

The lightest hydrides, witnesses of cosmochemical evolution

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The first molecular bonds: HeH⁺, together with He₂⁺, is predicted to form the first molecular bond in the primordial universe. While H₂⁺ was quickly destroyed by dissociative recombination, the abundance of HeH⁺ reached a first maximum at $z \sim 2000$ (0.1 Myr after the big bang), together with the rise of H₂⁺, H₂, H₃⁺, and their deuterated isotopologs (Fig. 1). After the recombination era ($z \sim 1000$), the steady increase of the abundances provided coolants for the collapse of halos forming population III stars ($z \sim 30$)*. When temperatures dropped to $T \sim 200$ K, rotational line cooling by HD and HeH⁺ became important (Fig. 2). HD was subsequently depleted by astration (Fig. 3) and HeH⁺ through dissociative recombination and proton transfer.

*Klessen & Glover 2023, ARA&A

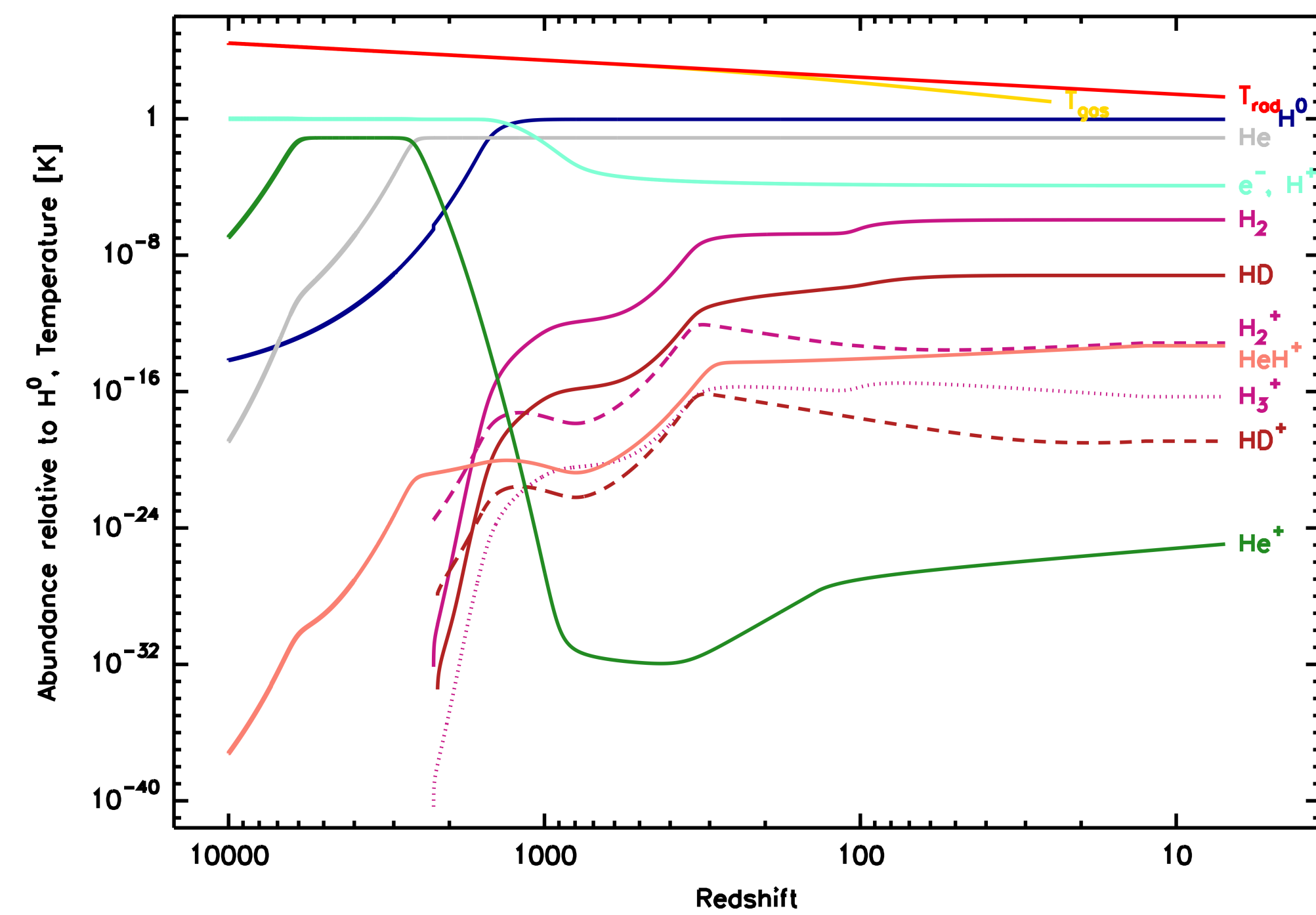


Fig. 1: Chemical and thermal evolution of the young universe, including H₂ cooling (Galli & Palla 1998). Processed with KROME package v14.08 (Grassi et al. 2014) and rates therein (except for the proton transfer of HeH⁺, Faure et al. 2024) under Λ CDM cosmology (final Planck data parameters, Tristram et al. 2024).

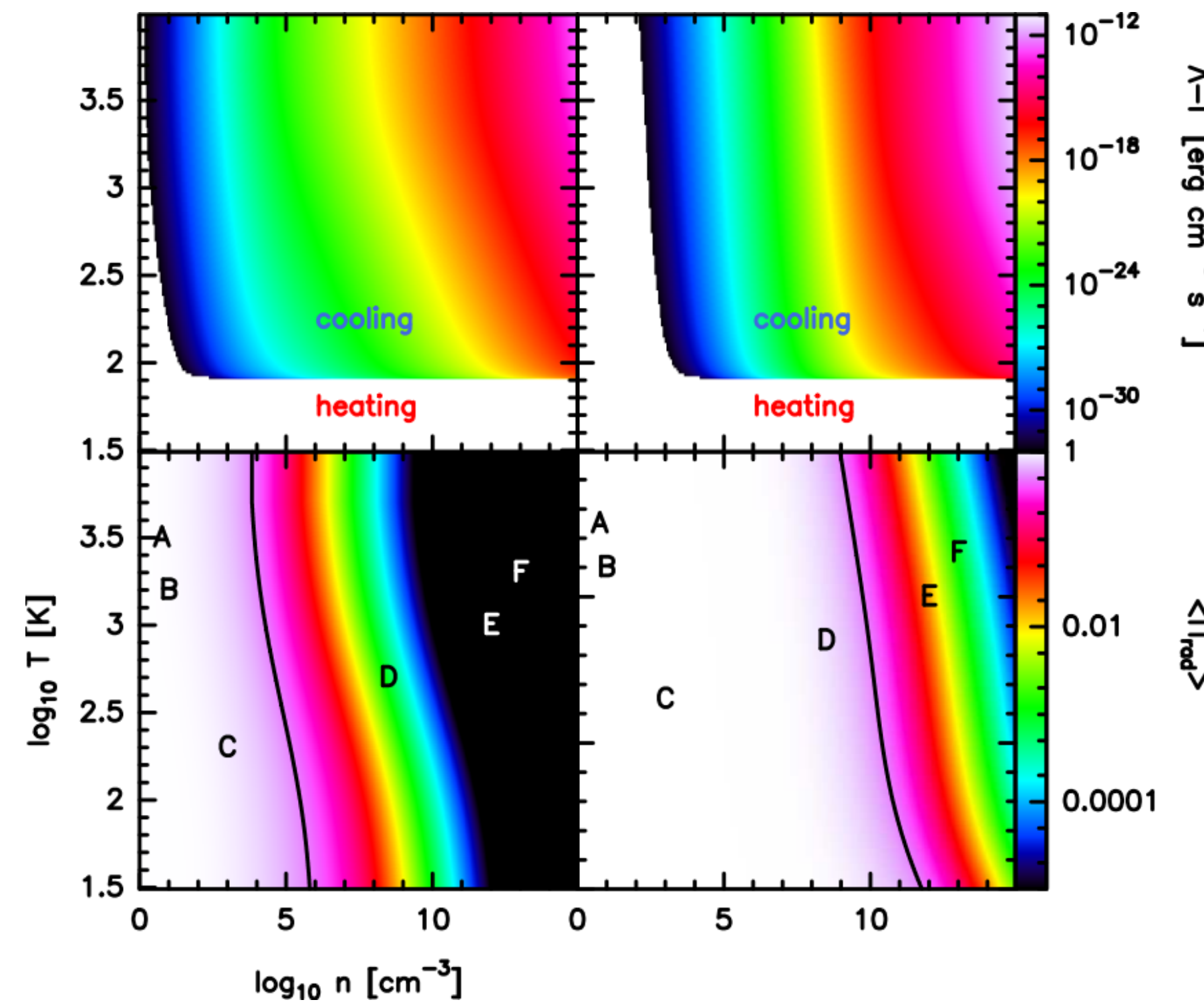


Fig. 2: Top - Cooling of a collapsing halo by HD (left) and HeH⁺ (right), for $z = 30$ and 10% escape probability. Bottom - Corresponding probabilities for radiative de-excitation. Evolutionary stages are labeled A (compression-heated flow into dark-matter halo), B - C (runaway H₂ cooling), C - D (PdV heating), E (gas fully molecular).

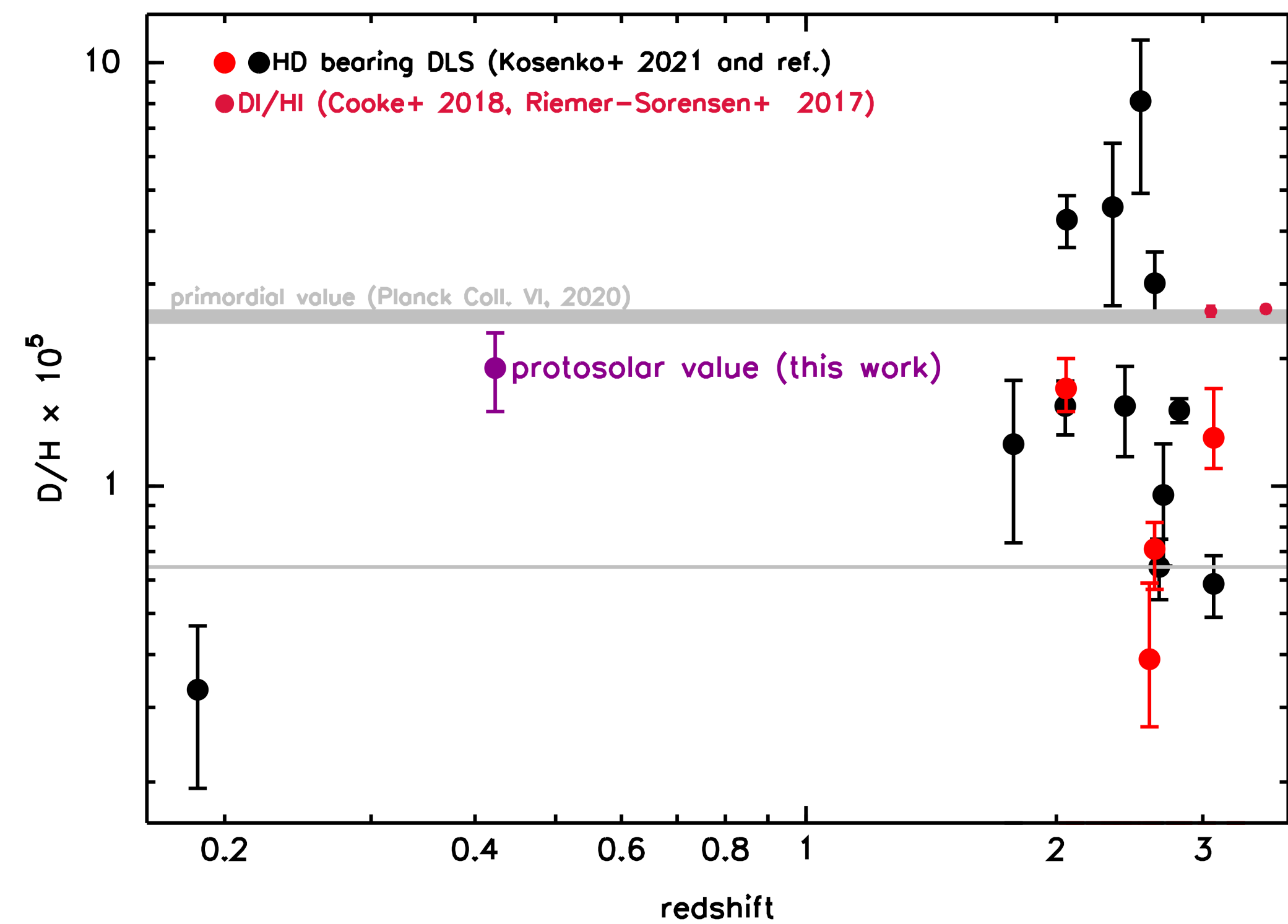


Fig. 3: Synopsis of cosmic deuterium fractions. Shown are the primordial value, D/H and HD/H₂ in damped Lyman α systems, and the protosolar value against redshift.

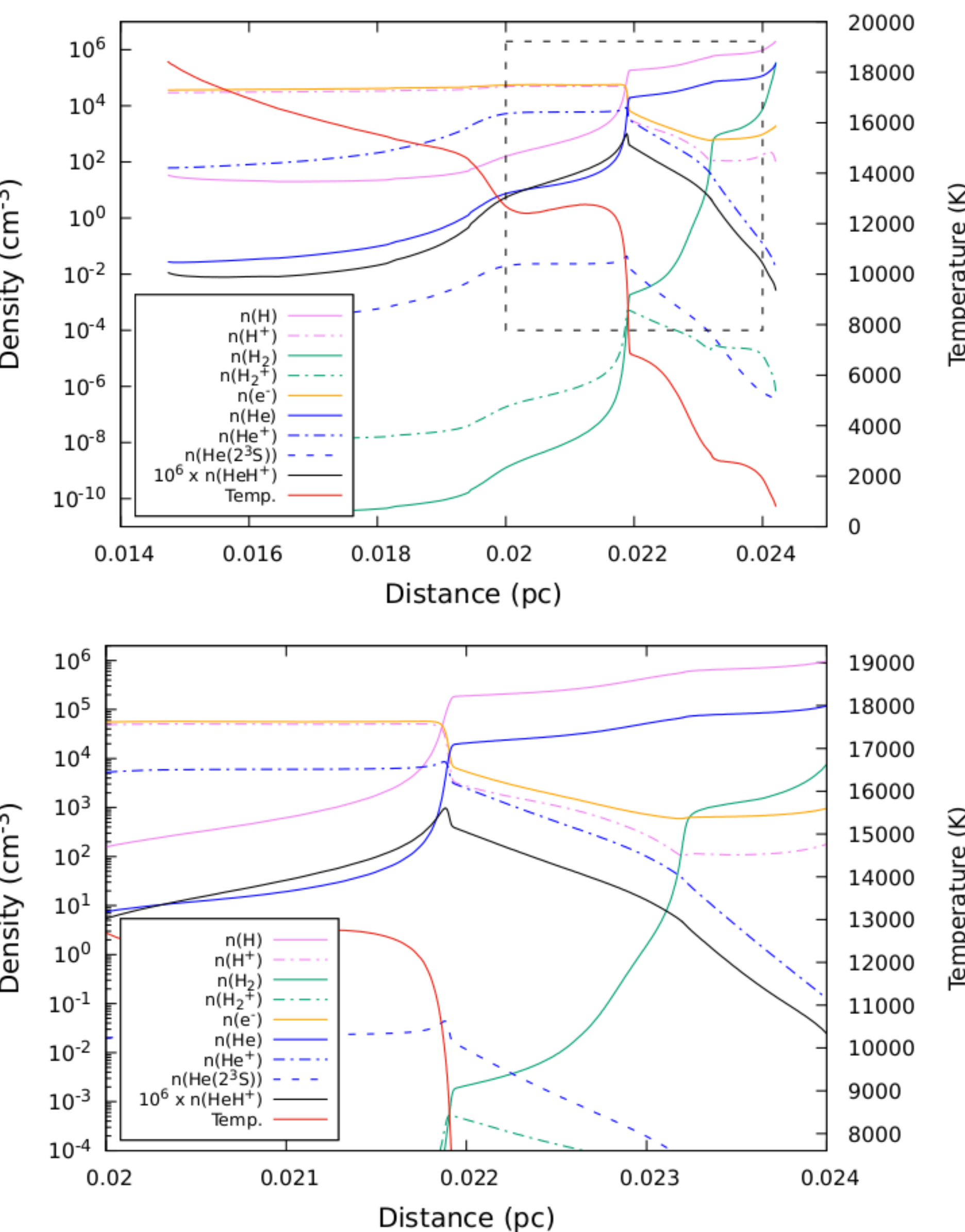


Fig. 4: Top - Equilibrium temperature and densities for an isobaric Cloudy* model of NGC 7027 as a function of distance from the 1.98×10^5 K hot central star, starting at the illuminated face of the nebula. Bottom - Zoom into the dashed area above (Sil+ 2025, A&A in press). *v23.01, Gunasekara+ 2023

Table 1: The chemistry of HeH⁺

Dominant production pathways (radiative association):

Present day Universe (k1): He⁺ + H \rightarrow HeH⁺ + photon
He(2³S) + H \rightarrow HeH⁺ + photon

Primordial Universe (k2): He + H⁺ \rightarrow HeH⁺ + photon

Dominant destruction pathways ($z < 200$ and NGC 7027):

Dissociative recombination: HeH⁺ + e⁻ \rightarrow He + H
Proton transfer: HeH⁺ + H \rightarrow He + H₂⁺

Table 2: NGC 7027* vs. primordial Universe¹

		NGC 7027 ²	$z = 2600$
T	[K]	5100	7100
n_H	[cm ⁻³]	2.6×10^5	7400
n_e	[cm ⁻³]	5960	7080
P/k	[K cm ⁻³]	1.6×10^9	5.3×10^7
$\int_{\nu_{Ly}} I_\nu d\nu$	[erg s ⁻¹ cm ⁻² sr ⁻¹]	160	20
$n(\text{He}^+)n(\text{H}^0)k_1$	[cm ⁻³ s ⁻¹]	2.9×10^{-8}	3.6×10^{-18}
$n(\text{He}^0)n(\text{H}^+)k_2$	[cm ⁻³ s ⁻¹]	2.0×10^{-12}	1.6×10^{-14}
		HeH ⁺ J=1-0	P(1) P(2)
measured / a-posteriori flux ratios ³		0.95(19)	0.86(9) 1.08(16)

¹ krome model, ² Cloudy17.02 model for HeH⁺ yielding layer, ³ Sil et al. 2025, MCMC

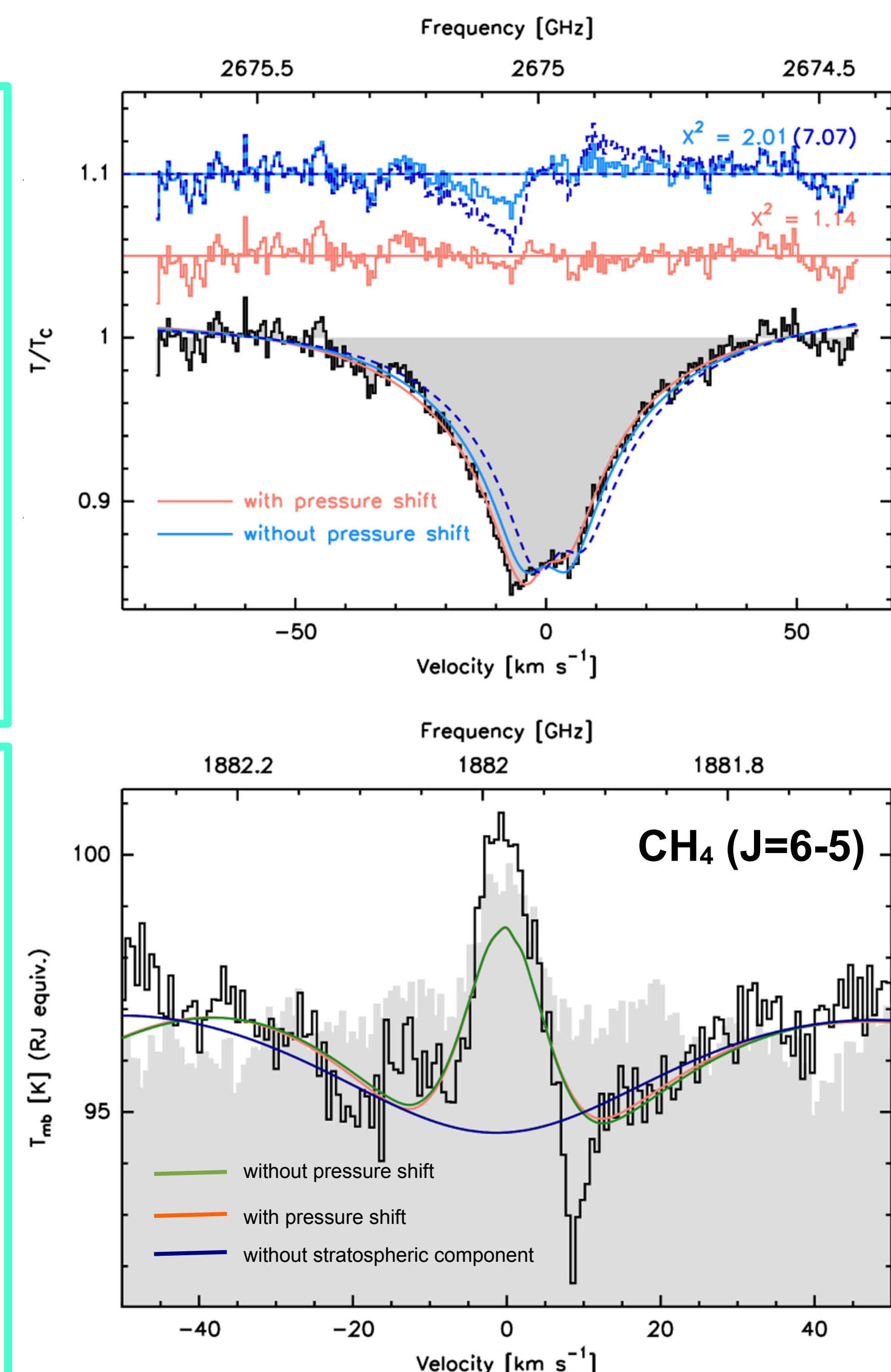


Fig. 3: Top - HD (J=1-0) line (4GREAT) of Jupiter and Voigt profile fits (best with inclusion of the pressure shift). Bottom - CH₄ (J=6-5) line (upGreat, equivalent from HIFI underneath) and fit for same model.

Results: The spectroscopy of rotational (FIR) and vibrational (NIR) lines of HeH⁺ in NGC 7027 confirms a chemistry controlled by ion-neutral reactions and photo-ionization (Güsten+ 2019; Neufeld+ 2020; Sil+ 2025). The Strömgren sphere of this young planetary nebula and the primordial universe form HeH⁺ on different pathways (radiative association of He + H⁺ and He⁺ + H, respectively) but share (for $z < 200$) the same destruction channels (dissociative recombination & proton transfer). Inclusion of He (2³S), the longest-lived metastable atomic state, reproduces the observed HeH⁺ abundance thanks to its 19.8 eV energy input. While reaction rates are measured in ion storage rings, removal of ambiguities between temperature and density requires further IR spectroscopy and high resolution to avoid blends (e.g., of HeH⁺ and CH). — **Why it matters:** The cooler stages in the formation of population III stars, when HeH⁺ and HD contend for the role of the major coolant, call for quantum-state selective reaction networks. Evidence for HD is as well limited to the local universe (except for a few $z \leq 3$ samples), where it traces, thanks to its weak fractionation, native D/H ratios. GREAT ($R > 5 \times 10^5$!) confirms the protosolar origin of Jupiter's deuterium fraction (Wiesemeyer+ 2024), significantly falling below the primordial value, by separating tropospheric absorption from stratospheric emission.