Rydberg States of H₃ and HeH as Potential Coolants for Primordial Star Formation

Gokul Kannan, Jeremy R. Chien, Anthony J. Benjamin, Niranjan Bhatia, and Richard J. Saykally

ABSTRACT: Current theory and measurements establish the age of the universe as ca. 13.8 billion years. For the first several hundred million years of its existence, it was a dark, opaque void. After that, the hydrogen atoms comprising most of the “ordinary” matter began to condense and ionize, eventually forming the first stars that would illuminate the sky. Details of how these “primordial” stars formed have been widely debated, but remain elusive. A central issue in this process is the mechanism by which the primordial gas (mainly hydrogen and helium atoms) collected via the action of dark matter cooled and further accreted to fusion densities. Current models invoke collisional excitation of H₂ molecular rotations and subsequent radiative rotational transitions allowed by the weak molecular quadrupole moment. In this work, we review the salient considerations and present some new ideas, based on recent spectroscopic observations of neutral H₃ Rydberg electronic state emission in the mid-infrared region.

INTRODUCTION

The early stages of primordial star formation have been the subject of extensive study for decades. For these first stars to form, it has been proposed that primordial gas clouds first condensed at nodes in a filamentary network organized by dark matter. These high density nodes proceeded to condense further through radiative cooling processes until they reached the Jeans mass, viz. the critical mass for gravity to become the dominant force driving star formation. However, as these nodes compressed, they would have gained massive amounts of energy, reaching temperatures above 10⁴ K. To sustain compression, the nodes would have had to cool via some highly effective radiative mechanism. Cooling in modern descriptions of secondary star-forming regions features extensive use of metal-based mechanisms—where “metal” refers to any elements heavier than H, He, and Li—but these fail in the primordial context due to the nearly exclusive presence of hydrogen and helium. Elucidating the requisite cooling mechanisms remains a major unsolved problem in the field.

Cooling mechanisms operative from 10⁴ to 10⁵ K are well-understood. Gas is cooled primarily via bremsstrahlung radiation (the deflection of charged particles by other charged particles, converting kinetic energy to photons). This drove the formation of “minihalos”—i.e. the “nodes” mentioned previously. It has been shown theoretically that each of these minihalos likely produced one single metal-free star, probably limited to ~300 solar masses. The size of these first stars is related to the Jeans mass for gravitational collapse, which is proportional to the square of the temperature and inversely proportional to the square root of the pressure. Pressures in primordial gas clouds were probably similar to those in star-forming clouds studied today, leaving temperature as the primary variable in determining the Jeans mass and, thus, as the defining factor in determining first star mass. Accordingly, efficient cooling of these stars to well below 10⁴ K is essential.

A number of simple primordial molecules have been identified as preceding star formation, and their abundances have been estimated theoretically (Figure 1). The formation and subsequent reactions of these molecules are limited by the presence of only ¹H, ²H (or D), ³He, ⁴He, and a trace amount of ⁷Li formed in the Big Bang. Accordingly, we can list most of the possible reactions according to the standard model (Table 1). Lepp and co-workers have examined these reactions in more detail. For the purposes of this paper, we are concerned primarily with the formation of H₂, HeH, H₃, and their derivatives. These molecules and their corresponding reactions give us a “toolbox” with which to begin examining potential

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primordial cooling mechanisms. However, we must recognize that this “toolbox” is limited; modeling abundances, reaction kinetics, and thermodynamics in primordial conditions remains an extraordinarily difficult task.

To cool from $10^4$ K to less than $10^3$ K, the currently accepted mechanism is via H$_2$ associative detachment (AD): $H + H^+ \rightarrow H_2^* + e^-$. Molecular hydrogen is also widely accepted as the predominant coolant at lower temperatures in primordial gas clouds, largely due to its high abundance and cooling effectiveness at temperatures relevant to the time period of interest ($<10^4$ K). This mechanism of cooling proceeds through the AD reaction, wherein translational energy from atomic H and H$^+$ is converted into internal energy of an excited H$_2$ through rotational–vibrational excitation of the molecule upon collision. The (nonpolar) molecule can then radiatively relax via electric quadrupole transitions, and the emitted photons can escape, cooling the gas.

Despite the apparent simplicity of this reaction, theory and experiment have failed to converge in terms of the magnitude and energy dependence of the corresponding rate coefficient (Figure 2).

The only experiments measuring the rate coefficient of H$_2$ AD at cosmological temperatures were carried out in 1967 by Schmeltekopf and co-workers. Virtually all early universe chemical models use their results. Subsequent computational studies of the reaction have mostly arrived at different numbers, mainly due to disagreements as to which reactions consume H$^+$ and which reactions produce negligible effects that can be omitted for simplification.

Despite the discrepancy in values of the rate coefficient, H$_2$ AD still remains the most widely accepted cooling mechanism of primordial gas clouds due to the high reactant abundance and cooling efficiency (Figure 3).

This mechanism, however, falls short when considering the predictions of early star masses. H$_2$-based cooling becomes ineffective at lower temperature, 200–300 K, as well as at sufficiently high density, establishing a lower limit for the temperature and thus for the Jeans mass, of the first stars—greater than 1000 solar masses, sufficient for supermassive stars and black holes to form instead. With the evolution of new theoretical results suggesting gravitational fragmentation of approximately one-fifth of the young first-generation stars, it is possible that this mechanism is the driver in cases of fragmentation. However, no experimental data supporting such fragmentation have been observed.

### H$_3$ RYDBERG MOLECULES

For the minihalos to effectively cool below 200 K, a non-H$_2$ based mechanism seems necessary, as the H$_2$ electric quadrupole-allowed rotational transitions are extremely weak. The driving molecule would have to have a high formation rate at low temperatures, and necessary intermediates must have sufficiently large rate constants and long lifetimes to allow effective cooling mechanisms to proceed. We find an interesting candidate in the recombination of H$_3^+$ with a free electron, producing an excited neutral H$_3$ Rydberg molecule intermediate.

Rydberg molecules have dissociative ground states and stable nonvalence excited states, parallel to those of the H atom in classic Bohr theory, and comprising orbitals energy-ordered by the increasing principal quantum number $n$. These excited species lose energy via strong dipole-allowed rovibrational radiative transitions as the electrons relax from high to lower $n$ states, and they have dense manifolds of rovibrational energy levels as well. This efficient radiative energy loss mechanism presents an opportunity for Rydberg molecules to release large amounts of energy on relatively short time scales—a potentially effective mechanism of cooling.

Herzberg first described H$_2$ Rydberg molecule emission spectra in the 1980s and detailed the transitions between the $n = 2$ and $n = 3$ Ry states. While the ground state of this molecule is unbound and very short-lived, the excited (Rydberg) states are metastable. As such, they either decay radiatively with lifetimes proportional to $n^3$ or predissociatively. As a prototype Rydberg molecule, H$_3$ has been studied extensively since Herzberg’s discovery by both theory and experiment, although not until recently in the context of primordial star cooling.

If H$_3^+$ forms favorably in primordial environments, then in collisions with H and He atoms, rotational transitions would be excited similar to H$_2$ molecule excitation. However, these H$_3^+$ excitations would have much stronger coupling to translation due to the net charge, so subsequently formed Rydberg states would likely exhibit rovibrationally excited ion cores, in addition to the electronic energy of the molecular n-state. This would engender detectable UV–visible and IR emissions, which could ultimately radiate away translational energy.

H$_3^+$ dissociative recombination (DR) occurs through an indirect mechanism involving the neutral H$_3$ Rydberg intermediate:

$$H_3^+ + e^- \rightarrow H_3^* \rightarrow \text{neutral products}$$

The H$_3^+$ DR process has been historically difficult to study due to two major factors: First, the vibrational degrees of freedom have three dimensions, usually requiring accessible theoretical models to reduce dimensionality and thus to lose information. Second, there have been major discrepancies in rate coefficients, cross sections, and various other metrics obtained via different experimental designs, similar to the issues described for H$_2$ AD.
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Table 1. Gas-Phase Reactions Relevant to First Star Formation and Their Rate Coefficients (Reprinted with Permission from Reference 4. Copyright 2002 IOP Publishing)a

| reaction | $a_1$ | $a_2$ | $a_3$ (K) |
|----------|-------|-------|----------|
| (1) $H + e^- \rightarrow H^+ + 2e^-$ | $7.57 \times 10^9$ | 5.50 \times 1 | 1.582 + 5d |
| (2) $D + e^- \rightarrow D^+ + 2e^-$ | $7.57 \times 10^9$ | 5.50 \times 1 | 1.582 + 5d |
| (3) $He + e^- \rightarrow He^+ + 2e^-$ | $4.12 \times 10^3$ | 0.5 | 2.85 + 5d |
| (4) $He^+ + e^- \rightarrow He^{2+} + 2e^-$ | $9.84 \times 11$ | 0.5 | 6.32 + 5d |
| (5) $Li + e^- \rightarrow Li^+ + 2e^-$ | $3.11 \times 8$ | 1.63 \times 1 | 6.27 + 4 |
| (6) $Li^+ + e^- \rightarrow Li^{2+} + 2e^-$ | $5.67 \times 12$ | 7.15 \times 1 | 8.77 + 5d |
| (7) $Li^{2+} + e^- \rightarrow Li^{3+} + 2e^-$ | $1.7 \times 12$ | 7.09 \times 1 | 1.42 + 6d |
| (8) $He^+ + e^- \rightarrow He + \nu$ | 3.66 \times 7 | 1.15 | 4.7 + 5d |
| (9) $He^{2+} + e^- \rightarrow He^+ + \nu$ | 1.97 \times 11 | 6.34 \times 1 | 1.32 + 6 |
| (10) $Li^+ + e^- \rightarrow Li + \nu$ | 1.33 \times 8 | 1.15 | 6.53 + 5d |
| (11) $Li^{2+} + e^- \rightarrow Li^+ + \nu$ | 1.87 \times 11 | 6.41 \times 1 | 1.76 + 6 |
| (12) $Li^{3+} + e^- \rightarrow Li^{4+} + \nu$ | 5.34 \times 8 | 1.23 | 9.23 + 5 |
| (13) $Li^{4+} + e^- \rightarrow Li^{5+} + \nu$ | 4.83 \times 11 | 6.21 \times 1 | 1.67 + 6 |
| (14) $H + D \rightarrow H + D^+$ | 1.97 \times 9 | 4.02 \times 1 | 3.71 + 1 |
| (15) $D^+ + H \rightarrow D + H^+$ | 1.97 \times 9 | 3.95 \times 1 | 3.30 + 1 |
| (16) $H^+ + H \rightarrow H + H$ | 1.40 \times 7 | 8.87 \times 1 | 2.93 + 4 |
| (17) $H^+ + D^+ \rightarrow H + D$ | 1.61 \times 7 | 8.87 \times 1 | 2.93 + 4 |
| (18) $H^+ + D \rightarrow H + D^+$ | 1.61 \times 7 | 8.87 \times 1 | 2.93 + 4 |
| (19) $D^+ + D \rightarrow D + D$ | 1.96 \times 7 | 8.87 \times 1 | 2.93 + 4 |
| (20) $Li^+ + H \rightarrow Li + H$ | 2.97 \times 11 | 7.17 \times 1 | 2.32 + 4 |
| (21) $Li^+ + H \rightarrow Li + H$ | 1.80 \times 7 | 6.77 \times 1 | 2.32 + 4 |
| (22) $Li^+ + D \rightarrow Li + D$ | 3.71 \times 7 | 5.10 \times 1 | 4.41 + 4 |
| (23) $Li^+ + D \rightarrow Li + D$ | 2.28 \times 7 | 5.10 \times 1 | 4.41 + 4 |
| (24) $H + \nu \rightarrow H^+ + e^-$ | 1.14 \times 7 | 0.98 | 1.57 + 5d |
| (25) $D + \nu \rightarrow D^+ + e^-$ | 1.14 \times 7 | 0.98 | 1.57 + 5d |
| (26) $He + \nu \rightarrow He^+ + e^-$ | 1.11 \times 7 | 1.23 | 2.80 + 5d |
| (27) $He^{2+} + \nu \rightarrow He^{3+} + e^-$ | 5.45 \times 5 | 1.63 | 5.90 + 5d |
| (28) $Li^+ + \nu \rightarrow Li^{2+} + e^-$ | 5.08 \times 6 | 1.45 | 6.05 + 4d |
| (29) $Li^{2+} + \nu \rightarrow Li^{3+} + e^-$ | 9.23 \times 6 | 1.37 | 8.40 + 5d |
| (30) $Li^{3+} + \nu \rightarrow Li^{4+} + e^-$ | 5.96 \times 2 | 2.63 | 1.27 + 6d |
| (31) $H + \nu \rightarrow H + e^-$ | 2.08 \times 4 | 2.13 | 8.82 + 3d |
| (32) $D + \nu \rightarrow D + e^-$ | 2.08 \times 4 | 2.13 | 8.82 + 3d |
| (33) $Li^+ + \nu \rightarrow Li^{2+} + e^-$ | 5.29 \times 5 | 1.40 | 8.10 + 3d |
| (34) $H_2 + D \rightarrow HD + H^+$ | 1.60 \times 9 | 4.85 \times 1 | -3.12 + 4 |
| (35) $H_2^+ + \nu \rightarrow H_2^{++} + e^-$ | 2.70 \times 10 | 4.85 \times 1 | -3.12 + 4 |

The rate coefficient fits presented on this table are given by the relation $a = a_1 (T/300)^{a_2} \times \exp(-T/a_3)$, $a_1$ is in cm$^3$ s$^{-1}$ for collision processes while it has units of s$^{-1}$ for photoprocesses. The notation A + B corresponds to A $\times 10^B$. Indicated reactions have an exponential term of $\exp(-a_3/T)$.

Experimental study has involved (1) storage ring experiments and (2) plasma afterglow experiments. The storage ring experiments comprise a particle accelerator, wherein energetic molecules are collided to drive reactions of interest. Plasma afterglow experiments utilize high-temperature, low-pressure plasmas, which also produce chemical reactions. While storage ring experiments yield results approximating the theoretical rate coefficients ($\sim 10^{-7}$ cm$^3$ s$^{-1}$), plasma afterglow experiments yield rates approximately an order of magnitude lower.

Theoretical treatments of $H_2^+$ DR prior to the early 2000s had neglected the Jahn–Teller effect, a non-Bohr–Oppenheimer phenomenon accounting for energy level splitting of degenerate electronic states due to geometric distortion. However, in 2001, Kokouline and co-workers showed that the inclusion of Jahn–Teller coupling provided dissociative recombination rates overlapping the range of experimental observations.

In 2003, Kokouline and Greene extended this theory to unify treatment of all $D_{3\alpha}$ trimeric ions, while...
In 2006, Glosik continued a series of promising afterglow experiments in Prague using cavity ringdown spectroscopy to record spectra of triatomic isomers in discharged mixtures of hydrogen and deuterium (H$_3^+$, H$_2$D$^+$, HD$_2$) originating from low rotational states. In subsequent low-temperature ion trap experiments at MPIK Heidelberg and TU Chemnitz, Glosik recorded near-infrared spectra of H$_3^+$, H$_2$D$^+$, and HD$_2$ and characterized the trapped ions at temperatures near 10 K. These low-energy interactions are directly relevant to interstellar conditions, especially in cold dense regions of space where deuterated molecules are abundant.

The Prague experiments performed prior to 2006 found that DR of H$_3^+$ is pressure dependent; the DR rate of H$_3^+$ rapidly falls when [H$_2$] $< 10^{12}$ cm$^{-3}$. These results suggested that the DR of H$_3^+$ is not exclusively a binary process and that previously measured DR rates were collective/effective (binary + ternary) values. This was the first time data suggested that ternary recombination is significant. In 2008, a flowing afterglow Langmuir probe experiment found similar pressure dependences of D$_3$ recombination on D$_2$ pressure. A D$_2$ low density limit was measured to give a pure binary recombination rate coefficient, while a new data analysis method improved determination of the effective recombination rates.

By 2010, a new Prague cryo-FALP design allowed afterglow experiments compatible with temperatures from 77 to 300 K and pressures from 400 to 2000 Pa to measure temperature and pressure dependences of H$_3$ recombination rates in He buffer gas. The effective recombination rate increased with increasing [H$_2$] and [He] from $\sim 10^{11}$ to $\sim 10^{13}$ cm$^{-3}$ and from $\sim 10^{17}$ to $5 \times 10^{17}$ cm$^{-3}$, respectively; however, the rate dropped significantly when [H$_2$] $< 10^{12}$ cm$^{-3}$ because lower concentrations cannot keep ortho- and para-H$_3^+$ in thermal equilibrium under recombination conditions (recombination is faster than rethermalization at this concentration). The effective recombination rate increased with increasing temperature from 77 to 170 K but decreased at higher temperatures. These results parallel later studies of D$_3^+$ recombination.

These authors describe H$_3^+$ ternary recombination as a two-step mechanism wherein the electron-H$_3^+$ collision creates a rotationally excited, neutral H$_3$ molecule, which then collides with He to form a "very long-lived Rydberg state with high orbital momentum." The rotationally excited H$_3$ and D$_3$ molecules respectively have lifetimes up to 300 and 1000 ps before autoionizing. This process proved to be 100 times more effective than Thomson, Bates, and Khare's ternary recombination process. Para-H$_3^+$ was found to have a larger He-collision rate than ortho-H$_3^+$, and this difference widens below 170 K, which is responsible for small measurement and calculation discrepancies for the ternary coefficient rate at that time. Including the ternary process in calculating the effective recombination rates and buffer gas factor represented the first time results from afterglow plasma experiments agreed with ion storage ring experiments and theory.

In 2010, Saykally et al. observed unexpected infrared lasing lines while performing cavity ringdown spectroscopy experiments on a pulsed supersonic rare gas plasma of hydrogen and rare gases. Upon consulting with Professor Chris Green, these were determined to be d→p lasing lines emitted from the H$_3$ Rydberg molecule. Calculations showed that while the d-states were long-lived, the p-states relaxed quickly, ostensibly providing an efficient lasing mechanism. The experimental-theoretical comparisons are included in Figure 4. While the experimental conditions under which these laser lines were discovered are not directly relevant to primordial gas conditions, their discovery and characterization of is a significant step toward understanding the energetics of excited H$_3$ Rydberg molecules.
In 2012, Galli and Palla summarized model cooling function calculations for various molecules.\textsuperscript{31} At low temperatures, the importance of H$_3^+$ becomes evident as an important coolant for primordial gas. While experimental data for actual H$_3$ Rydberg cooling remain elusive, the observed spectra and associated calculations for H$_3^+$ do suggest a potentially important role for H$_3$ Rydberg molecules in the cooling process (Figure 5).

During 2011–2013, a series of papers published by Glosi and co-workers were able to control the ratio of para- and ortho-H$_2$ to determine the binary recombination rates, and later, ternary recombination rates for both pure para- and ortho-H$_3^+$ ions. Population of H$_3^+$ in the para states is also temperature dependent.\textsuperscript{27,39} The first recombination rate coefficients were determined for ions in the lowest ground vibrational state, with specific nuclear and rotational states measured \textit{in situ}. These low-energy, state-specific recombination coefficient rates are in excellent agreement with theoretical predictions of binary DR. These efforts facilitated state-specific H$_3^+$ dissociative recombination experiments. At low temperatures (77–200 K), para- and ortho-H$_3^+$ dissociative recombination rates increasingly deviate as temperature decreases.\textsuperscript{39} Para-H$_3^+$ DR rates increase, while ortho-H$_3^+$ rates decrease. As such, the dissociative recombination patterns were experimentally determined below 100 K. Later, in 2015, it would be found that the 60 K binary recombination rate for para-H$_3^+$ (1.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}) is at least three times larger than for ortho-H$_3^+$ (0.5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}).\textsuperscript{45}

In 2013, studies extended conditions down to 50 K for the first time for both H$_3^+$ and D$_3^+$ DR. Differing from neutral ternary recombination (He assisted), electron-assisted ternary recombination (electron-collisional radiative recombination or E-CRR) may also substantially contribute to effective recombination rates, which was suggested by theory and observed in an Ar$^+$ dominated plasma. However, the contribution of E-CRR to the effective dissociative recombination rate could not be extracted in H$_3^+$ dominated plasma, even at 50 K.\textsuperscript{40} Moreover, E-CDR and N-CDR processes do not adequately explain existing experimental results. CRR at low temperatures competes with binary recombination. Collisional radiative recombination is a bigger factor than collisional dissociative recombination because CDR is only effective at low l states, while CRR occurs for both low and high l states and is statistically favored.

**THE HEH RYDBERG MOLECULE**

Recently, the role of HeH$^+$ as "the very first molecule to have been synthesized in the universe" has been elucidated via its discovery by radioastronomy.\textsuperscript{44} HeH$^+$ is generally considered important in the chemistry of the early universe, primarily as an intermediate in the synthesis of H$_2$:\textsuperscript{44}

\[
\text{H}^+ + \text{He} \rightarrow \text{HeH}^+ + \nu
\]

\[
\text{HeH}^+ + \text{H} \rightarrow \text{H}_2^+ + \text{He}
\]

\[
\text{H}_2^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+
\]

Here, we investigate its role as a potential primordial gas coolant. With a large dipole and a potential recombinant Rydberg state manifold, HeH$^+$ could indeed prove to be an interesting target for such a study. At high redshift, HeH$^+$ exhibits a fractional abundance multiple orders of magnitude higher than that of H$_3^+$, but still 5–10 orders of magnitude lower than that of neutral H$_2$. Similar to the case of H$_3^+$, electron–HeH$^+$ recombination processes could lead to an excited molecular core, IR and/or UV–vis radiation, and subsequent cooling. If neutral HeH Rydberg molecules do form, it may be necessary to account for such cooling effects (Figure 6).

Recent (2016) \textit{ab initio} theoretical studies have addressed such Rydberg states and have shown that they can evolve...
regularly, similar to the Born–Oppenheimer function for H2.\(^{45}\) Herzberg, in 1977, was able to experimentally characterize the lower energy levels of HeH\(^+\). This was possible due in part to the large dipole moment and its derivative, which generates strong rovibrational spectra in the infrared region. From these, it is possible to calculate the radiative energy loss from electron recombination.\(^{46}\)

The cooling functions for HeH\(^+\), H\(_3^+\), and other such molecules have previously been described. To evaluate the cooling function as a function of redshift, knowledge of the radiative and collisional transition probabilities and the frequencies of rovibrational transitions of each molecule is necessary. These data have been reported in the literature for common molecules and ions. The rate equations can thus be solved for the energy level populations. However, accurate collisional coefficients are available in only a limited number of cases, and approximations must be used for minor species, such as HeH\(^+\). The radiative cooling contribution for HeH\(^+\) was described by Coppola, Lodi, and Tennyson in 2011, and it is shown in Figure 7.\(^{38}\)

The cooling effects of HeH\(^+\) ostensibly contribute non-negligibly to the overall cooling, likely attributable to its strong dipole moment. While HeH Rydberg molecules retain the strong dipole moment, they additionally have the ability to radiate large quantities of energy upon recombining with an electron, as they decay from high to low \(n\)-states. Hence, HeH Rydberg molecules comprise an interesting candidate for further investigation of potential coolants in primordial gas.

In order to obtain astronomical data to exploit these laboratory and theoretical observations, it would be interesting to examine the 21 cm\(^{-1}\) hydrogen line to explore conditions at relevant redshifts, and then to ultimately scan appropriate frequency regions for emissions from candidate primordial molecules. In 1944, Hendrik van de Hulst predicted that atomic hydrogen should emit at a wavelength of 21.1 cm\(^{-1}\) corresponding to a transition between hyperfine levels of the 1s ground state in a spin-flip transition.\(^{47}\) While this magnetic dipole transition is very weak, the high abundance of neutral hydrogen atoms makes it possible to detect it using modern radio telescopes. Very interestingly, highly red-shifted \((z \approx 17)\) 21 cm\(^{-1}\) emission was recently detected at 78 MHz by the radiofrequency array in Australia.\(^{48}\) This light probes the universe only 180 million years after the Big Bang, as stars would have formed and emitted a background of Lyman-\(\alpha\) radiation, giving rise to the detected signal. Until now, it was believed that adiabatic cooling due to expansion of the universe was the primary initial cooling mechanism. While the observed line profile is consistent with what is expected of population III stars, the amplitude of the absorption is 0.5 K, which is more than twice the predicted value due to adiabatic cooling (the excess significance is 3.8\(\sigma\) per Barkana, 2018).\(^{49}\) Another possibility is a much hotter background, but this is unlikely since precise measurements of the background radiation from the Planck Collaboration et al. in 2018 indicate temperature anisotropies in line with estimates.\(^{50}\) Bowman et al., in 2018, reference Barkana (2016) who invokes velocity-dependent Rutherford/Coulomb scattering interactions between baryons and cold dark matter to explain the cooling and the large drop in amplitude of the absorption profile.\(^{48,51}\) However, Barkana et al. (2018) negated the possibility due to the requirement of strong interactions at \(z \sim 20\) and dominant dark matter to be cooled enough to explain the signal anomaly, pointing to the existence of additional cooling mechanisms.\(^{51}\)

If H\(_3^+\) and HeH Rydberg molecules did indeed produce strong emissions over large pathlengths from such massive objects as primordial stars, the resultant light may currently be detectable. Using the 21 cm\(^{-1}\) hydrogen line as a guide, we can make estimates, shifting the laboratory 7 \(\mu\)m emission from H\(_3^+\) into the far IR and the 0.2–0.4 \(\mu\)m HeH emission into the mid-IR. Examination of these regions with appropriate telescopes such as SOFIA and other HiFi instruments could yield interesting new insights to novel cooling mechanisms.

### CONCLUSIONS

While H\(_2\) associative detachment remains the accepted primary cooling mechanism for star formation in primordial gas, the weakness of quadrupole-allowed H\(_2\) rotational transitions remains a concern regarding cooling to the requisite low temperatures required for collapse to fusion densities. In the

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**Figure 6.** Fractional abundances of main species formed in the early universe as a function of redshift. Vertical lines indicate boundaries of the five main evolutionary phases, as described in Galli and Palla 2013. Reprinted with permission from ref 31. Copyright 2013 Annual Reviews.

**Figure 7.** HeH\(^+\) radiative cooling function contributions. Circles: 3 HeH\(^+\). Squares: 3 HeD\(^+\). Green solid curve: 3 HeH\(^+\) fit (Table 1). Blue dashed curve: 3 HeD\(^+\) fit. Reprinted with permission from ref 38. Copyright 2011 Oxford University Press.
search for alternative/additional coolants, $\text{H}_3^+$ and $\text{HeH}^+$ have been discussed. The laboratory observation and characterization of neutral $\text{H}_3$ Rydberg lasing processes in supersonic hydrogen/helium plasmas reveals another candidate for cooling. Rydberg molecules can radiate large amounts of energy on relatively short time scales. As such, the cooling per molecule could be extremely high, and Rydberg molecules could thus play an important role—even at their relatively low abundances. In addition to the $\text{H}_3$ Rydberg species, an increased understanding of $\text{HeH}$ in recent years presents another interesting candidate for cooling. With a strong dipole moment and derivative, as well as a Rydberg architecture, the $\text{HeH}$ Rydberg molecule could have an effect on high molecular cooling rates at relatively low abundances. We anticipate further experimentation into such Rydberg molecules in order to characterize their radiative cooling profiles, as well as further theoretical investigation into their cooling functions to elucidate their potential influence in primordial gas clouds.

Knowing that $\text{H}_3^+$ is formed in significant densities, we can infer that $\text{H}_3^+$ recombination with electrons to produce $\text{H}_3$ Rydberg molecules may have been prominent in the early universe. Strong IR emissions from these molecules would have occurred and could be detectable at very high redshifts. The IR emission results reported by Saykally et al. would be shifted deep into the far-IR/microwave region of the spectrum. High resolution telescope imaging of the 200−500 μm region for $\text{H}_3$ Rydberg and the 0.1−0.4 μm region for $\text{HeH}$ Rydberg could yield interesting results.

By searching for transitions of these Rydberg molecules in the context of primordial cooling, we could advance our understanding of the formation of the first stars in the universe. In order to assess the cooling potential of these novel systems, detailed chemical reaction modeling must be performed, and similarly detailed radiative transfer models must be developed. We hope that this brief review helps to stimulate such efforts.

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Notes
The authors declare no competing financial interest.

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Gokul Kannan is an undergraduate chemical engineer at the University of California, Berkeley, studying astrochemistry in the Saykally group for the past 3 years. Along with Jeremy Chien, Anthony Benjamin, and Niranjan Bhatia, he has focused on understanding $\text{H}_3$ and $\text{HeH}$ Rydberg emission spectra in the context of primordial gas cooling. He is planning to begin a graduate research position in the fall of 2021.

Jeremy Chien is an undergraduate researcher studying chemical biology at the University of California, Berkeley. His work with the Saykally group spans 3 years and looks into cooling mechanisms of the early universe in the formation of the first stars. He is applying to medical schools in the hopes of pursuing a career in surgery.

Anthony Benjamin is an undergraduate student and midshipman in the Chemical Biology program at the University of California, Berkeley. After graduating and commissioning, he will begin Navy Nuclear Power and Propulsion training to operate submarines.
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Richard Saykally is the Class of 1932 Endowed Professor of Chemistry at UC-Berkeley. He is coauthor of over 400 publications that have been cited over 50,000 times (h-index >100), and he is the recipient of over 75 honors and awards from 15 different countries.

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