H1-to-H2 Transitions in Dust-free Interstellar Gas

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Abstract

We present numerical computations and analysis of atomic-to-molecular (H1-to-H2) transitions in cool (∼100 K), low-metallicity, dust-free (primordial) gas in which molecule formation occurs via cosmic-ray-driven negative ion chemistry and removal is by a combination of far-UV photodissociation and cosmic-ray ionization and dissociation. For any gas temperature, the behavior depends on the ratio of the Lyman–Werner (LW) band FUV intensity to gas density, I LW/n, and the ratio of the cosmic-ray ionization rate to the gas density, ζ/n. We present sets of H1-to-H2 abundance profiles for a wide range of ζ/n and I LW/n for dust-free gas. We determine the conditions for which H2 absorption-line self-shielding in optically thick clouds enables a transition from atomic to molecular form for ionization-driven chemistry. We also examine the effects of cosmic-ray energy losses on the atomic and molecular density profiles and transition points. For a unit Galactic interstellar FUV field intensity (I LW = 1) with LW flux 2.07 × 107 photons cm−2 s−1 and a uniform cosmic-ray ionization rate ζ = 10−16 s−1, an H1-to-H2 transition occurs at a total hydrogen gas column density of 4 × 1021 cm−2, within 3 × 107 yr, for a gas volume density of n = 106 cm−3 at 100 K. For these parameters, the dust-free limit is reached for a dust-to-gas ratio Z′ d ≲ 10−5, which may be reached for overall metallicities Z′ ≲ 0.01 relative to Galactic solar values.

Unified Astronomy Thesaurus concepts: Interstellar medium (847); Photodissociation regions (1223); Cosmic rays (329)

1. Introduction

Atomic-to-molecular hydrogen (H1-to-H2) transitions are of fundamental importance for the structure of the interstellar medium (ISM) in galaxies (Sternberg et al. 2014, hereafter S14). Numerous observational studies show that dense molecular gas is closely correlated with star formation, from sub-pc to kpc scales and across cosmic time from low to high redshifts (Tacconi et al. 2020). H2 formation may promote cooling and high density cloud fragmentation and/or it may be accelerated in gravitationally collapsing regions where the gas becomes dense and optically thick to destructive radiation fields.

In star-forming galaxies, especially Milky Way-like systems containing diffuse to dense interstellar gas clouds, it is well established that hydrogen molecules are generally formed on the surfaces of dust grains (Gould & Salpeter 1963; Jura 1974; Le Bourlot et al. 2012; Girichidis et al. 2020). The formation efficiencies (via chemisorption and/or physisorption) depend on the solid-state dust compositions, the gas and grain temperatures, and the overall gas-to-dust mass ratios (Cuppen et al. 2010; Wakelam et al. 2017). For systems in which the heavy-element and dust abundances are very low, or if the grain surface temperatures are too high, the grain-induced formation rates vanish and molecules are instead formed by gas-phase processes, especially via the H− negative ion intermediary (McDowell 1961; de Jong 1972; Dalgarno & McCray 1973; Glover 2003; Larsson et al. 2012). For example, gas-phase production of H2 may dominate in protoplanetary disks where high temperatures inhibit gas-grain sticking (Glassgold et al. 2004) or in dust-poor outflow jets from protostars (Tabone et al. 2020). In metal-rich disks and jets, gas-phase H2 formation enables synthesis of heavy molecules (CO, OH, etc.) via the usual neutral–neutral and ion–molecule reactions, as occurs in dusty clouds (Herbst & Klepser 1973; Sternberg & Dalgarno 1995; Tielens 2013; van Dishoeck 2014; Bialy & Sternberg 2015; Öberg & Bergin 2021). Atomic-to-molecular conversion for dust-free conditions may also be important in low-metallicity, damped Lyα absorbers (DLAs) (Ranjan et al. 2018) or perhaps in dense condensations within cool filament in the circumgalactic medium (CGM) of galaxies and/or the cosmic web.

Gas-phase H2 formation was critically important in the dust-free early universe where even minute amounts of H2 enabled cooling to low (∼100 K) temperatures, reduction of the Jeans masses, and the collapse of the first objects (Peebles & Dicke 1968; Tegmark et al. 1997; Lepp et al. 2002; Haiman 2016). Feedback in the form of photodissociating Lyman–Werner (LW) band radiation from the first stars plausibly regulated the early star formation rates and the formation of seed black holes (Haiman et al. 1997; Latif et al. 2014; Visbal et al. 2014; Wolcott-Green et al. 2021). H1-to-H2 conversion for Galactic conditions and the structures of photodissociation regions (PDRs) in dense Milky Way molecular clouds are well understood (Federman et al. 1979; Tielens & Hollenbach 1985; Black & van Dishoeck 1987; Röllig et al. 2006; McKee & Krumholz 2010; Sternberg et al. 2014). But how do analogous H1-to-H2 PDR transitions occur for early universe conditions?

The astrophysics of H1-to-H2 conversion in the dusty interstellar medium (ISM) was reviewed in S14. That paper also presented numerical computations and analytic theory for H1-to-H2 transitions and the buildup of photodissociated H1 columns in dusty FUV-irradiated molecular cloud surfaces (PDRs). In Bialy & Sternberg (2016, hereafter BS16) we presented an analytic procedure for generating depth-dependent H1/H2 density profiles, again for dusty clouds, for a wide range of assumed gas-to-dust mass ratios. In all of these
computations, dust plays a dual role (a) in providing the molecular formation sites and (b) as shielding agents via FUV absorption (and scattering). Both roles, especially shielding, enable the atomic-to-molecular conversions.

In this paper, we extend the methodology presented in S14 and BS16 for a theoretical study of atomic-to-molecular transitions in dust-free environments. We consider simple idealized steady-state models consisting of FUV-irradiated plane parallel isothermal constant-density slabs, in which H₂ formation is via ionization-driven gas-phase processes and attenuation of the photodissociation rate is by H₂ absorption-line self-shielding only. This, as opposed to dusty clouds in which H₂ is formed on dust grains, and shielding includes dust absorption in addition to molecular self-shielding. We assume that the cloud ionization is provided by a flux of (low-energy) penetrating cosmic-ray particles. We do not consider irradiation by X-rays. We assume that the fractional ionizations are not affected by the presence of any heavy elements (“metals”) or by interactions with dust grains or large molecules such as polycyclic aromatic hydrocarbons (PAHs). Ionization drives the molecular hydrogen formation chemistry everywhere in the cloud, including the outer photodissociation regions (PDRs) and the inner optically thick cosmic-ray zones (CRZs). Ionization also serves as a H₂ removal mechanism in the cosmic-ray zones. We present analytic and numerical computations for the H I and H₂ density profiles for the dust-free conditions.

In Section 2, we present our model ingredients. This includes a review of the metal-free hydrogen–helium chemical network and a discussion of FUV photodissociation, H₂ self-shielding, and cosmic-ray propagation. In Section 3 we present an analytic model for the expected atomic to molecular profiles and dependence on the FUV field strength, gas density, and ionization rate. We also consider the timescales. We develop expressions for the total H I column densities in the PDRs and CRZs, as functions of FUV radiation intensity, cosmic-ray ionization rate, gas density, and temperature. In Section 4 we present numerical computations for the atomic and molecular density profiles and transition points for dust-free conditions. These computations include a fiducial model and a parameter study for a range of FUV intensities, gas densities, and ionization rates. We compare these to our analytic description. We summarize in Section 5.

2. Model Ingredients

2.1. Chemistry

We consider a steady state between formation of H₂ via cosmic-ray-driven negative ion chemistry and destruction by FUV photodissociation and cosmic-ray ionization and dissociation in a dust-free environment.

Our metal-free hydrogen and helium chemical networks are shown in Figure 1. The reactions and rate coefficients are listed in Tables 1 and 2. We solve for the steady-state abundances of H, H₂, H⁺, H²⁺, H₃⁺, He, He⁺, HeH⁺, and electrons. No heavy elements are included. The species abundances vary with cloud depth as the photodissociating FUV radiation is absorbed by the H₂ and as cosmic-ray energy losses reduce the ionization rates.

![Figure 1. Schematic of the metal-free two-body reaction gas-phase hydrogen–helium network. The dashed arrow indicates grain-surface formation of H₂ that we are explicitly excluding.](image)

2.1.1. Hydrogen Network

Molecular hydrogen is formed mainly via the well-known two-step catalytic sequence, starting with (slow) radiative attachment,

\[ H + e \rightarrow H^- + \nu \]  \hspace{1cm} (R1)

followed by (rapid) associative detachment

\[ H^- + H \rightarrow H_2 + e. \]  \hspace{1cm} (R2)

In regions with large fractional ionizations and/or low gas densities this sequence may be moderated by mutual neutralization

\[ H^- + H^+ \rightarrow H + H, \]  \hspace{1cm} (R3)

and photodetachment

\[ H^- + \nu \rightarrow H + e. \]  \hspace{1cm} (R4)

Photodetachment is by radiation shortward of the 1.6 \( \mu m \) (E > 0.75 eV) infrared threshold. For the high-gas-density parameter space we consider in this paper, [R3] and [R4] are slow in comparison to [R2] and do not reduce the molecular formation efficiencies. An additional H₂ formation route is radiative association

\[ H + H^+ \rightarrow H_2^+ + \nu \]  \hspace{1cm} (R5)

followed by charge transfer

\[ H_2^+ + H \rightarrow H_2 + H^+. \]  \hspace{1cm} (R6)

This channel is generally a minor contributor.

The H₂ formation sequence, [R1] and [R2], requires electrons and these are produced by an ionization source that we assume are nonthermal cosmic-ray particles,

\[ H + cr \rightarrow H^+ + e \]  \hspace{1cm} (R7)

and

\[ H_2 + cr \rightarrow H_2^+ + e. \]  \hspace{1cm} (R8)
Table 1
Rate Coefficients

| Reaction | Rate Coefficient (cm$^3$ s$^{-1}$) | Index | Reference |
|----------|----------------------------------|-------|-----------|
| H$^-$ + e $\rightarrow$ H$^+$ + $\nu$ | $1.67 \times 10^{-10}T_2^{0.64}e^{-0.052/T_2}$ | R1    | M13, Stancil & Dalgaro (1998) |
| H$^+$ + H $\rightarrow$ H$_2$ + e | $6.63 \times 10^{-9}T_2^{0.39}e^{-0.394/T_2}$ | R2    | M13, Bruns et al. (2010) |
| H$^+$ + H$^+$ $\rightarrow$ H + H$^+$ | $3.30 \times 10^{-7}T_2^{-0.50}$ | R3    | M13, Harada & Herbst (2008) |
| H$^+$ + H$_2$ $\rightarrow$ H$_2^+$ + $\nu$ | $2.31 \times 10^{-15}T_2^{0.50}$ | R4    | N20, Ramaker & Peek 1976 |
| H + H$_2$ $\rightarrow$ H$_2^+$ + H$^+$ | $6.40 \times 10^{-10}$ | R5    | M13, Karpas et al. (1979) |
| H$^+$ + e $\rightarrow$ H$^+$ + $\nu$ | $7.98 \times 10^{-12}T_2^{-0.75}$ | R6    | M13, Prasad & Huntress (1980) |
| H$_2^+$ + H$^+$ $\rightarrow$ H$_3$ + H$^+$ | $2.08 \times 10^{-9}$ | R7    | M13, Theard & Huntress (1974) |
| H$_2$ + e $\rightarrow$ H + H$^+$ | $1.59 \times 10^{-5}$ | R8    | N20, Schneider et al. (1994) |
| H$_2$ + H $\rightarrow$ H$_2^+$ + e | $9.12 \times 10^{-10}T_2^{-0.25}$ | R9    | M13, McCall et al. (2004) |
| H + He$^+$ $\rightarrow$ He + H$^+$ | $7.20 \times 10^{-15}$ | R10   | M13, McCall et al. (2004) |
| H$_2$ + He$^+$ $\rightarrow$ He + H$_2^+$ | $3.70 \times 10^{-14}e^{0.35/T_2}$ | R11   | M13, Barlow (1984) |
| He$^+$ + e $\rightarrow$ He + $\nu$ | $9.28 \times 10^{-12}T_2^{-0.50}$ | R12   | M13, Barlow (1984) |
| H + He$^+$ $\rightarrow$ HeH$^+$ + $\nu$ | $1.44 \times 10^{-6}$ | R13   | M13, Ercolan et al. (2006) |
| H$^+$ + He$^+$ $\rightarrow$ HeH$^+$ + $\nu$ | $1.77 \times 10^{-12}T_2^{-0.25}$ | R14   | N20, based on Vranckx et al. (2013) |
| H + HeH$^+$ $\rightarrow$ He + H$_2^+$ | $1.70 \times 10^{-9}$ | R15   | N20, Južek et al. (1995) |
| H$_2$ + HeH$^+$ $\rightarrow$ He + H$_2^+$ | $1.50 \times 10^{-9}$ | R16   | N20, Esposito et al. (2015) |
| HeH$^+$ + e $\rightarrow$ He + H$^+$ | $4.31 \times 10^{-9}T_2^{0.50}$ | R17   | M13, Bohme et al. (1980); Herbst et al. (1975) |

Note. Rate coefficients for the two-body reactions in our network, operating in the low-temperature ($T \leq 10^3$ K) regime. Here, $T_2 = T/(100$ K). The rate coefficients are from the UMIST2012 compilation (M13; McElroy et al., 2013) or the more recent (N20; Neufeld et al. 2020) compilation mainly for helium chemistry. We list the primary references as given by M13 and N20.

Table 2
Cosmic-Ray Rates

| Reaction | Relative Rate | Index |
|----------|---------------|-------|
| H + cr $\rightarrow$ H$^+$ + e | 0.46 | R7 |
| H$_2$ + cr $\rightarrow$ H$_2^+$ + e | 0.96 | R8 |
| H$_2$ + cr $\rightarrow$ H + H$^+$ | 0.7 | R11 |
| H$_2$ + cr $\rightarrow$ H + H$^+$ + e | 0.04 | R12 |
| He + cr $\rightarrow$ He$^+$ + e | 0.5 | R13 |

Note. Cosmic-ray reaction rates relative to the total H$_2$ cosmic-ray ionization rate ([R8] + [R16]).

Cosmic-ray ionization is also the main source of protons. The protons are removed by slow radiative recombination

$$H^+ + e \rightarrow H + \nu. \quad (R9)$$

The H$_2^+$ ions undergo rapid abstraction

$$H_2^+ + H \rightarrow H_3 + H. \quad (R10)$$

These reactions, together with charge transfer [R6], are the primary removal channels for the H$_2^+$ ions. Dissociative recombination

$$H_2^+ + e \rightarrow H + H, \quad (R11)$$

is a minor removal process unless the fractional ionizations become large. The H$_2^+$ may also be removed by far-UV photons

$$H_2^+ + \nu \rightarrow H + H^+, \quad (R12)$$

but this is a minor removal channel in our parameter space.

The saturated H$_3^+$ ions produced by [R10] recombine quickly with electrons

$$H_3^+ + e \rightarrow H + H + H \quad (R13)$$

and

$$H_3^+ + e \rightarrow H_2 + H \quad (R14)$$

leading back to H or H$_2$.

Cosmic-ray ionization [R8], and cosmic-ray dissociation

$$H_2 + cr \rightarrow H + H \quad (R15)$$

are the main H$_2$ removal mechanisms at cloud depths that are fully shielded from photodissociating far-UV radiation. Dissociative ionization

$$H_2 + cr \rightarrow H + H^+ + e \quad (R16)$$

is an additional (minor) removal channel. As we discuss further in our analysis below (Section 3), when the ionization, [R8], is followed by an abstraction, [R10], an additional H$_2$ molecule is removed for every H$_3^+$ ion that dissociatively recombines into three atoms, [R13].

A primary H$_2$ destruction process is photodissociation by 912-1108 Å Lyman–Werner (LW) photons

$$H_2 + \nu_{LW} \rightarrow H + H, \quad (R17)$$

in the $B^3\Sigma_u^+ - X^2\Sigma_g^+$ and $C^2\Pi_u - X^2\Sigma_g^+$ absorption-line systems. Photodissociation is generally the dominant H$_2$ removal mechanism unless self-shielding is very significant, as we discuss in Sections 3 and 4. (We are neglecting dust absorption.) We assume that any hydrogen-ionizing ultraviolet (EUV) radiation is absorbed outside the predominantly neutral atomic/molecular medium we are studying. Furthermore, we do not consider penetrating X-rays here. Local X-ray ionization is similar in its effects to cosmic-ray ionization. For simplicity of following the ionization driven chemistry, we assume that the ionization is provided by just cosmic-ray impacts throughout.
In sufficiently dense gas, \( \text{H}_2 \) is also produced by the three-body reaction
\[
\text{H} + \text{H} + \text{H} \rightarrow \text{H}_2 + \text{H}.
\] (R18)

However, this requires very dense gas \( \gtrsim 10^8 \text{ cm}^{-3} \), as may occur in collapsing clouds (Palla et al. 1983; Abel et al. 2002; Turk et al. 2012) and we do not consider this regime here. \( \text{H}_2 \) is also removed by collisional dissociation
\[
\text{H} + \text{H}_2 \rightarrow \text{H} + \text{H} + \text{H},
\] (R19)

however, this requires warm gas, with \( T \gtrsim 1000 \text{ K} \) (Martin et al. 1996), which is also outside our modeling regime that we are restricting to cool/cold gas.

2.1.2. Helium Network

For completeness we include the metal-free helium chemistry. Helium atoms are ionized by cosmic-ray impact
\[
\text{He} + \text{cr} \rightarrow \text{He}^+ + e,
\] (R20)

and neutralization is by rapid charge transfer and dissociative-charge transfer
\[
\begin{align*}
\text{He}^+ + \text{H} &\rightarrow \text{He}^+ + \text{H}^+ \quad (R21) \\
\text{He}^+ + \text{H}_2 &\rightarrow \text{He}^+ + \text{H}_2^+ \quad (R22) \\
\text{He}^+ + \text{H}_2 &\rightarrow \text{He}^+ + \text{H} + \text{H}^+. \quad (R23)
\end{align*}
\]

Radiative recombination
\[
\text{He}^+ + e \rightarrow \text{He} + \nu
\] (R24)
is an additional minor removal channel.

In cold, predominantly neutral gas, the molecular ion \( \text{HeH}^+ \) is produced by the radiative associations
\[
\begin{align*}
\text{H} + \text{He}^+ &\rightarrow \text{HeH}^+ + \nu \quad (R25) \\
\text{H}^+ + \text{He} &\rightarrow \text{HeH}^+ + \nu, \quad (R26)
\end{align*}
\]

and is removed by
\[
\begin{align*}
\text{HeH}^+ + \text{H} &\rightarrow \text{He} + \text{H}_2^+ \quad (R27) \\
\text{HeH}^+ + \text{H}_2 &\rightarrow \text{He} + \text{H}_2^+. \quad (R28)
\end{align*}
\]

In our models, dissociative recombination
\[
\text{HeH}^+ + e \rightarrow \text{He} + \text{H}
\] (R29)
is a very minor removal channel because the electron fractions remain low. Photodissociation
\[
\text{HeH}^+ + \nu \rightarrow \text{He} + \text{H}^+
\] (R30)
is also a minor removal channel in our parameter space.

Reactions [R25] and [R26],5 followed by [R27] and [R6] as well as [R5] followed by [R6], were primary sources of \( \text{H}_2 \) following cosmic recombination and prior to the introduction of the first reionization sources. At redshifts \( z \gtrsim 100 \) and at the prevailing mean gas densities, any \( \text{H}^+ \) produced via relic electron ions were rapidly photodetached by thermal background photons (Lepp et al. 2002; Galli & Palla 2013). In the

\[5\] Reaction [R25] dominates the formation of \( \text{HeH}^+ \) in the partially ionized interface zones in planetary nebulae where removal by [R29] is important in addition to [R27]. Interstellar \( \text{HeH}^+ \) was recently observed for the first time in the planetary nebula NGC7027 (Güsten et al. 2019; Neufeld et al. 2020). In such nebulae, associative ionization \( \text{H} + \text{He}(2\text{S}) \rightarrow \text{HeH}^+ + e \) involving the metastable helium produced via recombination is also an important source of \( \text{HeH}^+ \) (Roberge & Dalgarno 1982; Neufeld et al. 2020).

computations we consider here, we assume efficient formation of \( \text{H}^- \) via free electrons produced by local sources of ionizing cosmic rays, and the \( \text{H}_2 \) is formed mainly by [R1] and [R2]. The main parameters controlling the chemistry are the Lyman–Werner radiation intensity and associated photodissociation rate, the cosmic-ray ionization rate, the gas density, and the cloud temperature. We assume that photodetachment is by the same radiation source that also photodissociates the \( \text{H}_2 \). For our parameter space, and relatively dense gas conditions, photodetachment is therefore negligible, and our results are insensitive to the IR-to-UV spectral shapes as we discuss below.

2.2. FUV Radiation

In our study, we compute depth-dependent \( \text{H}1 \) and \( \text{H}_2 \) density profiles for dust-free clouds exposed to fluxes of far-UV photons and cosmic-ray particles. We determine conditions for which a \( \text{H}1 \)-to-\( \text{H}_2 \) transition occurs assuming steady-state conditions.

2.2.1. Radiation Spectra

We parameterize the far-UV radiation flux, in particular the dissociating Lyman–Werner band flux, relative to the standard Draine (1978) Galactic FUV interstellar field strength (Parra-vano et al. 2003; Bialy 2020).

For the Draine far-UV spectrum, the flux in the (narrow) 912–1108 Å LW band is \( f_{\text{LW}} = 2.07 \times 10^7 \text{ photons cm}^{-2} \text{ s}^{-1} \text{ fl}_{\text{LW}} \). \( f_{\text{LW}} \) is the radiation field strength relative to the free-space unattenuated Draine field in the LW band, for which \( \text{fl}_{\text{LW}} = 1 \).

The unattenuated \( \text{H}_2 \) photodissociation rate due to absorptions in all of the LW lines is \( D_0 = \sigma_D f_{\text{LW}} = 5.8 \times 10^{-11} \text{ s}^{-1} \text{ fl}_{\text{LW}} \).

Here \( f_{\text{LW}} \) is the mean flux density (photons cm\(^{-2}\) s\(^{-1}\) Hz\(^{-1}\)) in the LW band, and \( \sigma_D = 2.36 \times 10^{-3} \text{ cm}^2 \text{ Hz} \) is the total \( \text{H}_2 \)-line photodissociation cross section, summed over all the LW absorption lines (see S14). For the Draine spectrum, the \( \text{H}^- \) photodetachment rate is \( D_{\text{H}^-} = 5.6 \times 10^{-7} f_{\text{LW}} \text{ s}^{-1} \), and \( D_{\text{H}^-}/D_0 = 96.6 \). We computed the photodetachment rate using the Miyake et al. (2010) cross section (see their Figure 1) and integrating from the infrared threshold (1.6 \( \mu \)m) to the Lyman limit (912 Å).

More generally, the ratio \( D_{\text{H}^-}/D_0 \) depends on the shape of the radiation spectrum from the near-IR to the UV (Wolcott-Green et al. 2017). In Figure 2 we plot four radiation spectra, for pure Draine, combination Draine+MathisIR (Mathis et al. 1983), and \( 10^4 \) and \( 10^5 \) K blackbody fields.7 We normalize the spectra in Figure 2 such that they all have the same flux of \( 2.07 \times 10^7 \) photons cm\(^{-2}\) s\(^{-1}\) in the LW band, appropriate for \( \text{fl}_{\text{LW}} = 1 \). In Table 3 we list \( f_{\text{LW}} \) for these fields, defined as the flux densities at the Lyman limit in units of \( 10^{-21} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ Hz}^{-1} \text{ sr}^{-1} \).

Because the LW band is narrow, we make the simplifying approximation that for equal LW fluxes, the unattenuated \( \text{H}_2 \) dissociation rate is independent of the spectral shape and equal to \( D_0 = 5.8 \times 10^{-11} f_{\text{LW}} \text{ s}^{-1} \). However, the \( \text{H}^- \) photodetachment rate is very sensitive to the spectral shape. In Table 3 we list \( D_{\text{H}^-} \) and \( D_{\text{H}^-}/D_0 \) for the four radiation fields. In Figure 3 we

\[6\] In S14 we refer to the intensity parameter as \( I_{\text{UV}} \) and normalize to the entire 6–13.6 eV FUV band. Here we use the subscript “LW” to emphasize normalization relative to just the Lyman–Werner band.

\[7\] Mathis et al. (1983) represented their inferred IR Galactic stellar spectrum as a sum of diluted blackbodies at 3000, 4000, and 7500K, representing the late-type stars. The Draine (1978) field is due primarily to the early OB-type stars.
plot these quantities as functions of the radiation temperature, $T_{\text{rad}}$, for pure blackbody fields, all normalized such that $I_{LW} = 1$ at any $T_{\text{rad}}$. Figure 3 shows that $D_{-}/D_0$ grows rapidly for $T_{\text{rad}}$ below $\sim 2 \times 10^4$ K. In the computations in this paper we assume $10^5$ K spectra, appropriate for massive Population III stars, for which $D_{-} = 2.7 \times 10^{-9} I_{LW}$ s$^{-1}$, and $D_{-}/D_0 = 46.5$. However, even for this large ratio, photodetachment does not play a role in our model parameter space, as we discuss further below.

For reference, in Figure 2, we also plot the expected cosmological metagalactic radiation spectra (unnormalized) computed by Haardt & Madau (2012) at redshifts $z = 0.05, 1.05$, and 5.18. In Table 4 we list $J_{21}$, $I_{LW}$, $D_{-}$, and $D_{-}/D_0$, for these three cosmological radiation fields.

### 2.2.2. Shielding

We are considering dust-free gas for which any attenuation of the $\text{H}_2$ photodissociation rate is due entirely to self-shielding optical depth in the $\text{H}_2$ absorption lines. In the dust-free regime, the photodissociation rate at any depth into a semi-infinite plane-parallel slab is

\[
D(N) = \frac{1}{2} D_0 f_{\text{shield}} (N_{\text{H}_2}).
\]

Here, $N = N_{\text{H}_1} + 2 N_{\text{H}_2}$ is the total column density of hydrogen nuclei, atomic ($\text{H}_1$) plus molecular ($\text{H}_2$), from the surface to a depth, $z$ (cm), in the cloud. The factor of 1/2 accounts for reduction of the rate relative to free space by the cloud itself, with radiation incident from one hemisphere only and opaque to any radiation from the other side. This is the “semi-infinite”

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**Table 3**

| Stellar-based | $J_{21}$ | $D_{-}$ (s$^{-1}$) | $D_{-}/D_0$ | $(I_{LW}/n_0)_{\text{crit}}$ |
|---------------|---------|----------------|-------------|-------------------|
| Draine        | 13.5    | $5.58 \times 10^{-9}$ | 96.6        | $7.28 \times 10^3$ |
| Draine+Mathis | 13.5    | $2.73 \times 10^{-7}$ | 4.66        | $6.88 \times 10^3$ |
| $10^4$ K      | 14.6    | $1.77 \times 10^{-7}$ | 3.05        | $1.14 \times 10^4$ |
| $10^5$ K      | 61.8    | $2.77 \times 10^{-9}$ | 47.8        | $1.56 \times 10^6$ |

**Notes.**

$^a$ The radiation flux densities at the Lyman limit, in units of $10^{-21}$ ergs s$^{-1}$ cm$^{-2}$ Hz$^{-1}$ sr$^{-1}$, assuming each field is normalized to $I_{LW} = 1$.

$^b$ The $\text{H}^-$ photodetachment rates for the normalized fields.

$^c$ The ratio $D_{-}/D_0$ of the $\text{H}^-$ photodetachment rate and $\text{H}_2$ photodissociation rate.

$^d$ The critical ratios $(I_{LW}/n_0)_{\text{crit}}$ above which photodetachment reduces the $\text{H}^-$ abundance (see text).
Line overlap occurs when the dust abundance and associated continuum becomes small, decreasing to
where

\[ f_{\text{crit}} \] below which photodetachment reduces the \( H_2 \) abundance (see text).

\[ n_{\text{phot}} \] density relative to the mean cosmic baryon density \( n_b \) = 2.48 \times 10^{-7} (1 + z) \text{ cm}^{-3}.

The dissociation bandwidth in Equation (2) is given by the fit formula\(^{10}\) (Bialy & Sternberg 2016),

\[ W_d (N_{H_2}) = a_1 \ln \left[ \frac{a_2 + y}{1 + y/a_3} \right] \left( \frac{1 + y/a_3}{1 + y/a_4} \right)^{0.4}, \tag{4} \]

where

\[ y \equiv \frac{N_{H_2}}{10^{14} \text{ cm}^{-2}} \]
\[ a_1 = 3.6 \times 10^{11} \text{ Hz} \]
\[ a_2 = 0.62 \]
\[ a_3 = 2.6 \times 10^{13} \]
\[ a_4 = 1.4 \times 10^{7}. \]

Equation (4) is valid for \( y \geq 1 \). For complete line absorption of the dissociating radiation in the \( L \) band, \( W_{d,\text{tot}} = 8.8 \times 10^{13} \) Hz and the total dissociation flux absorbed in an optically thick cloud is \( \bar{F}_d W_{d,\text{tot}} = 2.2 \times 10^{16} \text{ LW photons cm}^{-2} \text{ s}^{-1} \). This is 10% of the total \( L \) flux and is reradiated as dissociation continuum. The remaining energy is reradiated as Lyman–Werner band emission lines (Sternberg 1989) terminating in mainly excited vibrational levels of the ground electronic state.

### 2.3. Cosmic Rays

Low-level ionization in the shielded ISM of galaxies is generally maintained by low-energy cosmic rays (Spitzer & Tomasko 1968; Dalgarno 2006). In localized environments, photionization by penetrating X-rays may also contribute in addition to the cosmic-ray impacts. Within molecular clouds, cosmic-ray ionization drives a rich ion–molecule chemistry and controls the dynamical coupling of magnetic fields to the gas. In the Milky Way, the characteristic \( H_2 \) cosmic-ray ionization rate is \( \sim 10^{-16} \text{ s}^{-1} \), although the rates may vary with location in the Galaxy and with cloud depth (Padovani et al. 2009; Neufeld & Wolfire 2017). The cosmic-ray fluxes and ionization rates may be substantially larger in galaxies with elevated star formation activity and FUV fields (Mashian et al. 2013; Bialy & Sternberg 2015; Bisbas et al. 2017; Bialy 2020).

Our parameter \( \zeta \) is the total cosmic-ray \( H_2 \) ionization rate (s\(^{-1}\)) due to nondissociative (IR8) plus dissociative (IR15) ionizations. We define the normalized rate \( \zeta_{\text{IR}} = \zeta / (10^{-16} \text{ s}^{-1})\). The relative rates of all of the cosmic-
ray ionization and dissociation processes in our network are listed in Table 2. An important parameter for the chemistry is the number of H2 dissociations per CR ionization, including the effects of the secondary electrons for both processes (Cravens & Dalgarno 1978; Li & Goldsmith 2003; Goldsmith & Li 2005). Following Padovani et al. (2018a) we assume 0.7 dissociations per ionization. This is the asymptotic ratio for large penetration depths.

The penetration and transport of cosmic rays and the possible attenuation of the associated ionization rates with cloud depth depend on a wide range of (uncertain) properties including the spectrum of the low-energy particles, the distributions and orientations of the magnetic fields, the particle gyroradii, free-streaming ionization energy losses, particle production, and the characteristics of MHD turbulent diffusion (Ivlev et al. 2018; Padovani et al. 2020).

We therefore construct two families of models for (a) constant ionization rates through the clouds, and (b) attenuation of the ionization rates assuming a power-law form for the energy losses. For model family (b), we adopt the Padovani et al. (2018b) results for the particle energy losses and transport for the “Voyager-1-based” cosmic-ray input spectrum (Cummings et al. 2016). The Padovani et al. (2018b) CR ionization rates, for low- and high-ionization cosmic-ray spectra (their models L and H) may be expressed as simple power laws

\[ \zeta = \zeta_0 \times \left( \frac{N_{\text{eff}}}{10^{19} \text{ cm}^{-2}} \right)^{-q}, \]  

where \( N_{\text{eff}} \) is the effective cosmic-ray-absorbing gas column. The effective column depends on the orientation angle \( \theta \) of the magnetic field along which the cosmic-ray protons propagate relative to the cloud normal so that \( N_{\text{eff}} = N / \mu \), where \( \mu \equiv \cos \theta \). Equation (5) is valid for \( N_{\text{eff}} \) between \( 10^{19} \) and \( 10^{24} \text{ cm}^{-2} \), the relevant range for our considerations. We find that \( q = 0.280 \) and \( q = 0.385 \) for the Padovani models L and H, respectively, with an accuracy of 37% and 6%. For \( N_{\text{eff}} < 10^{19} \text{ cm}^{-2} \) we assume \( \zeta = \zeta_0 \).

3. Analysis

In Section 4 we present our numerical solutions to the chemical rate equations and resulting H1/H2 density profiles, including computations of the atomic-to-molecular transition points, for the dust-free conditions we are considering. Before presenting our numerical calculations we first provide an analytic description as a guide.

3.1. H1/H2 Balance

In a steady state, we write the H2 formation–destruction equation as

\[ R \cdot n \chi_{11} = \left\{ \frac{1}{2} D_0 f_{\text{shield}}(N_{\text{H2}}) + [0.96 f_3 (1 + f_3) \right. \]

\[ + 0.7 + 0.04] \chi \frac{1}{n}\]

\[ \left( \int_{\text{H}} \right) \]  

In this expression, \( x_{11} \equiv n_{11} / n \) and \( x_{16} \equiv n_{16} / n \) are the depth-dependent atomic (H) and molecular (H2) abundance fractions, and \( n = n_{11} + 2n_{16} \) is the total hydrogen volume density. We are assuming that the additional constituents all have very low abundances compared to H1 or H2. On the left-hand side, \( R \) is the effective rate coefficient for H2 formation via the H− sequence, [R1] and [R2] (Bialy & Sternberg 2019). The first term on the right-hand side is the depth-dependent photodissociation rate in the photodissociation region (PDR). It vanishes in the inner cosmic-ray zone (CRZ) where cosmic-ray ionization and dissociation become the main H2 removal mechanisms. These are included in the second term in brackets multiplied by \( \zeta \). The numerical factors are the relative rates for [R8], [R14], and [R15], respectively (see Table 2).

In Equation (6), the factor 0.96\( \zeta \) for cosmic-ray ionization is multiplied by the branching ratio

\[ f_d = \frac{k_{10} \chi_{11}}{k_{10} \chi_{16} + k_{6} \chi_{11}}. \]  

This is the probability that the production of H2+ via ionization is followed by the abstraction reaction [R10] to H2 rather than charge transfer [R6] back to H2 (see Eq (15) in Bialy & Sternberg 2015). Dissociative recombination of H2+ [R11] may be ignored because the fractional ionizations are small. The additional factor

\[ 1 + f_3 = 1 + \frac{k_{13}}{k_{13} + k_{4}}, \]  

where \( f_3 = 0.65 \) is the branching ratio for dissociative recombination fragmentation of H2+ into three atoms, [R13], rather than back to H2, [R14] (see Figure 1). The product, \( (1 + f_3) f_d \) is then the net number of H2 molecules removed per ionization event [R8]. This number is depth-dependent because \( f_d \) depends on the atomic and molecular factions, \( x_{11} \) and \( x_{16} \). Thus, for \( x_{11} \approx 1 \), e.g., in photodissociated gas, \( f_d = 0 \) and cosmic-ray ionization [R8] is ineffective in further reducing the small molecular fraction. For \( x_{16} \approx 0.5 \), the branching ratio \( f_d = 1 \), and 1.65 hydrogen molecules are removed per cosmic-ray ionization event. Cosmic-ray dissociation [R15] remains operative throughout. It is important in the CRZ, but is a minor H2 removal process in the PDR.

Following Bialy & Sternberg (2019) we write

\[ R_- = \eta k_1 x_e \]  

where \( x_e \equiv n_e / n \) is the electron fraction and \( k_1 \) is the rate coefficient of the radiative attachment reaction [R1]. The branching ratio

\[ \eta = \frac{k_2 x_{11}}{k_2 x_{11} + k_3 x_{11} + D_- / n} \]  

is the fraction of radiative attachments that are followed by associative detachment [R2] rather than mutual neutralization [R3] or photodetachment [R4]. For \( \eta = 1 \), all radiative attachments result in H2 formation.

Throughout the PDR and into the CRZ, including where the gas is molecular, the electron and proton fractions are equal, i.e., the positive charge is carried mainly by protons. This is because the positive molecular ions produced by CR ionization of H2 [R8] are rapidly removed by abstraction [R10], followed by rapid dissociative recombination [R13], and [R14]. The fraction of H2 ionizations leading to H+ [R15] is small and CR ionization of atomic hydrogen [R7] is the dominant source of electrons throughout. With the further assumption that the gas is neutral, i.e. \( x_e \ll 1 \), and with the neglect of helium
ionization), we have that
\[
x_e = \left( \frac{0.46\zeta}{n\Omega_B} \chi_{H_1} \right)^{1/2} = 2.4 \times 10^{-6} \left( \frac{\zeta_{16}}{n_6} \right)^{1/2} T_{2}^{1/8} \chi_{H_1}^{1/2},
\]  
(11)

where \(\alpha_B\) is the electron–proton recombination rate coefficient, \(n_6 = n/(10^6 \text{cm}^3)\), and \(T_2 = T/100\text{K}\). In this approximation, \(x_{H_1} = x_e\).

The branching ratio \(\eta\) becomes small (\(< 0.5\)) if the proton fraction \(x_{H_1} \geq (k_2/k_1)x_{H_1}\), or if \(D_\ast \geq k_2x_{H_1}\). For atomic gas (\(x_{H_1} = 1\)), \(\eta < 0.5\) for \(x_{H_1} > 0.3\). This requires \(\zeta_{16}/n_6 > 2.21 \times 10^8\) as given by Equation (11) (for \(T = 100\text{K}\)). For the \(T = 10^9\text{K}\) spectrum we assume in our computations, \(\eta < 0.5\) and photodetachment becomes important for \(I_{L,W}/n_6 > (I_{L,W}/n_6)_{\text{crit}} = 1.6 \times 10^6\). In Table 3 we list the critical UV intensity-to-density ratios, \((I_{L,W}/n_6)_{\text{crit}}\), at which \(\eta = 0.5\) for the different spectral shapes.

For comparison, in Table 4 we give the critical densities, \(n_{6,crit}\) below which \(H^+\) photodetachment becomes important for the (unnormalized) metagalactic fields at various redshifts. We also list these densities relative to the cosmic mean baryon densities \(n_0\) at the different epochs. Relative to the cosmic mean densities, photodetachment by the evolving metagalactic field is more effective at lower redshift.

For the parameter space we are considering, it is safe to assume \(\eta = 1\), and we then have
\[
R_- = 4 \times 10^{-22} \left( \frac{\zeta_{16}}{n_6} \right)^{1/2} T_{2}^{1/2} e^{-0.09/T} \chi_{H_1}^{1/2} \text{ cm}^3 \text{s}^{-1}. 
\]  
(12)

Equation (11) is valid for \(\zeta_{16}/n_6\) up to \(\sim 1.7 \times 10^8\) for which \(x_e \lesssim 0.1\) (for \(x_{H_1} = 1\)). For this maximal ionization fraction (with the gas still mainly neutral) \(R_- \sim 1.6 \times 10^{-17} \text{ cm}^3 \text{s}^{-1}\) at 100 K. Remarkably, this is comparable to the characteristic \(R_{\text{dust}} = 3 \times 10^{-17} \text{ cm}^3 \text{s}^{-1}\) for grain-surface catalysis of \(H_2\) for typical Galactic dust-to-gas ratios, \(Z' = 1\). However, for \(\zeta_{16} = 1\) this requires extremely low density, \(n_6 \sim 6 \times 10^{-10}\) \((n = 6 \times 10^{-4} \text{cm}^{-3})\). In general, \(R_- \ll R_{\text{dust}}\) for typical ISM conditions. For \(\zeta_{16} = n_6 = 1\), \(R_- = 3.65 \times 10^{-22} \text{ cm}^3 \text{s}^{-1}\) at 100 K (for \(x_{H_1} = 1\)), and gas-phase formation becomes important for very small dust-to-gas ratios \(Z' \lesssim 3 \times 10^{-3}(\zeta_{16}/n_6)^{1/2}\). However, such low dust-to-gas ratios may not require correspondingly small metallicities because the dust abundances may decline sharply and nonlinearly. For example, given the Rémy-Ruyer et al. (2013) broken power-law representation for the gas-to-dust ratio, \(Z'\), versus overall metallicity, \(Z\), into the low-metallicity regime (see also Bialy & Sternberg 2019; Li et al. 2019) gas-phase \(H_2\) formation dominates for \(Z \lesssim 0.01(\zeta_{16}/n_6)^{1/2}\) at 100 K. Furthermore, \(R_-\) increases with temperature, whereas \(R_{\text{dust}}\) probably declines (Cuppen et al. 2010), so the relative efficiencies of the gas-phase processes may grow in warmer gas (Glover 2003).

In dusty clouds, electrons are provided by the photoionization of heavy elements and dust neutralization processes may reduce the ionization fractions. As we discuss in Appendix A, heavy-element ionization is negligible for \(Z' \lesssim 0.01(\zeta_{16}/n_6)^{1/2}\) and dust-grain neutralization is unimportant for \(Z' \lesssim 10^{-5}\). Coincidentally, this is the gas-to-dust ratio for which \(H_2\) formation on dust may be ignored as well.

Because \(R_-\) is proportional to \((\zeta/n)^{1/2}\), whereas destruction is proportional to \((\zeta/n)^{-1}\), the molecular fraction decreases with \(\zeta/n\) in the CRZ as we discuss further below. For any \(\zeta\), the effective rate coefficient \(R_- \sim n^{-1/2}\), due to the lower electron fractions at larger densities. The rate of gas-phase \(H_2\) formation, \(R_- \sim n^{-1/2}\), is therefore proportional to \(n^{1/2}\).

Equation (11) may also be used to estimate the \(H^+\) abundance. Assuming formation via \(R[11]\) and removal by just \(R[2]\), we obtain the upper limit
\[
x_{H_1} \gtrsim \frac{k_1}{k_2} x_e \approx 6.04 \times 10^{-14} T_{2}^{1.41} e^{0.3/T} \left( \frac{\zeta_{16}}{n_6} \right)^{1/2} \chi_{H_1}^{1/2}. 
\]  
(13)

Although the \(H^-\) anions are critical intermediaries for \(H_2\) formation, their abundance remains extremely small for steady-state conditions.

### 3.2. PDR

In the PDR, Equation (6) may be written as
\[
x_{H_1} = \frac{1}{2} \alpha_{\text{shield}} (N_{H_2}) x_{H_2}
\]  
(14)

where
\[
\alpha = \frac{D_0}{R_-} = \frac{\sigma_d F_{\nu,L,W}}{R_-} = 1.45 \times 10^6 \left( \frac{I_{L,W}}{n_6} \right) \left( \frac{\zeta_{16}}{n_6} \right)^{-1/2} T_2^{-1.02} \chi_{H_1}^{-1/2}
\]  
(15)

The unattenuated photodissociation rate, \(D_0\), depends on the far-UV field strength, \(I_{L,W}\), so the dimensionless parameter \(\alpha\) is a function of the two ratios \(I_{L,W}/n\) and \(\zeta/n\) (via \(R_-\)). In general, the gas is atomic (\(x_{H_1} = 1\)) at the unshielded cloud boundary and the \(H_2\) fraction is
\[
x_{H_2} = \frac{2}{\alpha} = 1.38 \times 10^{-5} \left( \frac{I_{L,W}}{n_6} \right)^{-1} \left( \frac{\zeta_{16}}{n_6} \right)^{1/2}
\]  
(16)

For fiducial parameters, \(I_{L,W} = \zeta_{16} = n_6 = 1\), the molecular fraction \(x_{H_2} = 1.38 \times 10^{-5}\) at the cloud boundary and a molecular self-shielding column of \(\gtrsim 10^{21} \text{cm}^{-2}\) for which \(f_{\text{shield}} \lesssim 10^{-5}\) is required to enable an \(H^+\)-to-\(H_2\) transition.

Equation (14) may be written as the differential equation
\[
dN_{H_1} = \frac{1}{2} \alpha f_{\text{shield}} (N_{H_2}) dN_{H_2}
\]  
(17)

for the \(H_1\) column as a function of the \(H_2\) column. For a constant \(\alpha\), independent of cloud depth, integrating gives
\[
N_{H_1}(N_{H_2}) = \frac{\alpha}{2} \int_0^{N_{H_2}} f_{\text{shield}} (N_{H_2}) dN_{H_2} = \alpha W_{d}(N_{H_2}) \sigma_d
\]  
(18)

where \(\sigma_d\) is the line-dissociation cross section (\text{cm}^2 \text{Hz}) and \(W_d(N_{H_2})\) is the dissociation bandwidth as given by Equation (4). In pulling \(\alpha\) out of the integral, we are assuming (a) constant gas density for the given \(I_{L,W}\) and \(\zeta_{16}\), (b) that \(x_{H^+_1} \approx 1\), i.e., the gas is largely atomic, where photodissociation dominates the production of the \(H_1\) column, and (c) no CR attenuation so...
that $\zeta_{-16}$ is constant. Equation (18) can also be written as

$$N_{H_1}(N_{H_2}) = \frac{1}{2} \frac{F_{L,W}W_d(N_{H_2})}{R_n}. \tag{19}$$

The numerator, $F_{L,W}W_d(N_{H_2})/2$, is the radiation flux absorbed in dissociations up to a molecular column $N_{H_2}$, and this is equal to the product $R_n N_{H_1}(N_{H_2})$, i.e., the rate at which molecules are produced within $N_{H_2}$.

For sufficiently large $N_{H_2}$ ($\gtrsim 10^{22}$ cm$^{-2}$) the H$_2$ absorption lines fully overlap and all of the LW-band photons are absorbed by the H$_2$. The total H$_1$ column maintained by photodissociation by LW-band photons is then

$$N_{H_1}^{LW}_{\text{tot}} = \frac{\alpha}{\sigma_d} \frac{W_d}{2} \left( \frac{I_{L,W}}{n_e} \right)^{-0.5} \text{ cm}^{-2}. \tag{20}$$

In the third equation, we have set $T_2 = 1$ and $x_{H_1} = 1$ in the expression for $R_n$ with the assumption that the photodissociated H$_1$ is built up in an extended fully atomic PDR and the transition from H$_1$ to H$_2$ is sharp. This assumption is valid if the transition occurs as the absorption lines overlap, in which case the dissociation rates are reduced exponentially, leading to sharp transitions. Setting $x_{H_1} = 1$ is more approximate when the transition points occur before the lines overlap in which case further LW absorptions out of the damping wings enable continued gradual growth of the photodissociated H$_1$ columns. Sharp transitions induced by line overlap occur when $N_{H_1}^{LW}_{\text{tot}} \gtrsim 10^{22}$ cm$^{-2}$.

We select fiducial parameters, $I_{L,W} = \zeta_{-16} = n_e = 1$ (or $I_{L,W}/n_e = \zeta_{-16}/n_e = 1$) such that the resulting H$_1$ photodissociation column, $N_{H_1}^{LW}_{\text{tot}} = 2.7 \times 10^{21}$ cm$^{-2}$, is comparable to the H$_2$ shielding column $\sim 10^{22}$ required for line overlap.

It is of interest to compare Equation 20 to the S14 formula for the total H$_1$ photodissociation column in dusty clouds where molecule formation is via grain catalysis and opacity is provided by FUV dust absorption in addition to H$_2$ self-shielding. The S14 formula (for beamed fields) is

$$N_{H_1}^{LW}_{\text{tot}} = \frac{1}{\sigma_g} \ln \left( \frac{1}{2} \frac{\sigma_g F_{L,W} W_{d,\text{tot}}}{R_{\text{dust}} n} + 1 \right), \tag{21}$$

where $\sigma_g$ is the dust absorption cross section, $R_{\text{dust}}$ is the grain-surface H$_2$ formation-rate coefficient, and $W_{d,\text{tot}}$ is the “H$_2$ dust-limited dissociation bandwidth” (see S14). For vanishing dust abundance, $\sigma_g \rightarrow 0$, $W_{d,\text{tot}} \rightarrow W_d$, and $R_{\text{dust}}$ may be replaced with the gas-phase coefficient $R_n$. Expanding the logarithm, $\sigma_g$ cancels out and this yields our Equation (20) for dust-free conditions. We further discuss Equation (20) versus (21) in Appendix B.

### 3.3. CRZ

The transition from the outer PDR to the inner CRZ occurs as self-shielding reduces the H$_2$ photodissociation rate below the CR destruction rate. In the CRZ, H$_2$ formation continues to be driven by CR ionization. Removal is by a combination of CR ionization and dissociation.

Moving from the PDR to CRZ may or may not give rise to an atomic-to-molecular transition, depending on $\zeta/n$, as follows. In the CRZ, Equation (6) may be written as

$$R_n x_{H_1} = [0.96 f_d (1 + f_3) + 0.74] \zeta x_{H_2}. \tag{22}$$

In analogy to Equation (14) for the PDR, this may be written as

$$x_{H_1} = \beta x_{H_2}. \tag{23}$$

where implicitly $\beta = [0.96 f_d (1 + f_3) + 0.74] \zeta / R_n$. Expanding the logarithm,

$$\zeta = \ln \left( \frac{1}{1 + k_{6,\text{H}_1}/k_{10,\text{H}_2}} \right) + 0.74 \left( \frac{x_{-16}}{n_6} \right)^{1/2} \times T_2^{1.02} e^{0.092/T_2} x_{\text{H}_1}^{1/2}. \tag{24}$$

Here we have used Equations (7), (9), and (11), with $\eta = 1$. It follows that the atomic and molecular mass fractions are equal, $(x_{H_1} = 2x_{H_2}$, or $\beta = 2$) for the critical ratio

$$\zeta_{-16} \left( n_6 \right)_{\text{crit}} \approx 10.88 \times T_2^{0.03} e^{-0.18/T_2} = 9.02, \tag{25}$$

Equation (22) is the algebraic equation

$$3.96 \left( \frac{x_{-16}}{n_6} \right)^{1/2} x_{H_1}^{1/2} T_2^{0.02} e^{-0.092/T_2} = \left[ \frac{0.96 (1 + f_3)}{1 + k_{6,\text{H}_1}/k_{10,\text{H}_2}} + 0.74 \right] \frac{x_{-16}}{n_6} x_{\text{H}_2}. \tag{26}$$

The left-hand side is the formation rate per unit volume and is proportional to $(\zeta/n)^{1/2}$. The right-hand side is the destruction rate per unit volume and is proportional to $\zeta/n$. For $\zeta/n$ less than the critical value given by Equation (25), the gas becomes molecular in the CRZ, and a H$_1$-to-H$_2$ transition then occurs in moving from the PDR to the CRZ. For larger $\zeta/n$, the gas remains atomic and a H$_1$-to-H$_2$ transition does not occur.

In Figure 4 we plot the atomic and molecular fractions as functions of $x_{-16}/n_6$ as given by the solution to Equation (26) (dashed curves) compared to the numerical solutions (solid curves) of the full rate equations within the CRZ. The agreement is excellent. The vertical dotted line indicates the critical ratio of 9.02 as given by Equation (25). This is close to our numerically computed value of 11.84 indicated by the vertical solid line.

#### 3.4. Analytic Profiles

Our procedure to generate analytic profiles is based on the formation–destruction equation

$$x_{H_1} = \left[ \frac{1}{2} \alpha_{\text{shield}} (N_{H_2}) + \beta \right] x_{H_2}, \tag{27}$$

and mass conservation

$$x_{H_1} + 2x_{H_2} = 1. \tag{28}$$

$^{11}$ This expression for the critical ionization-to-density ratio is more accurate than Equation (21) in Bialy & Sternberg (2015) for which $x_{H_1} = 2x_{H_2}$ at $\zeta_{-16}/n_6 = 11.4$. In that paper we made the approximations $f_d = 1$, and $1 + f_3 = 2$ and we set the cosmic-ray dissociation rate to $0.1 \zeta$ (as incorrectly listed in UMIST12) rather than to $0.7 \zeta$ as here.
With our expressions for \( \alpha \) and \( \beta \) (Equations (15) and (24)), the local abundances \( x_{\text{H}1} \) and \( x_{\text{H}2} \) may be computed as functions of the molecular column density \( N_{\text{H}2} \) for any given \( \zeta/n \) and \( I_{\text{LW}}/n \). The parameters \( \alpha \) and \( \beta \) themselves depend on \( x_{\text{H}1} \) and \( x_{\text{H}2} \). We integrate Equation (27) assuming that they are constant, writing them as \( \bar{\alpha} \) and \( \bar{\beta} \), independent of cloud depth, and assuming no CR attenuation. For \( \bar{\alpha} \), we set \( x_{\text{H}1} = 1 \) in Equation (15). For \( \bar{\beta} \), and for any \( \zeta/\bar{n}_6 \), we set \( f_d \) as given by Equation (7) for the constant (asymptotic) \( x_{\text{H}1}/x_{\text{H}2} \) ratio in the optically thick CRZ.

We have computed \( f_d \) and \( \bar{\beta} \) using our full numerical solutions for \( x_{\text{H}1}/x_{\text{H}2} \) in the CRZ shown in Figure 4. We find that for \( 50 \text{ K} < T < 10^3 \text{ K} \), the power-law fit

\[
\bar{\beta} = 0.75 \times \left( \frac{\zeta/16}{n_6} \right)^{0.37} T_2^{-0.79} \tag{29}
\]

is accurate to within 11% for \( 0.1 < \zeta/\bar{n}_6 < 10 \) and 34% for \( 0.01 < \zeta/\bar{n}_6 < 100 \). With these approximations,

\[
N_{\text{H}1}(N_{\text{H}2}) = \frac{\bar{\alpha}}{2} \frac{W_d(N_{\text{H}2})}{\sigma_d} + \bar{\beta} N_{\text{H}2}. \tag{30}
\]

The first term on the right is the atomic column built up in the PDR; the second term is the column built up in the CRZ.

The depth-dependent atomic and molecular densities may then be constructed in the following simple procedure:

1. Select the ratios \( I_{\text{LW}}/n \) and \( \zeta/n \).
2. Compute \( \bar{\alpha} \) using Equation (15) assuming \( x_{\text{H}1} = 1 \).
3. Compute \( \bar{\beta} \) using Equation (29) given the assumed \( \zeta/n \).
4. Solve Equations (27) and (28) for \( x_{\text{H}1} \) and \( x_{\text{H}2} \) using \( \bar{\alpha} \) and \( \bar{\beta} \) given any \( N_{\text{H}2} \) and the shielding function Equation (3).
5. Compute \( N_{\text{H}1}(N_{\text{H}2}) \) using Equation (18) and with Equation (4) for \( W_d(N_{\text{H}2}) \).
6. Plot the density profiles \( x_{\text{H}1}(N) \) and \( x_{\text{H}2}(N) \), with \( N = N_{\text{H}1} + 2N_{\text{H}2} \).

As we demonstrate below, this procedure provides an accurate representation for the density profiles and H-1-to-H2 transition points for models without CR attenuation compared to full numerical solutions to the depth-dependent rate equations for the hydrogen/helium network.

### 3.5. Timescales

We have been assuming steady-state conditions for the atomic and molecular densities. The timescales required to reach a steady-state equilibrium may be estimated by considering the time-dependent \( \text{H}_2 \) formation–destruction equation (Goldsmith et al. 2007; Liszt 2007). In our problem, this may be written as

\[
\frac{dx_{\text{H}2}}{d\tau} = 1 - \left[ 2 + \frac{1}{2} \sigma_{\text{shield}}(N_{\text{H}2}) + \bar{\beta} \right] x_{\text{H}2} \tag{31}
\]

where here the dimensionless time \( d\tau \equiv R. ndt \). Making the assumption that \( \alpha \) and \( \beta \) are independent of \( x_{\text{H}1} \) and \( x_{\text{H}2} \) as the system evolves, e.g., by setting \( \alpha = \bar{\alpha} \) and \( \beta = \bar{\beta} \), the solution is

\[
x_{\text{H}2}(0) = 1/a + \left[ x_{\text{H}2}(0) - 1/a \right] e^{-\alpha \tau} \tag{32}
\]

where \( x_{\text{H}2}(0) \) is the initial molecular fraction, and

\[
a = 2 + \frac{1}{2} \sigma_{\text{shield}}(N_{\text{H}2}) + \bar{\beta}. \tag{33}
\]

The \( \text{H}_1 \)-to-\( \text{H}_2 \) equilibration timescale for any shielding column \( N_{\text{H}2} \) is then

\[
\tau_{\text{eq}} = \frac{1}{a}, \tag{34}
\]

or

\[
t_{\text{eq}} = \frac{t_{\text{H}2}}{a} = \frac{1}{R.n} \times \frac{1}{2 + \frac{1}{2} \sigma_{\text{shield}} + \bar{\beta}}, \tag{35}
\]

where the \( \text{H}_2 \) formation time

\[
t_{\text{H}2} = \frac{1}{R.n} = \frac{8.0 \times 10^7 \left( \frac{\zeta/16}{n_6} \right)^{-1/2}}{n_6 x_{\text{H}2}^{-1/2} T_2^{-1.02}} \text{yr} \tag{36}
\]

using Equation(12) for \( R. \).

In general, \( \alpha \gg 1 \) and \( \beta \) is of order unity (see Equations (15) and (24)). Therefore, in the outer PDR where \( f_{\text{shield}} \rightarrow 1, a \gg 1 \), and the equilibration timescale is short, with

\[
t_{\text{eq}} \approx \frac{2}{D_0} = \frac{1.1 \times 10^3}{I_{\text{LW}}} \text{ yr}. \tag{37}
\]

In this limit, the equilibration time is the dissociation time, independent of the gas density. If the gas is initially molecular \( x_{\text{H}2}(0) = 1/2 \) photodissociation to the equilibrium atomic state is rapid. Or, if initially fully atomic \( x_{\text{H}2}(0) = 0 \) the small equilibrium molecular abundance is reached within a short time. In the inner shielded CRZ, where \( f_{\text{shield}} \rightarrow 0 \), and with \( \beta \ll 1 \), we have \( a \approx 1/2 \), and

\[
t_{\text{eq}} \approx \frac{1}{2R.n} = \frac{3.96 \times 10^7 \left( \frac{\zeta/16}{n_6} \right)^{-1/2}}{n_6 x_{\text{H}2}^{-1/2} T_2^{-1.02}} \text{ yr}. \tag{38}
\]

The equilibration time is then long and comparable to the \( \text{H}_2 \) formation time. In this limit, \( t_{\text{eq}} \) is independent of the photodissociation rate, is inversely proportional to the gas density for fixed \( \zeta/n \), and decreases as \( \zeta^{-1/2} \) for fixed density.
For our fiducial parameters, $I_{LW} = \zeta_{-16} = n_6 = T_2 = 1$, we have that $\alpha = 1.45 \times 10^5$, and $\beta \approx 0.75$. Thus, in the unshielded PDR, $t_{eq} \approx 1.1 \times 10^3$ yr. In the CRZ, $t_{eq} \approx 4.3 \times 10^7$ yr. In Figure 10, we show computations of the depth-dependent timescales, short to long, and shown as $n_6 \times t_{eq}$, for a range of $I_{LW}/n_6$ and $\zeta_{-16}/n_6$. We discuss these results as part of our parameter study in Section 4.4.

### 4. Numerical Models

We now present solutions for the atomic and molecular abundance profiles and the H\textsubscript{1}-to-H\textsubscript{2} transition points, obtained by solving the rate equations (Equation (38)) for our hydrogen–helium chemical network (Figure 1 and Table 1). We refer to these solutions as our “numerical models.” We write down the rate equations and then present our results as part of our numerical models. We solve the rate equations for the steady-state abundances, $x_i \equiv n_i/n$ of the atomic and molecular hydrogen/helium species in our chemical network described in Section 2. Here, $n_i$ is the density of species $i$ and $n$ is the total hydrogen gas density. The rate equations are

$$
\sum_{j} k_{ij}(T) x_j x_i + \frac{\zeta}{n} \sum_{j} a_{ij} x_j x_i = x_i \left( \sum_{j} k_{ij}(T) x_j + \frac{\zeta}{n} \sum_{j} a_{ij} + \frac{I_{LW}}{n} \sum_{j} b_{ij} \right) \tag{38}
$$

The $k_{ij}$ are the temperature-dependent rate coefficients (cm$^3$ s$^{-1}$) for two-body reactions of species $j$ and $l$ that lead to the formation of $i$. We use the rate coefficients as given in the UMIST2012 database (McElroy et al. 2013) as updated by Neufeld et al. (2020). We list these in Table 1. The $a_{ij}$ are the direct cosmic-ray ionization and dissociation factors for the five hydrogen/helium CR reactions in our network as listed in Table 2, multiplied by the CR attenuation factor. The $b_{ij}$ are the normalized photorates for H$^+$ photodetachment, H$_2^+$, and He$^+$ photodissociation, and local H$_2$ photodissociation including self-shielding. The incident LW field intensity is specified by $I_{LW}$ and $\zeta$ is the cosmic-ray ionization rate at the cloud edge.

Mass conservation is

$$
\sum_{i} \alpha_{im} x_i = X_m \tag{39}
$$

where $\alpha_{im}$ is the number of atoms of element $m$ (hydrogen or helium) contained in species $i$. The hydrogen abundance $X_H = 1$ by definition. For helium we assume a cosmic value $X_{He} = 0.1$. Charge conservation is the (dependent) equation

$$
\sum_{i} q_i x_i = 0 \tag{40}
$$

where $q_i$ is the net charge of species $i$.

For any temperature $T$, and for a given H$_2$ column density $N_{H_2}$, the solutions to the rate equations depend on the two ratios $I_{LW}/n_6$ and $\zeta/n_6$. $N_{H_2}$ determines the local photodissociation rate via the self-shielding factor. If CR attenuation is included, the local solutions also depend on the total gas column $N = N_{H_2} + 2N_{He}$, but $N_{He}$ may still be used as the single independent-depth variable. Thus for isothermal conditions the depth-dependent abundance profiles are determined by the two ratios $I_{LW}/n_6$ and $\zeta/n_6$ at the cloud boundaries. Equation (38) is nonlinear and we solve this numerically by integrating the time-dependent differential rate equations to equilibrium via a Newton iteration of the steady-state algebraic equations. We compute the species abundances, including $x_{H_1}$ and $x_{H_2}$, as functions of cloud depth, integrating inward for $N_{H_2}$ and $N_{He}$, given the initial conditions $N_{H_1} = N_{He} = 0$ at the outer boundary. We have verified (as a numerical consistency check) that for fixed temperature, the solutions depend only on the ratios $I_{LW}/n_6$ and $\zeta/n_6$ for any FUV intensity, cosmic-ray ionization rate, and gas density.

#### 4.2. Fiducial Case

For our fiducial parameters we set $I_{LW}/n_6 = 1$ and $\zeta_{-16}/n_6 = 1$. In Figure 5 we show the resulting H\textsubscript{1} and H\textsubscript{2} mass fractions, $x_{H_1}$ and $x_{H_2}$, as functions of total gas column $N$ (cm$^{-2}$) for gas temperatures $T = 50, 100$, and 500 K. In these computations we do not include any cosmic-ray attenuation. With these choices, (a) the gas is predominantly atomic in the outer PDR (Equation (16)), (b) the gas is primarily molecular in the CRZ (Equation (25)), and (c) the transition points occur at total gas columns $\approx 10^{12}$ cm$^{-2}$ (Equation (20)). The effective gas-phase formation-rate coefficient varies linearly with $T$ (Equation (12)), so as the temperature increases, the transition points occur at smaller gas columns and are at $1.4 \times 10^{22}$, $3.7 \times 10^{21}$, and $2.3 \times 10^{20}$ cm$^{-2}$, for $T = 50, 100$, and 500 K. In the CRZ, the molecular fractions are 0.58, 0.71, and 0.90. It is evident that higher temperatures induce stronger H\textsubscript{1}-to-H\textsubscript{2} transitions.

In Figure 6 we present more details for the $T = 100$ K case (left-hand panels), and we compare these to models that include cosmic-ray attenuation (right-hand panels). We set $\zeta_{-16}/n_6 = 1$ at the cloud surface, and assume the $q = 0.385$ power law (Equation (5)) for $\zeta(N)$ for the Padovani et al. (2018b) model-H particle-energy distribution. In the upper right-hand panel, the solid curves are the H\textsubscript{1} and H\textsubscript{2} mass fractions assuming any magnetic field is normal to the cloud surface ($\mu = 1$ in Equation (5)). The dashed curves are for a highly inclined magnetic field ($\mu \equiv \cos \theta = 0.1$).
At the unshielded cloud edge, the molecular fraction \( x_{\text{H}_2} = 1.3 \times 10^{-5} \) (Equation (16)) for all three models. Without CR attenuation (upper left panel), the H\textsubscript{1}-to-H\textsubscript{2} transition point \((x_{\text{H}_1} = 1/2)\) occurs at \( N = 4 \times 10^{24} \) cm\(^{-2}\), where \( N_{\text{H}_1} = 2.9 \times 10^{24} \) and \( N_{\text{H}_2} = 5.7 \times 10^{20} \) cm\(^{-2}\). The HI column at the transition point is consistent with Equation (20) for the total HI column produced by photodissociation. A HI-to-H\textsubscript{2} transition is expected because \( \zeta - 16/n_6 < 11.87 \) (see Figure 4).

In the CRZ, the atomic and molecular mass fractions are constant, with \( x_{\text{H}_1} = 0.28 \), and \( x_{\text{H}_2} = 0.72 \).

With CR attenuation, the transition point is shifted to slightly larger gas columns of \( 1.31 \times 10^{25} \) and \( 2.41 \times 10^{25} \) cm\(^{-2}\), \( \mu = 1 \) and 0.1. This is because of the lowered ionization rate and reduction of the effective gas-phase formation-rate coefficient \( R_\text{cr} \) (Equation (12)) within the PDR. In the CRZ, the atomic fractions continue to decrease with depth, in accordance with Equation (26) and Figure 4, as \( \zeta \) decreases and the molecular destruction rate is reduced.

The middle panels of Figure 6 show the abundances of electrons, H\textsuperscript{+}, H\textsuperscript{-}, and H\textsuperscript{3+} ions, without (left) and with (right) CR attenuation. As expected, the protons carry the positive charge and the curves for \( x_e \) and \( x_{\text{H}_1} \) overlap. In the PDR, \( x_e = 2.5 \times 10^{-6} \) as given by Equation (11). The electron fraction drops in the CRZ, due to the reduced atomic fraction there. The abundance of the H\textsuperscript{-} intermediary is everywhere proportional to the electron fraction (Equation (13)). Mutual neutralization \([R3]\) and photodetachment \([R4]\) are negligible compared to associative detachment \([R2]\) and \( \eta = 1 \). The H\textsuperscript{3+} abundance rises as the H\textsubscript{2} density grows. When CR attenuation is included, the H\textsuperscript{3+} abundance declines slightly with depth as the ionization rate is diminished.

The bottom panels of Figure 6 show the LW photodissociation and CR destruction rates as functions of the total gas column. For both models, the onset of molecular self-shielding occurs at \( N \approx 5 \times 10^{19} \) cm\(^{-2}\) where \( N_{\text{H}_1} = 2.1 \times 10^{15} \), without CR attenuation, and 1.5 \times 10\(^{15}\), and 7.2 \times 10\(^{14}\) with CR attenuation (for \( \mu = 1 \) and 0.1), and the photodissociation rate drops with increasing cloud depth. Without CR attenuation, the LW and CR destruction rates are equal at \( N = 9.3 \times 10^{21} \) cm\(^{-2}\), near to the H\textsubscript{1}-to-H\textsubscript{2} transition point. The CR destruction rate is slightly larger in the CRZ due to the increase in the \( f_\text{d} \) branching ratio (Equation (7)). With CR attenuation, the
curves are the H2 mass fractions calculated using the analytic procedure (Section 3.4). The red markers indicate the H I-to-H2 transition points where \( x_{\text{HI}} = 2x_{\text{H2}} \).

destruction rates are equal at \( 3.8 \times 10^{22} \) and \( 6.6 \times 10^{22} \text{ cm}^{-2} \) (for \( \mu = 1 \) and 0.1) and the CR destruction rates continue to decline within the CRZ.

### 4.3. Model Grids

In Figure 7 we present a 5 × 5 numerical model grid for the H I and H2 density profiles, for \( I_{\text{UV}}/n_6 \) ranging from 0.1 to 10 in steps of 0.5 dex (rows), and \( \zeta_{-16}/n_6 \) from 0.1 to 10 (columns) also in steps of 0.5 dex. These computations are all for \( T = 100 \text{ K} \), without CR attenuation. The middle panel (blue curves) is our fiducial model. In Figure 7 we also plot (dashed curves) the H2 abundances computed using our analytic procedure (Section 3.4). The agreement between the analytic and numerical results is excellent.

As expected, for fixed \( \zeta_{-16}/n_6 \), the molecular fractions in the PDRs are reduced as \( I_{\text{UV}}/n_6 \) is increased and photodissociation becomes more effective relative to the fixed formation rates (Equation (16)). The transition points (indicated by the red markers) therefore occur at larger gas columns as \( I_{\text{UV}}/n_6 \) is increased. For example, for \( \zeta_{-16}/n_6 = 1 \), and for \( I_{\text{UV}}/n_6 \) from 0.1 to 10, the molecular fraction ranges from \( 1.26 \times 10^{-4} \) to \( 1.26 \times 10^{-6} \) at the cloud edges. The transition columns increase from \( 1.2 \times 10^{20} \) to \( 5 \times 10^{22} \text{ cm}^{-2} \). The molecular fractions remain unaltered in the CRZs (Equation (26) and Figure 4), where \( 2x_{\text{H}} = 0.71 \) and \( x_{\text{HI}} = 0.29 \), independent of \( I_{\text{UV}}/n_6 \).

For increasing \( \zeta_{-16}/n_6 \) at fixed \( I_{\text{UV}}/n_6 \), the molecular fractions increase in the PDRs but decrease in the CRZs. This is because the H2 formation efficiency via CR ionization is enhanced for larger \( \zeta/n \) relative to the fixed photodissociation rates in the PDR (Equation (16)). However, in the CRZ, the molecular fraction decreases with \( \zeta/n \) because removal by CR ionization is more effective than CR-driven formation (Equation (26)) and Figure 4. The transition columns therefore first decrease for increasing \( \zeta_{-16}/n_6 \), but above \( (\zeta_{-16}/n_6)_{\text{crit}} = 11.84 \) (see Figure 4) a conversion point does not occur and the gas remains predominantly atomic in the CRZ. For example, for \( I_{\text{UV}}/n_6 = 1 \) and for \( \zeta_{-16}/n_6 \) from 0.1 to 10, the H2 mass fraction at the PDR edge increases from \( 8.38 \times 10^{-6} \) to \( 8.38 \times 10^{-5} \). In the CRZ, it decreases from 0.86 to 0.52. For \( \zeta_{-16}/n_6 \) from 0.1 to 3.16, the transition column decreases from \( 1.27 \times 10^{22} \) to \( 2.38 \times 10^{21} \). For \( \zeta_{-16}/n_6 = 10 \), a transition just barely occurs at \( 5.81 \times 10^{21} \text{ cm}^{-2} \).

In Table 5 we list the H I and H2 column densities and the total hydrogen column at the atomic-to-molecular transition points (\( x_{\text{HI}} = 2x_{\text{H2}} \)) for each of the models in the grid. The required H2 shielding columns range from \( \sim 10^{19} \) to a few \( 10^{21} \text{ cm}^{-2} \), corresponding to shielding factors, \( f_{\text{shield}} \), from \( 1.9 \times 10^{-4} \) to \( 4.4 \times 10^{-7} \). We also list the equilibration timescales required to reach the transition points, assuming fully atomic initial states. These range from \( n_6 \times t_{\text{eq}} = 8.0 \times 10^6 \) to \( 8.9 \times 10^7 \text{ yr} \).

In Figure 9 (left panel) we plot the hydrogen gas columns at which the transition points occur as functions of \( \zeta_{-16}/n_6 \) for the various \( I_{\text{UV}}/n_6 \) ratios for models without CR attenuation. For \( I_{\text{UV}}/n_6 = 1 \), the transition column decreases from \( 3.62 \times 10^{22} \)
The HI, H₂, and total hydrogen column densities, \( N_{\text{HI}}, N_{\text{H}_2}, \text{and } N_{\text{total}} \), are listed in Table 5 for models without cosmic-ray attenuation. The shield factors and the timescales at the transition points are also listed for each model. In Figure 7, these models are shown with CR attenuation. The column densities initially decrease with increasing CR attenuation as functions of the ionization-rate-to-density ratio at the cloud edge, \( \xi_{-16}/n_0 \), for the various \( I_{\text{UV}}/n_0 \) models including CR attenuation. For any \( I_{\text{UV}}/n_0 \) the transition columns initially decrease with \( \xi_{-16}/n_0 \) due to the overall enhanced ionization and molecular formation rates in the PDRs. For these branches the atomic to molecular transitions are governed by self-shielding of the H₂ against LW photodissociation. The (dotted) lines in Figure 9 are contours of constant local attenuated ratios \( \xi_{-16}/n_0 \), for our assumed CR attenuation function. The intersections with the solid curves give the local attenuated values of \( \xi_{-16}/n_0 \) at the transition points. For example, for \( I_{\text{UV}}/n_0 = 1 \), and \( \xi_{-16}/n_0 \text{ at the CRZs. The local values of } \xi_{-16}/n_0 \text{ must then equal } \xi_{-16}/n_0 \text{ at the CRZs. The local values of } \xi_{-16}/n_0 \text{ must then equal } \xi_{-16}/n_0 \text{ at the CRZs.}

4.4. Depth-dependent Timescales

Figure 10 shows the depth-dependent equilibrium timescales, plotted as the product \( n_{\text{eq}} \) (Equation (34)) versus gas column density \( N \). These are for models with CR attenuation. We compute \( \alpha \) and \( \beta \) locally at every depth (rather than using \( \hat{\alpha} \) and \( \hat{\beta} \)). As expected, for fixed \( I_{\text{UV}}/n_0 = 1 \) (top panel) the timescale approaches the short dissociation limit of \( n_{\text{eq}} \approx 1.1 \times 10^3/I_{\text{UV}} \) yr in the PDR at low gas columns, independent of \( \xi_{-16}/n_0 \). At large depths in the CRZ, the timescale approaches the long H₂ formation limit, with \( n_{\text{eq}} \approx 4 \times 10^7 \xi_{-16}/n_0^{1/2} \) yr. At intermediate gas columns, e.g., at \( 10^{21} \text{ cm}^{-2} \) in Figure 10, the timescale increases with \( \xi/n \) because elevating the H₂ formation rate within the PDR increases the shielding column, thereby reducing the dissociation rate and associated equilibrium time. At fixed \( \xi_{-16}/n_0 = 1 \) (bottom panel) the product \( n_{\text{eq}} \) decreases linearly.

Table 5

| Models without Cosmic-Ray Attenuation |
|---------------------------------------|
| \( \log(I_{\text{UV}}/n_0) \) | \( \log(\xi_{-16}/n_0) \) | -1 | -0.5 | 0 | 0.5 | 1 |
|---------------------------------------|
| \( N_{\text{HI}} \text{ (cm}^{-2}) \) | 4.2(1) | 1.8(2) | 8.2(19) | 4.8(19) | 2.1(20) |
| \( N_{\text{H}_2} \text{ (cm}^{-2}) \) | 7.7(19) | 3.5(19) | 1.8(19) | 1.3(19) | 9.2(19) |
| \( N_{\text{total}} \text{ (cm}^{-2}) \) | 5.6(20) | 2.5(20) | 1.2(20) | 7.4(19) | 3.9(20) |
| \( f_{\text{shield}} \) | 6.5(5) | 1.1(4) | 1.6(4) | 1.9(4) | 5.7(5) |
| \( \xi_{-16}/n_0 \times \text{eq} \text{ (yr)} \) | 7.7(7) | 4.3(7) | 2.5(7) | 1.4(7) | 8.0(6) |
|---------------------------------------|
| -0.5 | 2.3(21) | 1.1(21) | 5.2(20) | 3.1(20) | 9.5(20) |
|---------------------------------------|
| 0 | 3.6(20) | 2.0(20) | 1.1(20) | 8.5(19) | 4.1(20) |
|---------------------------------------|
| 1 | 1.0(22) | 5.2(21) | 2.7(21) | 1.6(21) | 1.6(21) |
|---------------------------------------|
| 0.5 | 1.2(21) | 7.4(20) | 4.8(20) | 3.8(20) | 1.3(21) |
|---------------------------------------|
| 1 | 1.3(22) | 6.7(21) | 3.6(21) | 2.4(21) | 5.8(21) |
|---------------------------------------|
| 0.5 | 6.4(6) | 1.0(5) | 1.6(5) | 1.9(5) | 7.6(7) |
|---------------------------------------|
| 1 | 7.7(7) | 4.4(7) | 2.5(7) | 1.4(7) | 8.0(6) |

Note. The HI, H₂, and total hydrogen column densities, \( N_{\text{HI}}, N_{\text{H}_2}, \text{and } N_{\text{total}} \), at the transition points for each model in the grid shown in Figure 7. These are models without CR attenuation. The shielding factors and the timescales at the transition points are also listed for each model. In Table 6 we list the HI, H₂, and total hydrogen column densities initially decrease with \( \xi_{-16}/n_0 \) due to the additional contribution of cosmic-ray H₂ destruction near the inner edge of the PDR, which moderates the shape of the transition profile.

In Figure 8, we display the 5 \times 5 model grid, now including CR attenuation. For these models, we again use Equation (5) assuming a Padovani model-\( \mathcal{H} \) \( (q = 0.385) \) for a normally inclined magnetic field \( (\mu = 1) \). The atomic fractions in the PDRs are increased and the transition points generally occur at greater depths due to the lowered ionization and reduced H₂ formation rates through the PDRs. However, in the CRZs, the molecular fractions are always larger for models with CR attenuation because of the reduced H₂ destruction rates and transitions always occur.

In Table 6 we list the HI, H₂, and total hydrogen column densities at the transition points for the model grid shown in Figure 8 as well as the shielding factors and equilibrium timescales. As expected, with CR attenuation the required H₂ shielding columns are larger, reaching up to \( 10^{22} \text{ cm}^{-2} \), corresponding to \( f_{\text{shield}} \times 1.7 \times 10^{-27} \).

Figure 9 (right panel) shows the hydrogen gas columns (solid curves) at the transition points for models with CR attenuation as functions of the ionization-rate-to-density ratio at the cloud edge, \( \xi_{-16}/n_0 \text{ at the CRZs. For these branches the atomic to molecular transitions are governed by self-shielding of the H₂ against LW photodissociation. The (dotted) lines in Figure 9 are contours of constant local attenuated ratios } \xi_{-16}/n_0, \text{ for our assumed CR attenuation function. The intersections with the solid curves give the local attenuated values of } \xi_{-16}/n_0 \text{ at the transition points. For example, for } I_{\text{UV}}/n_0 = 1, \text{ and } \xi_{-16}/n_0 \text{ when the transitions occur within the CRZs. The local values of } \xi_{-16}/n_0 \text{ must then equal } \xi_{-16}/n_0 \text{ at the CRZs. The local values of } \xi_{-16}/n_0 \text{ must then equal } \xi_{-16}/n_0 \text{ at the CRZs.}
with $I_{\text{LW}}/n_6$ at the cloud edges in the dissociation limit. The timescale lengthens as self-shielding sets in, finally reaching the long H$_2$ formation time in the CRZ, independent of $I_{\text{LW}}/n_6$.

5. Summary and Discussion

We have presented an analytic and numerical study of the atomic and molecular hydrogen-density profiles and H I-to-H$_2$ transitions that may occur in dense, dust-free (primordial) interstellar photodissociation regions (PDRs) and optically thick cosmic-ray zones (CRZs). Our models are highly idealized. We focus on 1D, steady-state, cold, isothermal, constant-density gas slabs, irradiated by stellar-type far-UV fields and fluxes of nonthermal cosmic-ray particles. Molecular hydrogen formation is by ionization-driven gas-phase (two-body) chemistry only, primarily via the H$^-$ intermediary rather than by dust-catalysis as in standard ISM clouds. H$_2$ absorption-line self-shielding enables the atomic-to-molecular transitions, even without any dust opacity.

For this idealized setup, we solve the rate equations for the depth-dependent abundances of H I and H$_2$ as well as the trace species, H$^+$, H$_2^+$, H$_3^+$, H$^-$, He, He$^+$, HeH$^+$, and electrons. The basic parameters in the problem are (a) the unattenuated LW radiation-field intensity $I_{\text{LW}}$, (b) the gas density $n$, (c) the cosmic-ray ionization rate $\zeta$, and (d) the gas temperature $T$. For any temperature, the depth-dependent abundances and the H I-to-H$_2$ transition points depend on the two ratios $I_{\text{LW}}/n$ and $\zeta/n$. The cosmic-ray-driven gas-phase H$_2$ formation route may be represented by an effective rate coefficient $R_-$ depending on the ionization fraction (Equations (6)–(9)).

Because gas-phase H$_2$ formation is inefficient compared to molecule production on dust-grain surfaces, we focus on relatively dense gas for which the formation rates are enhanced. Our fiducial model is for $n = 10^6$ cm$^{-3}$ at $T = 100$ K. The illuminating FUV radiation is for a (Pop III) $10^5$ K blackbody field normalized to a Galactic interstellar LW intensity, $I_{\text{LW}} = 1$, with LW flux $2.07 \times 10^7$ photons cm$^{-2}$ s$^{-1}$. The H$_2$ cosmic-ray ionization rate $\zeta = 10^{-16}$ s$^{-1}$. We also present results for $I_{\text{LW}}/n$ and $\zeta/n$ ranging $\pm 1$ dex around our fiducial case. For this range of parameters, H$^-$ photodetachment is negligible and the resulting H I and H$_2$ density profiles are insensitive to the IR to UV spectral shapes of the radiation fields. For our fiducial model, a H I-to-H$_2$ transition occurs at a total hydrogen gas column density of $4 \times 10^{21}$ cm$^{-2}$ within an equilibration timescale of $3 \times 10^7$ yr. This is comparable to the transition column and H$_2$ formation time for typical dusty Galactic clouds with densities $\sim 10^2$ cm$^{-3}$.

We examine the effects of cosmic-ray energy losses on the H I and H$_2$ density profiles and transition points. CR attenuation moves the transition points to larger cloud depths due to the reduced ionization fractions and lowered molecular formation efficiencies in the PDRs. However, in the CRZs, the...
reduced cosmic-ray destruction rates lead to enhanced molecular fractions.

For our parameter space, the dust-free limit is reached for dust-to-gas ratios \( Z' \lesssim 10^{-5} \) (relative to Galactic), depending slightly on the ionization rate and gas density. In this limit, gas-phase \( \mathrm{H}_2 \) formation dominates, and dust-gas neutralization processes do not affect the hydrogen–helium chemistry and ionization structures. Given the probable super-linear dependence of interstellar dust-to-gas mass ratios on the ambient metallicity in differing environments, the dust-free limit may be reached for metallicities \( Z' \lesssim 10^{-2} \) (relative to solar) depending slightly on gas density and ionization rate.

Our theoretical study is relevant for systems such as low-metallicity dwarf galaxies at low and high redshift, possibly dense condensations in the circumgalactic medium of galaxies, and intergalactic filaments, as well as for protoplanetary disks and dust-depleted outflow jets from protostars. As for dusty systems, the long \( \mathrm{H}_2 \) formation timescales suggest that cloud evolution, dynamical turbulence, and variability of the radiation sources must be considered for a complete description of the \( \mathrm{H}_1 \) and \( \mathrm{H}_2 \) abundances in specific astrophysical systems.

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### Appendix A

#### Metals, Dust, and the Fractional Ionization

In Equation (11) we are assuming that free electrons provided by the ionization of heavy elements are negligible and that dust grains do not affect the hydrogen–helium chemistry and associated ionization fractions. In standard Galactic PDRs, free electrons are produced by the photoionization of atomic carbon and other heavy elements with low ionization potentials. For example, in the outer CII zones, photoionization of atomic carbon provides an ionization floor of \( \chi_c \sim 2.6 \times 10^{-4} \) for solar metallicity (e.g., Sternberg & Dalgarno 1995). Equation (11) is then valid for metallicities \( Z' \lesssim 0.01(\zeta_{16}/n_e)^{1/2} \). Photoionization of heavy elements in dust-free gas could enhance the gas-phase \( \mathrm{H}_2 \) formation efficiency, but we do not consider such effects in this paper.

Charge transfer between dust grains and ions, or “dust-assisted recombination,” may enhance the neutralization of gas-phase ions, including \( \mathrm{H}^+ \) and \( \mathrm{He}^+ \) (Weingartner & Draine 2001). The presence of small dust particles (e.g., polycyclic aromatic hydrocarbons, PAHs) may further alter the gas-phase ionization fractions via electron attachment and the formation of negatively charged dust particles (Lepp et al. 1988). For any ion, the dust-assisted recombination rate coefficient depends on the overall dust-to-gas ratio and the grain charge. We recall that the dust-assisted recombination coefficient is a monotonically decreasing function of the grain charge parameter \( \psi = n_e \sqrt{\tau} / n_e \), where \( n_e \) is the electron density. The grain-assisted recombination rate coefficient is maximal for small \( \psi \). For Galactic dust abundances, the maximal dust-assisted recombination rate for \( \mathrm{H}^+ \) is \( \alpha_{g,\omega} n \) where \( \alpha_{g} \sim 10^{-13} \text{ cm}^3 \text{s}^{-1} \) (Weingartner & Draine 2001). Dust
recombination is therefore negligible for 
\[ Z_{\text{H}}^{16}/n_6 \] 10

For the effects of small grains, we have verified by explicit computation for our model parameter space described in Section 4, that any PAHs are present mainly as neutral or negatively charged particles. We calculated the relative PAH\(^{+}/PAH^{-}\) abundances using the rate coefficients for recombination and attachment with electrons and charge-transfer reactions with H and H\(^{+}\), as summarized in Wolfire et al. (2003) (see their Appendix C2), and the photoionization and photodetachment cross sections recommended by Lepp et al. (1988). For a characteristic PAH abundance \[ x_{\text{PAH}} = 6 \times 10^{-7} \] for \[ Z_{\text{H}}^{16}/n_6 \] (Lepp et al. 1988; Weingartner & Draine 2001) we find that the PAHs do not alter the hydrogen–helium chemistry and ionization structure for \[ Z_{\text{H}}^{16}/n_6 \] -1. This can also be seen analytically. The dominant neutralization process is attachment (PAH\(^+\) + e \rightarrow PAH\(^-\) + ν), with a rate coefficient \[ \kappa_{-} = 1.34 \times 10^{-6} \text{ cm}^3 \text{s}^{-1} \]. This reaction is negligible compared to radiative recombination with protons for \[ Z_{\text{H}}^{16}/n_6 \] 10

Appendix B

Comparison to Sternberg et al. (2014)

As discussed in S14, in dusty optically thick PDRs the total HI column density maintained by photodissociation for beamed radiation is

\[
N_{\text{HI,tot}} = \frac{1}{\sigma_g} \log \left[ \frac{\alpha G}{2} + 1 \right] = \frac{1}{\sigma_g} \log \left[ \frac{1}{2} \frac{\sigma_g \bar{F}_{\text{LW}} W_{\text{g,tot}}}{R_{\text{dust}} n} + 1 \right],
\]

where the dimensionless parameters

\[
\alpha \equiv \frac{D_0}{R_{\text{dust}} n},
\]

and

\[
G \equiv \frac{\sigma_g W_{\text{g,tot}}}{\sigma_d}.
\]

In these expressions, \( \bar{F}_{\text{LW}} \) is the mean LW-band flux density (photons cm\(^{-2}\) s\(^{-1}\) Hz\(^{-1}\)), \( \sigma_d \) is the total H\(_2\) photodissociation cross section (cm\(^2\) Hz), \( D_0 = \sigma_d \bar{F}_{\text{LW}} \) is the free-space Figure 9. Left panel: total hydrogen gas columns at the atomic-to-molecular transition points as functions of \( \zeta_{\text{PAH}}/n_6 \) for \( I_{\text{LW}}/n_6 \) ranging from 0.1 to 10 for models without CR attenuation. The vertical dashed line indicates the critical ratio \( \zeta_{\text{PAH}}/n_6 \)crit = 11.84 (at 100 K). Right panel: transition columns for models with CR attenuation (for \( \mu = 1 \)). The dotted lines are contours of constant local attenuated \( \zeta_{\text{PAH}}/n_6 \). The dashed line is the contour for the critical value.

Figure 10. Depth-dependent equilibration timescales for \( I_{\text{LW}}/n_6 = 1 \) with \( \zeta_{\text{PAH}}/n_6 \) from 0.1 to 10 (upper panel), and for \( \zeta_{\text{PAH}}/n_6 = 1 \), with \( I_{\text{LW}}/n_6 \) from 0.1 to 10 (lower panel).

recombination is therefore negligible for 
\[ Z_{\text{H}}^{16}/n_6 \leq 1 \times 10^{-5}(\zeta_{\text{PAH}}/n_6)^{1/2} \] at 100 K.

For the effects of small grains, we have verified by explicit computation for our model parameter space described in Section 4, that any PAHs are present mainly as neutral or negatively charged particles. We calculated the relative PAH\(^{+}/PAH^{-}\) abundances using the rate coefficients for recombination and attachment with electrons and charge-transfer reactions with H and H\(^{+}\), as summarized in Wolfire et al. (2003) (see their Appendix C2), and the photoionization and photodetachment cross sections recommended by Lepp et al. (1988). For a characteristic PAH abundance \[ x_{\text{PAH}} = 6 \times 10^{-7} \] for \[ Z_{\text{H}}^{16}/n_6 \] (Lepp et al. 1988; Weingartner & Draine 2001) we find that the PAHs do not alter the hydrogen–helium chemistry and ionization structure for \[ Z_{\text{H}}^{16}/n_6 \] -1. This can also be seen analytically. The dominant neutralization process is attachment (PAH\(^+\) + e \rightarrow PAH\(^-\) + ν), with a rate coefficient \[ \kappa_{-} = 1.34 \times 10^{-6} \text{ cm}^3 \text{s}^{-1} \]. This reaction is negligible compared to radiative recombination with protons for \[ Z_{\text{H}}^{16}/n_6 \leq 1 \times 10^{-5}(\zeta_{\text{PAH}}/n_6)^{1/2} \]. We conclude that for \( \zeta_{\text{PAH}} = 1 \) dust-grain neutralization and H\(_2\) formation on dust surfaces (as discussed in Section 3.1) are, coincidentally, both negligible at dust-to-gas ratios \( Z_{\text{H}}^{16}/n_6 \approx 1 \).
photodissociation rate (s⁻¹), \(W_{\text{tot}}\) (Hz) is the total H₂-dust limited dissociation bandwidth (see S14), \(\sigma_g\) is the H₂ dust-continuum absorption cross section (cm²), \(R_{\text{dust}}\) is the dust-grain H₂ formation rate coefficient (cm³ s⁻¹) and \(n\) is the gas density (cm⁻³). The dimensionless parameter, \(\alpha\) is the ratio of the free-space dissociation rate to the H₂ formation rate, and \(G\) (also dimensionless) is the dust-opacity-averaged H₂ self-shielding factor (see Equation (45) in S14).

In the strong field limit, \(\alpha G \gtrsim 1\), and

\[
N_{\text{H}^1, \text{tot}}^{\text{LW}} \approx \frac{1}{\alpha G} \ln \left[ \frac{\sigma_g F_{\gamma, \text{LW}} W_{\text{tot}}}{2 R_{\text{dust}} n} \right]. \tag{B4}
\]

In this limit, the H I dust opacity \(\sigma_g N_{\text{H}^1, \text{tot}}^{\text{LW}}\) associated with the photodissociated H I column is large. The H I column is only logarithmically sensitive to \(\alpha G\) because the H I column is self-limited by the H I dust absorption that competes with H₂ photodissociations. The dominating H I dust opacity leads to sharp H I-to-H₂ transitions due to the exponential dust shielding factor, and \(\alpha G\) limited dissociation bandwidth. Thus, \(\sigma_g \rightarrow 0\). Furthermore, \(R_{\text{dust}}\) is replaced with a nonvanishing \(R_n\). So for dust-free conditions \(\alpha G\) is small by definition and

\[
N_{\text{H}^1, \text{tot}}^{\text{LW}} \approx \frac{1}{2} \frac{F_{\gamma, \text{LW}} W_{\text{tot}}}{R_n}. \tag{B5}
\]

In this limit the H I dust opacity is negligible and the H I column is linear with \(\alpha G\), i.e., with the incident LW flux. The H I-to-H₂ transitions are controlled by H₂ self-shielding in nonoverlapping absorption lines and the transitions are gradual (not sharp). In the weak-field limit a large fraction of the photodissociated H I column is built up past the transition points inside the molecular zones (see Figure (7) in S14).

We now consider dust-free systems. For these, \(\sigma_g \rightarrow 0\), and \(W_{\text{tot}} \rightarrow W_{\text{dust}}\), where \(W_{\text{dust}}\) is the dust-free H₂ dissociation bandwidth. Thus, \(\alpha G \rightarrow 0\). Furthermore, \(R_{\text{dust}}\) is replaced with a nonvanishing \(R_n\). So for dust-free conditions \(\alpha G\) is small by definition and

\[
N_{\text{H}^1, \text{tot}}^{\text{LW}} \approx \frac{1}{2} \frac{F_{\gamma, \text{LW}} W_{\text{dust}}}{R_n}. \tag{B6}
\]

This is formally analogous to the weak-field limit (Equation (B5)) for dusty clouds for which (a) the H I dust opacity is negligible (b) the transitions are controlled by H₂ self-shielding, and (c) the H I is linearly proportional to the incident LW flux. However, for dust-free clouds a different distinction between weak and strong fields remains. For \(N_{\text{H}^1, \text{tot}}^{\text{LW}} \gtrsim 10^{22}\) cm⁻², which is the H₂ column density required for complete line-overlap, the H I-to-H₂ transitions are sharp due to the exponential cutoff of the dissociation rates. This is the strong-field limit for dust-free clouds. For \(N_{\text{H}^1, \text{tot}}^{\text{LW}} \lesssim 10^{22}\) cm⁻², the transitions occur before the absorption lines overlap. The conversions are then gradual with significant H I in the molecular zones up to the point where the lines finally do overlap and the LW-band photons are fully absorbed. This is the weak-field limit for dust-free clouds. As discussed in Section 3.1 and Appendix A, for \(\lesssim 16/\eta_6 \sim 1\) the dust-free limit is reached for dust-to-gas ratios \(Z' \lesssim 10^{-5}\), and overall metallicities \(Z' \lesssim 10^{-2}\), relative to characteristic Galactic values.
