( z_{\text{rei}} = 6 \) and 8, correspondingly. In the right panel, the radiation temperature at the moment of reionization is 10000 K, with dilution coefficients \( \alpha_{\text{III-6}} = 6.0 \cdot 10^{-11} \) and \( \alpha_{\text{III-8}} = 8.6 \cdot 10^{-17} \) for \( z_{\text{rei}} = 6 \) and 8, correspondingly. In the bottom panels the energy densities of the first light in the halos are \( 10^3 \) (dotted line) and \( 10^2 \) (solid lines) times higher than the energy densities in the corresponding models in the top panels shown by solid lines. In all the panels, the lines for \( H_2 \) and HD are superimposed. We can see that these molecules are quite destroyed before reionization. The larger is the spectral density of the first light, the earlier they disappear because of photodissociation.

The number density of HeH+ molecular ions in the halo evolves quite differently. It starts to change early over the low threshold of dissociation and changes nonmonotonically over the competition of formation and destruction reactions (\( \text{He}8, \text{He}10, \text{He}11, \text{He}12, \text{He}14, \) and \( \text{He}15 \) in Table 1) in the medium with the growth of dilution coefficients \( n_{\text{III}}, n_p, \) and \( n_e \). Moreover, in the models of the first light with \( \alpha \leq 10^{-14} \) and \( T \sim 10000 \) K, the number density of these molecules increases by \( 10^2 \) \( \sim 10^3 \) times on \( z_{\text{rei}} \) when other molecules are destroyed in their entirety. It gives us the chance to observe the epoch of reionization in the lines of helium hydride ions.

In order not to overload the paper we do not present the figures for models of the first light Ic and Id, in which the spectral energy distributions on \( z_{\text{rei}} \) are the same as in the models Ia and Ib but with slower growth of temperature and energy density rate. As in the case of the inter-halo medium, the qualitative behavior is similar to the cases with Ia and Ib models, but the effect of the first light in the models Ic and Id is already noticeable at larger redshifts because its energy density is higher there.

### 5.3. Luminescence of halo in the molecular lines

We went on to analyze the impact of the first light on the luminescence of a halo in the lines of the first molecules. Since the first light with temperature, \( T_{\text{III}} \sim 10^3 \), can excite the rotational-vibrational energy levels of the first molecules the luminescence of halos in the Cosmic Dawn would complicatedly depend on the spectral energy density of background radiation and the number density of the molecules.

To evaluate the luminescence of the halo in the molecular lines, we must compute the population of rotational levels. We integrate for that
the kinetic equations of population or depopulation of rotational levels:

$$\frac{dn_i}{dt} = \sum_{j \neq i} n_j R_{ji} - n_i \sum_{j \neq i} R_{ij} + 3Hn_i,$$

(9)

where the indices, \(i\) and \(j\), mark the rotational levels, \(n_i\) is the number density of molecules at the rotational level \(i\), and

\[ R_{ij} = A_{ij} + B_i U_{ij} + C_{ij}, \quad R_{ji} = B_j U_{ij} + C_{ji} \]

are the rates of transitions between them. Here, \(i > j\), \(A_{ij}\) is the rate of spontaneous transition from \(i\)-level to \(j\)-level, \(B_i\) and \(B_j\) are the rates of induced transition and absorption at frequency \(\nu_{ij}\), accordingly, \(C_{ij}\) and \(C_{ji}\) are the rates of collisional excitation of \(i\)-level from \(j\)-level and de-excitation from the \(i\)-level to the \(j\)-level. \(U_{ij} = U_{ij}^{\text{CMB}} + U_{ij}^{\text{pd}}\) is the total energy density of radiation at any redshift from cosmological recombination to reionization. We used the same approximations for excitation and de-excitation rates of rotational levels of molecules H\(_2\), HD, and HeH\(^+\) as in our previous papers, Novosyadlyj et al. (2020) and Kulinich et al. (2020), and references therein.

Solution of the system of equations for populations of rotational levels with \(J = 0 \rightarrow 5\) gives us the possibility to compute the excitation temperature from the \(i\)-level to the \(j\)-level:

$$T_{ji} = \frac{h\nu_{ij}}{k_B} \ln \frac{n_i g_i}{n_j g_j},$$

where \(h\) is the Planck constant, \(k_B\) is the Boltzmann constant, and \(g_i, g_j\) are statistical weights of levels. This, in turn, makes it possible to calculate the optical depths in the rotational lines, \(\tau_{ij}\), along the diameter of the spherical homogeneous top-hat halo,

$$\tau_{ij} = \frac{1.55 \times 10^{10} n_i \frac{g_i A_{ij}}{g_j \nu_{ij}} \sqrt{\frac{m_i}{T_i}}}{1 - \exp \left( -\frac{h\nu_{ij}}{k_B T_i} \right)} \frac{1}{r_h},$$

(10)

where \(m_i\) is the atomic number of a molecule, \(n_i\) is the radius of the halo in units of kpc, and the rest values are in the CGS system. The results show that the maximum values of \(\tau_{H_2}^{H_2}, \tau_{D^+}^{H_2}, \tau_{H_2}^{H_2}\) and \(\tau_{HeH^+}^{HeH^+}\) after virialization are in the range of \(10^{-7} \rightarrow 10^{-9}\), which means that such halos are optically thin. Our estimation shows that they are also optically thin in the frequencies of photo-dissociations of molecules (\(\tau_{pd} \leq 10^{-10}\)). Thus, the use of the optically thin halo approximation in the molecular lines and in the continuum is justified. Since the column densities of the molecules \(N(H_2), N(HD), N(HeH^+) \ll 10^{19} \text{ cm}^{-2}\), the self-shielding effect is not important for such halos (Draine & Bertoldi 1996).

Traditionally, the intensity of microwave radiation is expressed in units of brightness temperature:

$$T_{ij}^\text{br} = \frac{l_{ij}}{2k_B \nu_{ij}}.$$

Since the luminescence of the Dark Ages and Cosmic Dawn halos in the lines of the first molecules occurs on the cosmic microwave background at the same frequencies, it is reasonable to calculate the differential brightness temperature:

$$\delta T_{ij}^\text{br} = T_{ij}^\text{br} - T_{\text{CMB}}.$$
Fig. 11. Differential brightness temperature of warm halos ($T_p \approx 280$ K) in the base rotational lines of molecules $\text{H}_2$, HD, and $\text{HeH}^+$ (from top to down) with and without of the first light: solid dark line – without first light, solid red and blue lines with background first light which reionize the medium at $z=6$ and $z=8$ accordingly, dotted and dashed blue lines with the first light with energy density $10^3$ and $10^6$ times higher than the background one ($z_{rei} = 8$). In the left column, the first light is Ia, in the right one it is Ib.

In the case of an optically thin top-hat halo the radiative transfer equation gives the next expression for the differential brightness temperature; for details, see Novosyadlyj et al. (2020):

$$\delta T_{br} = \frac{5 \cdot 10^{35} \nu_{ij} A_{ij}}{(1+z)^2 \nu_{ij}} \sqrt{\frac{m_i}{T_B}} \left[ \exp\left(\frac{\hbar \nu_{ij}}{k_B T_B}\right) - \exp\left(\frac{\hbar \nu_{ij}}{k_B T_{xen}}\right) \right] r_{ij}. \quad (11)$$

Using it we compute the evolution of luminescence of warm and hot halos in the rotational lines of molecules $\text{H}_2$, HD, and $\text{HeH}^+$ during the Dark Ages and Cosmic Dawn with the different energy densities of the first light. The results are presented in Figs. 11 and 12 for the same models of the first light as in Fig. 10.

We can see that the luminescence of a single halo in the rotational lines of $\text{H}_2$ and HD molecules appears after the turn-around point of seed perturbation, when adiabatic heating of baryon matter becomes noticeable and disappears before hydrogen reionization of the intra-halo medium caused by photodissociation of molecules. It has formed a plateau with sharp uphill and downhill. Their detection could be very informative about the first halos, first molecules, and first light. Unfortunately, the amplitude of the differential brightness temperature is too low to be detected by current telescopes. However, in the case of the “hotter” first light with lower energy density, the differential brightness temperature of hot halos can reach a few hundredths or even tenths of a microkelvin (Fig. 12, right panels in the top and middle rows), at the
sensitivity level of existing and planned advanced telescopes for the microwave range.

The time dependence of the luminescence of a single halo in the rotational lines of HeH$^+$ molecular ions is as interesting with regard to both warm halos as well as hot ones. It has three phases of sharp changes: increasing after the turn-around point of seed perturbation, decreasing during the Cosmic Dawn caused by photodissociation of molecules in the case of the warm halo (Fig. 11, bottom row), or by collision in the case of the hot halo and a noticeable increase during the reionization. Thus, the halo could exhibit luminescence at the reionization epoch in the rotational lines of HeH$^+$ molecular ions only (from the studied ones, of course). Again, however, the amplitude of differential brightness temperature in the basic rotational lines is too low to be detected by existing telescopes.

The magnitude of fluxes in the rotational lines of the first molecules obtained in this work and in Novosyadlyj et al. (2020) without reionizing by the first light practically coincides with that predicted in the early works (Dubrovich 1977; Maoli et al. 1994, 1996; Kamaya & Silk 2002; Ripamonti et al. 2002; Kamaya & Silk 2003; Omukai & Kitayama 2003; Mizusawa et al. 2004, 2005; Dubrovich et al. 2008) despite completely different source models. The main conclusion about their marginal detectability by modern and planned telescopes coincides with the conclusions of these and other authors. The novel result presented here is the luminescence of H$_2$ and HD molecules in the lines long before the...
reionization of atomic hydrogen and their disappearance due to photodissociation of these molecules shortly prior. The halo luminosity with $M \propto 10^{10} - 10^{13}$ $M_\odot$ at $7 \leq z \leq 24$ has been estimated using GIZMO cosmological simulations (see, e.g., Liu et al. (2019)). The interpolation of their results to smaller halo masses shows a good agreement (up to orders of magnitude of fluxes) with our results in the models without the first light. The fact that there is no disappearance of H$_2$ emission at $z \leq 8 - 9$ due to photodissociation can be explained by the underestimation of UV radiation, since the model of reionization is not self-consistent in this case.

The results presented here were obtained within the framework of the simplest models of halo and first light, which can be far from real, as well as a limited set of chemical reactions and energy levels of molecules. Complicating the models by expanding the number of reactions and energy transitions in the molecules will be a task for further research.

6. Discussion and conclusions

We analyzed the ionization of the hydrogen atoms and the formation and destruction of the first molecules in the inter-proto-galactic medium of Cosmic Dawn, assuming the thermal energy distribution of the background radiation of the first sources of light. The spectral energy distribution at those epochs was presented by the Planck function with a certain temperature dependent on redshift, along with a dilution factor constrained by data about the redshift of reionization. The latter was assumed to be $x_{\text{HII}} = 0.5$ at $6 \leq z \leq 8$. We used the simplest model of the first light with a minimal number of parameters (temperature and dilution coefficient). Such radiation is not in thermodynamic equilibrium but features Planck energy distribution, which essentially simplifies the computations of all activation and deactivation and photodissociation of atoms and molecules, according to the generalized formula (5). It corresponds to the following scenario: the sources of the first light, proto- and PopIII stars, evolve, while the average energy density and temperature of their radiation increase according to Equations (6) and (4). The parameters in Equation (6) could be constrained using the observational data on the luminosities of halos in the lines of molecules, which we have evaluated here. However, in this paper, we set them arbitrarily in order to clarify the effect of the star formation rate on our estimates. Mathematically, the problem has consisted of the numerical integration of the system of kinetic equations of the ionization and recombination of atoms and molecules, as well as the formation and destruction of molecules and their ions together with the equations of expansion of the Universe and the thermal energy balance for the baryonic component. We only took into account the most important reactions (Table 1) that are connected with the most abundant atoms and molecules: atomic hydrogen H, helium He, deuterium D, molecular hydrogen H$_2$, hydrogen deuteride molecule HD, and helium hydride ion HeH$^+$. The obtained results lead to conclusions that provide a clearer understanding of the possible physical conditions at Cosmic Dawn and the epoch of reionization. Our conclusions are summarized as follows:

1. The number densities of hydrogen atoms, kinetic temperature, and the radiation field in the inter-proto-galaxy medium of Cosmic Dawn are such that the atoms are in the base state mainly and the case of A of photoinization is realized (Fig. 1).

2. The thermal radiation with a temperature of $T_{\text{IR}} = 5000$ K and dilution factor of $x_{\text{HII}} = 2 \cdot 10^{-5} - 10^{-10}$ ionizes the atomic hydrogen up to $x_{\text{HII}} = 0.5$ at $6 \leq z \leq 8$. At the current epoch, the spectral energy density of such radiation is a few orders lower than the spectral energy density of CIB at frequencies of $<30$ THz ($\lambda > 10\mu m$). At higher frequencies, it would be detected by the current radio telescopes. For higher radiation temperatures, the dilution factor is lower and the current energy density of such radiation becomes too low for its detection. For the first light with comoving radiation temperature, $T_{\text{IR}} = 10000$ K, which ionizes the inter-proto-galaxy medium at $6 \leq z \leq 8$, the dilution factor is ~10$^{-12}$. Its spectral flux is in the range of the frequency maximum at the current epoch, which is ~Jy, and masks in the Wien range of CIB. The range of values for the dilution factor $x_{\text{HII}}$ is narrow for any fixed radiation temperature of the first light, $T_{\text{IR}}$, at the moment of reionization, but the dependence $a_{\text{IR}}(T_{\text{IR}})$ is steep since the potential of ionization of the atomic hydrogen is in the Wien range of spectral energy distribution (Figs. 2-3).

3. The first light heats the baryonic gas in the interproto-galaxy medium up to dozens or hundreds of kelvins at $z_{\text{re}}$, which depends on its radiation temperature and dilution factor. In any case, the change of baryonic temperature $T_{\text{B}}$ becomes noticeable not long before the ionized hydrogen fraction reaches 1/2. The different history of increasing of radiation temperature, $T_{\text{IR}}$, forms the temperature history of the baryonic component at that time (Fig. 4).

4. The number densities of negative hydrogen ion H$^-$ and molecular ions H$_2^+$ start to decrease long before reionization, since the thresholds energy of photodissociation for them are essentially lower than the potential of ionization of the atomic hydrogen (Figs. 5-6).

5. The most abundant molecules in the Dark Ages, namely, H$_2$ and HD, are destroyed over the course of the Cosmic Dawn not long before hydrogen reionization since the threshold of photodissociation for them is lower than the potential of ionization of atomic hydrogen (Figs. 5-7).

6. The dependence of the number density of the helium hydride ion HeH$^+$ on redshift in the Cosmic Dawn is intriguing via the competition of photodissociation by the first light and its formation in the reaction $\text{He} + \text{H}^+ \rightarrow \text{HeH}^+ + \gamma$ when the number density of H$^+$ increase. The number density of HeH$^+$ decreases in the models of the first light with a large number density of photons, and increases for diluted first light with higher radiation temperature (Figs. 5-7). We consider whether these molecules can survive in the remote corners of the intergalactic medium? This is an interesting task for further research with more realistic models of the spectral energy distribution of radiation in the different periods of the evolution of the Universe.

7. The time dependence of the luminoscence of a single top-hat halo in the rotational lines of H$_2$ and HD molecules has a form of plateau with sharp uphill and downhill and maximal amplitude of a differential brightness temperature of $\sim 10^{-10} - 10^{-8}$ K for warm halos and $\sim 10^{-5} - 10^{-6}$ K for hot ones (Figs. 11-12). The beginning of the plateau is connected with the formation and adiabatic heating of the forming halo, while the ending of the plateau is caused by photodissociation of the molecules before reionization.

8. The time dependence of the luminoscence of a single halo in the rotational lines of HeH$^+$ molecular ions has three phases of sharp changes: increasing during virialization halo (heating), decreasing during Cosmic Dawn (photodissociation or collision destruction of molecules), and increasing during the reionization epoch. The maximal amplitude of differential brightness temperature does not exceed $10^{-7}$ K.

9. The detection of the luminoscence of the Dark Ages and Cosmic Dawn halos in the rotational lines of the first molecules could provide very important information about formation of the first halos, first molecules, and the first sources of light.

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References

Appendix A: Rates of photorecombination and effective cross-sections of photoionization for HI and DI

Before the epoch of reionization, during epochs of the Dark Ages and Cosmic Dawn, hydrogen atoms were mainly in the ground electron state. To obtain the total rate of electron recombination on the second level, we use the analytical approximation of the total rate of recombination on all levels by Ferland & Ferland (1996):

$$\alpha_s(T) = \frac{a}{\sqrt{T/T_i} \left(1 + \sqrt{T/T_i} \right)^{\beta} \left(1 + \sqrt{T/T_i} \right)^{1.5}}$$

with the coefficients \(a = 7.982 \times 10^{-11}\), \(b = 0.748\), \(T_1 = 3.148\), \(T_2 = 7.036 \times 10^5\), and the approximation of the rate of recombination on the base level by Ferland et al. (1992):

$$\alpha_1(T) = 10^{0.5(T/3)/T}$$

$$F(1, T) = \frac{a_1 + c_1 x + c_2 x^2 + g_1 x^3 + h_1 x^4}{1 + b_1 x + d_1 x^2 + f_1 x^3 + h_1 x^4}, \quad x = \lg T,$$

with refined values of approximation coefficients from the publicly available code Cloudy (Ferland et al. 2017) \(a_1 = -10.781359\), \(b_1 = -0.38790005\), \(c_1 = 4.6748385\), \(d_1 = 0.063898347\), \(e_1 = -0.87297469\), \(f_1 = -5.0923340 \times 10^{-3}\), \(g_1 = 0.081445619\), \(h_1 = 2.4935490 \times 10^{-3}\), and \(i_1 = -3.9043790 \times 10^{-3}\). So, the expected value of the recombination rate coefficient for case B is as follows:

$$\alpha_B(T) = \alpha_1(T) - \alpha_1(T)$$

The testing shows that this approximation of the rate B of recombination \(\alpha_B(T)\) matches the values \(\sum_{n=0}^{\infty} \alpha(n, T)\) in the range of electron temperature \(3 \leq T \leq 10^5\) K computed by Cloudy with an accuracy of about 0.01%.

The rate of photoionization of atomic hydrogen from the level \(n\) by radiation with intensity, \(I(\nu)\), we can compute, for the known effective cross-section of photoionization from this level \(\sigma_\nu(\nu)\), according to Abel et al. (1997), as follows:

$$R_{\nu n} = 4\pi \int_{\nu n}^{\infty} \sigma_\nu(\nu) \frac{I(\nu)}{h\nu} d\nu,$$

where \(\nu_n\) is the threshold frequency of photoionization from level \(n\). For the intergalactic cold rarediffuse medium of the Dark Ages and Cosmic Dawn, photoionization goes mainly from base \((n = 1, l = 0)\) or second metastable levels \((n = 2, l = 0)\). We use the analytical approximation proposed by Ferland et al. (1996) with a small correction:

$$\sigma_\nu(E) = \sigma_0(x - 1)^{2}\frac{x^{1.5}}{1 + \sqrt{x}} / \left(1 + \alpha(E - E_{\min})\right),$$

where \(x = \frac{\nu}{\nu_0}, \sigma_0, E = h\nu, E_0, P, y_\nu\), and \(\alpha\) are the best-fit parameters, which we re-determined using the open source codes by Bauman et al. (2001) for computations the cross-sections of photoionization of hydrogen from the base level \((n = 1, l = 0)\) and the second one \((n = 2, l = 0)\) and \((n = 2, l = 1)\) shown in Fig. A.1 as solid lines. The best-fit coefficients and accuracy of approximation are presented in Table A.1.

The effective cross-sections of photoionization of HI from the base and second levels are shown in Fig. A.1 by the dotted red line. We assume that the rates of photorecombination and effective cross-sections of photoionization for deuterium atoms are the same as for atomic hydrogen.

Appendix B: Rates of photodissociation of molecules H₂ and HD

At the Cosmic Dawn, energetic photons appear and they are capable to ionize of atoms and molecules and dissociate the last. The threshold of direct photodissociation of \(H_2 (H_2 + \gamma \rightarrow H + H)\) is 4.53 eV, so, it can be important long before the reionization. The physics and computations of the cross-section of this reaction are well described in Glover & Jappsen (2007); Heays et al. (2017) (see also citations therein). Here, we use the photodissociation cross-section of molecule H₂ computed by Heays et al. (2017) and presented on the site of Leiden University\(^9\) in the table form with high wavelength resolution \((4 \times 10^{-5})\). We illustrate these data in Figure B.1 using low wavelength resolution data table data \((0.1\mu m)\). We computed the rate of dissociation according to (A1) with \(I(\nu) = B(\nu)\) for range of temperatures \(10^5 < T < 2 \times 10^8\) K. The result is shown in the right panel of Fig. B.1 by open circles. We also propose the analytical approximation of this dependence by the formula:

$$R_{\nu H}(T) = \sigma_0(1 + e^{T^4}) \exp(f(T)).$$

with the best-fit parameters \((a, b, c, d, f) = (2394.9, 0.62681, 2.4635, 0.56957, 140050)\) for \(T \leq 15000\) K and \((a, b, c, d, f) = (6.44711 \times 10^7, 0.322, 6.5341 \times 10^{-8}, 1.4752, 153570)\) for \(T > 15000\) K. Its deviation from the numerical result is not larger than 1% in the interested temperature range (bottom small panel of the left figure). We present also in the main panel of the right figure the analytical approximation by Glover & Jappsen (2007); Schleicher et al. (2008) for comparison. We can see that in the low temperature range \((T < 5000\) K), they are close. We assume here that the rate of direct photodissociation of molecule HD \((HD + \gamma \rightarrow D + H)\) is the same as for molecule H₂.

\(^9\) https://home.strw.leidenuniv.nl/ ewine/photo/cross_sections.html
Table A.1. Coefficients of approximation (A2) for cross-sections of photoionization of HI from the first and second energy levels.

<table>
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<th>n</th>
<th>l</th>
<th>$E_{\text{min}}$ (eV)</th>
<th>$E_{\text{max}}$ (eV)</th>
<th>$E_0$ (eV)</th>
<th>$\sigma_0$ ($10^{-18}$ cm$^2$)</th>
<th>$\gamma_0$</th>
<th>$P$</th>
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<th>Max. dev. (%)</th>
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<tr>
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Fig. B.1. Effective cross-sections of hydrogen molecule H$_2$ photodissociation from Heays et al. (2017) shown in the left panel and the rate of dissociation computed here in the right panel. The solid red line is the analytical approximation (B1), the dotted blue line is from Glover & Jappsen (2007); Schleicher et al. (2008). The deviation of analytical approximation (B1) from the numerical results is shown in the low panel.