CO/H$_2$, C/CO, OH/CO, and OH/O$_2$ in Dense Interstellar Gas: From High Ionization to Low Metallicity

Shmuel Bialy$^1$ and Amiel Sternberg$^1$

$^1$Raymond and Beverly Sackler School of Physics & Astronomy, Tel Aviv University, Ramat Aviv 69978, Israel; shmuelbi@mail.tau.ac.il

Received: 2014 September 21

ABSTRACT

We present numerical computations and analytic scaling relations for cold-gas, ionization-driven interstellar ion-molecule chemistry, down to the very low metallicities ($\lesssim 10^{-3}$× solar) associated with the Pop-III to Pop-II star transition and the early enrichment reionization epoch. We focus on the behavior for H$_2$, CO, CH, OH, H$_2$O and O$_2$. We consider shielded or partially shielded one-zone gas parcels, and solve the chemical rate equations for steady-state conditions for a wide range of ionization parameters, $\zeta/n$, and metallicities, $Z'$. We find that the OH abundances are always maximal at the H-to-H$_2$ conversion points, and that large OH abundances persist at very low metallicities even when the hydrogen is predominantly atomic. We study the OH/O$_2$, C/CO and OH/CO abundance ratios, from large to small, as functions of $\zeta/n$ and $Z'$. Cold dense star-forming clouds for the Pop-II generation may have been OH-dominated and atomic rather than CO-dominated and molecular.

Key words: ISM: molecules – galaxies: abundances – reionization, first stars

1 INTRODUCTION

In this paper we present a numerical and analytic study of interstellar gas-phase ion-molecule chemistry, from standard Galactic conditions into the relatively unexplored domain of very low metallicity gas, appropriate for the early cosmic transition from Pop-III to Pop-II stars and the reionization epoch. We consider the behavior for a wide range of initiating hydrogen ionization rates and gas densities. Our focus is mainly on the molecular cold-cloud chemistry for H$_2$, CO, CH, OH, H$_2$O and O$_2$, and the relative steady-state abundances of these species, for varying metallicities and ionization parameters. Our discussion includes a detailed analysis of the hydrogen-carbon-oxygen chemical networks in the transition to the low metallicity limit.

There are several motivations for this work. First, observations of Population-II stars in the Galactic halo (Beers & Christlieb 2005) have revealed stars with heavy element abundances orders of magnitude smaller than in the Sun and the interstellar medium (ISM) of the star-forming disk. In the primitive halo star SDSS J102915+192927, for example, an overall metallicity of less than $10^{-4}$×solar has been reported (Caffau et al. 2011). In many metal-poor stars the carbon/iron ratios are significantly enhanced (e.g. Norris et al. 2013, Yong et al. 2013, Carollo et al. 2013), but even so the absolute carbon and oxygen abundances are very low, down to $\lesssim 10^{-3}$ compared to solar photospheric values. The very existence of these stars shows that interstellar cloud condensation, gravitational collapse, and low-mass star-formation occurred in gas with metallicities far lower than in present-day star-forming regions. Here we ask, and considering gas-phase ion-molecule formation-destruction chemistry within an idealized interstellar gas parcel, how do the atomic and molecular constituents for the heavy elements, especially carbon and oxygen, depend on the overall metallicity, from solar down to very subsolar?

Star formation, and the processes that led to the metal poor Pop-II stars, probably included molecule formation to a level that enhanced gas cooling and regulated the Jeans masses. In pristine or in very low metallicity environments, even partial conversion to H$_2$ enables efficient rotational line cooling in addition to atomic and ionic metal fine-structure emissions (Bromm & Loeb 2003, Santoro & Shull 2006, Omukai, Hosokawa & Yoshida 2010, Glover & Clark 2013). At high metallicities such as in Milky Way star-forming regions, complete conversion to H$_2$ (Sternberg et al. 2014) and the associated production of heavy molecules, especially CO but also many other species (Graedel, Langer & Frerking 1982, van Dishoeck 1998, Tielens 2013), appears essential for the coupled cooling and gravitational collapse. What are the most abundant molecules containing heavy elements? For normal Galactic conditions at solar metallicity this is CO, especially in regions shielded from photodissociating radiation. Is this true also for a metallicity of $10^{-3}$?

Very low metallicity stars have also been detected in nearby dwarf-spheroidal (dSph) galaxies (Tafelmeyer et al. 2010), e.g., most recently in the Galaxy satellite Segue 1 (Frebel, Simon & Kirby 2014). These dwarf galaxies may be directly related to the low-metallicity damped Ly$_\alpha$ absorbers (DLAs) observed from low to high redshifts (e.g. Pettini et al. 2008, Penprase et al. 2010, Rafelski et al. 2012). The low DLA metallicities, e.g. down to $\sim 2 \times 10^{-2}$ in the ($z=5.1$) absorber toward the QSO J1202+3235 (Rafelski et al. 2012), and the similar elemental abundance patterns, suggest that the DLAs may represent the initial conditions for the low-metallicity Pop-II stars and dSphs. The relative abundance patterns, including $\alpha$-element enhancements, appear consistent with nucleosynthetic production in massive (initially metal-free) Population-II stars at the reionization epoch. Then, if ultra-low metallicity molecular clouds existed...
at the reionization transition from Pop-III to Pop-II objects, what were their chemical properties?

A second motivation is the large range in ionization rates that may be expected for the neutral atomic/molecular ISM in galaxies from low to high redshift and with varying star-formation rate. For the standard neutral Galactic ISM, the ion-molecule chemistry and the production of “heavy molecules” is driven by (low-energy) cosmic-ray ionization. The ionization rate, as probed by observations of H$_3^+$, HCO$^+$, OH, OH$^+$, or H$_2$O$^+$, in diffuse and dense gas, and in the intercloud medium (e.g., van Dishoeck & Black 1986; van der Tak & van Dishoeck 2000; Neufeld et al. 2010; Indriolo & McCall 2012) may vary with location in the Galaxy and with individual cloud thickness, but overall it seems to lie within the fairly narrow range $\sim 10^{-16}$ to $10^{-15}$ s$^{-1}$ (Dalgarno 2006; Indriolo & McCall 2012). In as much as cosmic-ray production depends on star-formation and the subsequent supernova explosions and shock particle accelerations, the internal ionization rates may be significantly larger in more rapidly star-forming and/or compact galaxies, compared to $3$ M$_\odot$ yr$^{-1}$ within $\sim 10$ kpc for the Milky Way. At high redshift and along the upper end of the main-sequence for star-forming galaxies (Whitaker et al. 2012), or for merging star-bursting systems, the surface star-formation rates may be orders of magnitude larger than for the Galaxy (e.g., Förster Schreiber et al. 2009; Tacconi et al. 2013), and this may imply correspondingly very high cosmic-ray fluxes (Papadopoulos 2010; Mashian, Sternberg & Loir 2013). The galaxy mass-metallicity relation (Tremonti et al. 2004; Mannucci et al. 2010) may then also imply a correlation between metallicity and global ionization rate for the neutral ISM in galaxies.

The ionization rates may also be much larger than the characteristic Galactic value in localized environments exposed to X-rays. Penetrating X-rays and cosmic-rays are largely equivalent in their chemical effects, since the hydrogen ionization is always due to the secondary electrons produced by either primary X-ray photoionization or cosmic-ray impact ionization (Lepp & Dalgarno 1996; Maloney, Hollenbach & Tielens 1996; Meijerink & Spaans 2005). X-ray irradiation may play a dominating role in the inner envelopes and disks around young stellar objects (Igea & Glassgold 1999; Stüuber et al. 2003; Vasyunin et al. 2008). External to the Galaxy, X-ray driven chemistry may be especially important for any molecular gas around accreting massive black holes, from active galaxies in the local Universe (e.g., Hailey-Dunsheath et al. 2012) to high-redshift minihalos around the time of cosmic reionization (Volonteri & Silk 2014; Chen et al. 2014). Interstellar chemistry is a complex interplay of myriad processes, and the observed and predicted abundances of even the simplest molecules vary greatly with environmental conditions. Controlling quantities and processes include the gas density, the gas-phase elemental abundances, dust grain properties and dust-gas interactions including freeze out ice-processing and desorption, the gas and dust temperatures as set by local heating and cooling, photodissociating far-ultraviolet radiation field strengths, the cosmic-ray and/or X-ray ionization rates, time-scales, dynamical states, and evolutionary histories. The early Universe, including the Pop-III to Pop-II reionization epoch during which the first metal enrichment occurred, may have been simpler than today. In particular, the role of dust may have been much more important compared to gas-phase molecular production pathways. However, as noted by Dalgarno (2006) dust may have already been produced in the supernova ejecta of the Pop-III stars. The presence of dust could have provided shielding for molecule formation sites.

In this paper we consider “one-zone” models for the basic hydrogen, carbon, and oxygen gas-phase formation-destruction chemistry for idealized representative gas parcels, and we study the behavior as a function of the overall metallicity, $Z/\odot$, of the gas. We wish to understand how the molecular production efficiencies and pathways for the most abundant oxygen and carbon bearing species vary as the metallicity becomes very small, down to the Pop-II star regime. Oxygen and carbon were likely the most abundant heavy elements produced by the Pop-III supernova explosions (Heger & Woosley 2010). For simplicity we assume fixed (solar) relative abundances for the heavy elements as the metallicity is varied, importantly with O/C $> 1$. The second basic parameter that enters is the ratio of the driving ionization rate, $\zeta$, to the gas density, $n$. For any metallicity we vary the ionization parameter, $\zeta/n$, over a wide range relative to characteristic Galactic values. We imagine that the ionization is provided by cosmic-rays and/or an X-ray source. Our focus is on the varying chemical behavior for “cold cloud” conditions. We adopt a constant gas temperature of 100 K throughout, as a compromise between the colder to warmer ambient conditions in cool neutral star-forming gas from low to high redshift. We also consider the effects of partially attenuated background far-ultraviolet (FUV) radiation when or if dust shielding becomes ineffective, but we do not include any radiative transfer for the FUV.

We presented preliminary results for some of the computations presented in this paper in Sternberg et al. (2011). There have also been other discussions of heavy element molecular chemistry in the early Universe and at low-metallicity (see Yan 1997; Harwit & Spaans 2003; Dalgarno 2004; vonlanthen et al. 2009; Penteado, Cuppen & Rocha-Pinto 2014). Discussions of gas phase chemistry at very high ionization rates have also been presented (Lepp & Dalgarno 1996; Lepp & Tinsley 1998; Béav et al. 2011) but these have been restricted to local Universe environments, for solar or near-solar metallicities. Our focus and motivation is the gas phase astrochemistry of the Pop-III to Pop-II reionization era, and for this purpose we consider a very wide range of metallicities and ionization parameters.

In 3 we present our chemical networks and describe the dominant formation-destruction reactions and pathways from high to low-metallicity, and from the molecular to atomic regimes. We also present a discussion of photoprocesses for partially shielded gas parcels. In 4 we write down and discuss the chemical rate equations, and define our adjustable parameters, $Z/\odot$, $\zeta/n$, and $I_{\odot}/n$. In 5 we present an analytic treatment for the atomic to molecular hydrogen balance, and for the steady-state H$_2$ formation time scales. In 6 we present 1D numerical model sequences for the chemical behavior as a function of metallicity at fixed ionization parameter, and vice versa. Our focus is on H$_2$, CO, CH, OH, H$_2$O, and O$_3$, and we discuss how the molecular abundance ratios vary with the parameters. We also develop analytic scaling relations for the heavy molecule abundances and molecular ratios, as functions of $Z/\odot$ and $\zeta/n$. In 7 we present comprehensive full 2D computations for the chemical behavior, spanning the range from low metallicity to high ionization parameter. We summarize our results in 8.
2 CHEMICAL NETWORKS

We consider simplified (“minimal”) interstellar gas phase networks (Figures 1, 2, and 3) for the formation and destruction of H and H₂, and for the metal-bearing molecules, OH, H₂O, O₂, CH, and CO, which are our primary focus. The networks consist of standard ionization-driven two-body ion-molecule sequences, including selective neutral-neutral atom-exchange reactions, and moderated by dissociative and radiative recombination (Herbst & Klemperer 1973; Dalgarno & Black 1976; van Dishoeck 1988; Sternberg & Dalgarno 1995; van Dishoeck 1998; Le Teuff, Millar & Markwick 2000; McElroy et al. 2013; Wakelam et al. 2012). We assume that the ionization of H, H₂, and He is provided by a flux of penetrating cosmic-rays and/or X-rays, with a total (primary plus secondary) H ionization frequency ζ (s⁻¹). We also consider destructive photoprocesses due to background FUV radiation. Except for the formation of H₂, we ignore all gas-grain interaction and ice processes. Negative-ion chemistry (Dalgarno & McCray 1973; Walsh et al. 2009) plays a role only for H₂, via the H⁺ formation route, as described below. Negative ion production reactions for the heavy molecules are included in our set but they remain negligible throughout. Our focus is on low-temperature T ≤ 300 K gas for which the formation sequences are unaffected by direct H₂ neutral-neutral reaction with large endothermicities or activation barriers. Our networks include a total of 74 atomic and molecular hydrogen, carbon, oxygen, silicon, and sulfur species, and a set of 986 reactions, of which around 80 play a significant role as we describe below.

We wish to study the basic variation trends of the steady-state abundances of the chemical species within isothermal and uniform density “gas parcels”, as functions of the gas phase elemental abundances or metallicity of the gas, the ionization rate, and the total hydrogen gas density. We are particularly interested in the behavior at very subsolar metallicities, and/or high ionization rates. We parameterize the metallicity by a scaling factor Z′, such that Z′ = 1 corresponds to the heavy element abundances in the solar photosphere (Asplund et al. 2009) as listed in Table 1. We consider the solutions to the formation-destruction equations with and without the presence of a moderating and partially attenuated background FUV radiation field. Lyman continuum radiation is always excluded. When a background FUV field is present we assume that for sufficiently high metallicities the gas parcels are fully shielded by surrounding optically thick columns of dust. As Z′ becomes small we allow the gas to become optically thin to dust-absorption. However, we assume that the parcels are always shielded by sufficiently large columns of H₂ such that the 912-1108 Å Lyman-Werner (LW) band is fully blocked by fully overlapping H₂ absorption lines. We introduce this assumption to allow for optimal conditions for molecule formation in the parcels even at very low metallicity.

In our description of the networks we describe the dominant formation and destruction pathways in the limits of high and low metallicity. As we discuss in 1 and 2 for any Z′ the hydrogen makes the transition from predominantly atomic to molecular form at a critical ratio of the ionization rate ζ to the total hydrogen gas density n. In our discussion, the high-metallicity formation-

1 e.g., H⁻ + O → OH + e
2 e.g., O + H₂ → OH + H; OH + H₂ → H₂O + H

destruction pathways usually (but not always) correspond to predominantly H₂ gas. The low-metallicity pathways usually correspond to predominantly H gas. The transition from the fully H₂ "molecular regime" to the fully H "atomic regime" is important for the chemical behavior, as we describe below.

We begin with a description of the hydrogen/helium networks, and then consider the oxygen, and carbon/oxygen sequences.

2.1 Hydrogen and Helium

We illustrate the hydrogen-helium networks in Figure 1. These networks include the species H, H₂, H⁺, H⁻, H₂⁺, H₂⁺, He, He⁺, and HeH⁺. The formation of H₂ is essential for the efficient ion-molecule production of metal-bearing molecular species in the gas phase. At high metallicity H₂ formation is dominated by dust-grain catalysis

\[ H + H : gr \rightarrow H_2 + gr \]  

(R1)

At sufficiently low metallicity the main H₂ formation route is in the gas phase via the formation of H⁻ negative ions

\[ H + e \rightarrow H^- + \nu \]  

(R2)

\[ H^- + H \rightarrow H_2 + e \]  

(R3)

This radiative-attachment associative-detachment sequence is moderated by mutual neutralization

\[ H^- + H^+ \rightarrow H + H^- \]  

(R4)

which limits the H⁻ abundances when the proton density becomes large. Gas phase H₂ production also proceeds via radiative association

\[ H + H^+ \rightarrow H_2^+ + \nu \]  

(R5)

followed by charge transfer

\[ H_2^+ + H \rightarrow H_2 + H^+ \]  

(R6)

However, at the low gas temperatures (T ≤ 300K) we are considering, and in the absence of photodetachment, the H⁻ sequence, [R2] and [R3], always dominates.

In the absence of FUV photodissociation, the H₂ is removed by (primary plus secondary) cosmic-ray and/or X-ray ionization and radiative dissociation. We refer to these processes collectively as “crx-ionization”. Thus

\[ H_2 + crx \rightarrow H_2^+ + e \]  

(R7)

\[ \rightarrow H^+ + H + e \]  

(R8)

Depending on the H/H₂ density ratio, the H₂⁺ ions are removed by

| Element | n/H |
|---------|-----|
| He      | 0.1 |
| C       | 2.9 × 10⁻⁴ |
| N       | 6.8 × 10⁻⁴ |
| O       | 4.9 × 10⁻⁴ |
| Si      | 3.2 × 10⁻⁵ |
| S       | 1.3 × 10⁻⁵ |

Table 1. Elemental abundances relative to hydrogen.
charge transfer (reaction (R4)), leading back to H$_2$, and by proton transfer

$$H_2^+ + H_2 \rightarrow H_3^+ + H,$$  \hspace{1cm} (R9)

leading to H$_3^+$. The H$_3^+$ ions are removed by dissociative recombination

$$H_3^+ + e \rightarrow H + H + H \rightarrow H_2 + H,$$  \hspace{1cm} (R10)

and also by

$$H_3^+ + CO \rightarrow HCO^+ + H,$$ \hspace{1cm} (R12)

when the e/CO ratio is small.

The H/H$_2$ density ratio is a critical parameter affecting the overall chemical behavior. The main sources of free hydrogen atoms are direct dissociative ionization of the H$_2$, or H$_2$ ionization ([R3] and [R7]) followed by proton-transfer formation of H$_3^+$ ([R9]). At high metallicity, the H atoms are removed by the H$_2$ grain surface formation process. At low metallicity the H atoms are removed by ionization

$$H + crx \rightarrow H^+ + e.$$  \hspace{1cm} (R13)

The ionization of H is a major source of protons at low metallicity where the atomic fraction becomes large. When the gas is primarily H$_2$, the protons are produced by dissociative ionization of the H$_2$ (reaction [R8]). At high metallicity the protons are removed mainly by charge transfer with atomic oxygen

$$H^+ + O \rightarrow H + O^+.$$  \hspace{1cm} (R14)

Reactions with molecules

$$H^+ + OH \rightarrow OH^+ + H,$$  \hspace{1cm} (R15)

$$H^+ + SiO \rightarrow H + SiO^+,$$  \hspace{1cm} (R16)

may also contribute to the removal of H$^+$ in some parts of our parameter space. At low metallicity, radiative recombination

$$H^+ + e \rightarrow H + \nu,$$ \hspace{1cm} (R17)

is the dominant H$^+$ removal mechanism.

As we discuss further below, ionization of atomic hydrogen is the major source of free electrons at low metallicity, and the protons then carry all of the positive charge. At high metallicity, electrons are provided by ionization of heavy elements, and the positive charge is carried by metal ions and/or molecular ions.

Helium atoms and ions interact with hydrogen species and also with CO molecules. He$^+$ is produced by crx-ionization

$$He + crx \rightarrow He^+ + \nu.$$ \hspace{1cm} (R18)

At high metallicity, He$^+$ is neutralized by dissociative charge transfer with CO

$$He^+ + CO \rightarrow He + O + C^+.$$ \hspace{1cm} (R19)

At low metallicity, the He$^+$ ions are removed rapidly by charge transfer and dissociative charge transfer with H and H$_2$

$$He^+ + H \rightarrow He + H^+,$$ \hspace{1cm} (R20)

$$He^+ + H_2 \rightarrow He + H_2^+ \rightarrow He + H^+ + H.$$ \hspace{1cm} (R21)

Because these reactions are rapid, the He$^+$ fraction remains small. Finally, the molecular ion HeH$^+$ is produced via

$$He + H_2^+ \rightarrow HeH^+ + H,$$ \hspace{1cm} (R23)

and is removed by

$$HeH^+ + H_2 \rightarrow He + H_3^+,$$ \hspace{1cm} (R24)

or by

$$HeH^+ + H \rightarrow He + H_3^+,$$ \hspace{1cm} (R25)

depending on the H/H$_2$ ratio. In our parameter space the formation of HeH$^+$ via radiative association

$$He + H^+ \rightarrow HeH^+ + \nu,$$ \hspace{1cm} (R26)

followed by reactions [R25] and [R6] is a negligible source of H$_2$ compared to the H$^+$ formation route. But in the recombination era, prior to the appearance of ionization sources and with the rapid removal of the H$^+$ by the thermal background radiation (at redshifts $z \gtrsim 100$), this was a major source of H$_2$, as was the sequence [R5]-[R6].

### 2.2 Oxygen: OH, H$_2$O, and O$_2$

Our oxygen network includes O, O$^+$, OH$^+$, H$_2$O$^+$, H$_3$O$^+$, OH, H$_2$O and O$_2$, and also silicon-oxygen and sulfur-oxygen species, and the carbon-oxygen branches described in [23]. In Figure 2 we show the oxygen-hydride portion of the network, with our focus on the formation and destruction of OH, H$_2$O, and O$_2$. At temperatures $\lesssim 300$ K, the production of OH and H$_2$O is initiated by charge transfer

$$O + H^+ \Rightarrow O^+ + H,$$ \hspace{1cm} (R14)

$$O^+ + H_2 \rightarrow OH^+ + H,$$ \hspace{1cm} (R27)

or by proton transfer

$$O + H_3^+ \rightarrow OH^+ + H_2,$$ \hspace{1cm} (R28)
followed by the rapid abstractions

\[
\begin{align*}
\text{OH}^+ + \text{H}_2 & \rightarrow \text{H}_2\text{O}^+ + \text{H} \quad \text{(R29)} \\
\text{H}_2\text{O}^+ + \text{H}_2 & \rightarrow \text{H}_2\text{O}^+ + \text{H} \quad \text{(R30)}
\end{align*}
\]

The sequence is terminated by dissociative recombination

\[
\begin{align*}
\text{H}_2\text{O}^+ + e & \rightarrow \text{OH} + \text{H} + \text{H} \quad \text{(R31)} \\
\text{H}_2\text{O}^+ + e & \rightarrow \text{OH} + \text{H}_2 \quad \text{(R32)} \\
& \rightarrow \text{H}_2\text{O} + \text{H} \quad \text{(R33)} \\
& \rightarrow \text{O} + \text{H}_2 + \text{H} \quad \text{(R34)}
\end{align*}
\]

which yields the \text{OH} and \text{H}_2\text{O} molecules. When the fractional ionization is large, the abstraction sequence may be interrupted by dissociative recombination of the reactive ions

\[
\begin{align*}
\text{H}_2\text{O}^+ + e & \rightarrow \text{OH} + \text{H} \quad \text{(R35)} \\
& \rightarrow \text{O} + \text{H}_2 \quad \text{(R36)} \\
& \rightarrow \text{O} + \text{H} + \text{H} \quad \text{(R37)}
\end{align*}
\]

and

\[
\text{OH}^+ + e \rightarrow \text{O} + \text{H} \quad \text{(R38)}
\]

Importantly, at high metallicities \text{OH} is removed mainly by rapid reactions with oxygen atoms

\[
\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H} \quad \text{(R39)}
\]

Additional removal reactions are

\[
\begin{align*}
\text{OH} + \text{C} & \rightarrow \text{CO} + \text{H} \quad \text{(R40)} \\
\text{OH} + \text{C}^+ & \rightarrow \text{CO}^+ + \text{H} \quad \text{(R41)} \\
\text{OH} + \text{Si}^+ & \rightarrow \text{SiO}^+ + \text{H} \quad \text{(R42)}
\end{align*}
\]

At low metallicity, \text{OH} is removed mainly by charge transfer with protons

\[
\text{OH} + \text{H}^+ \rightarrow \text{OH}^+ + \text{H} \quad \text{(R43)}
\]

Reaction \text{[R44]} is a destruction channel because some of the \text{OH}^+, \text{H}_2\text{O}^+, and \text{H}_2\text{O}^+ ions undergo dissociative-recombination leading directly to atomic oxygen and to the complete breakup of the chemical bonds. The transition from \text{OH} removal by oxygen atoms to removal by protons is crucial for the behavior of the \text{OH} abundances with varying metallicity and ionization parameter, as we describe in detail in \text{[3]} and \text{[6]}.

In addition to \text{OH}, the dissociative recombination of \text{H}_2\text{O}^+ yields \text{H}_2\text{O} molecules (reaction \text{[R33]}). At high metallicities the \text{H}_2\text{O} is removed by rapid reactions with metal species

\[
\begin{align*}
\text{H}_2\text{O} + \text{C}^+ & \rightarrow \text{HCO}^+ + \text{H} \quad \text{(R44)} \\
\text{H}_2\text{O} + \text{Si}^+ & \rightarrow \text{SiOH}^+ + \text{H} \quad \text{(R45)} \\
\text{H}_2\text{O} + \text{HCO}^+ & \rightarrow \text{H}_2\text{O}^+ + \text{CO} \quad \text{(R46)}
\end{align*}
\]

but it is also removed by

\[
\text{H}_2\text{O} + \text{H}_3^+ \rightarrow \text{H}_2\text{O}^+ + \text{H}_2 \quad \text{(R47)}
\]

At low metallicity the \text{H}_2\text{O} is removed by

\[
\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_2\text{O}^+ + \text{H} \quad \text{(R48)}
\]

This is a removal mechanism for the \text{H}_2\text{O} (as is \text{[R15]} for \text{OH}) because some of the \text{H}_2\text{O}^+ ions are removed by dissociative recombination rather than reentering the abstraction sequence that leads back to \text{H}_2\text{O}.

Following the formation of \text{OH} via \text{[R14]}–\text{[R32]}, \text{O}_2 is produced by

\[
\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H} \quad \text{(R39)}
\]

which as stated above is also the primary \text{OH} removal reaction at high metallicity. At high metallicity, the \text{O}_2 is removed by

\[
\begin{align*}
\text{O}_2 + \text{C} & \rightarrow \text{CO} + \text{O} \quad \text{(R49)} \\
\text{O}_2 + \text{C}^+ & \rightarrow \text{CO} + \text{O}^+ \quad \text{(R50)} \\
& \rightarrow \text{CO}^+ + \text{O} \quad \text{(R51)} \\
\text{O}_2 + \text{Si} & \rightarrow \text{SiO} + \text{O} \quad \text{(R52)}
\end{align*}
\]

The \text{O}_2 is also removed by internal photodissociation induced by secondary electron excitations of the \text{H}_2 (\text{Sternberg, Dalgarno & Lepp 1987; Gredel et al. 1989; Heays et al. 2014}). Here and below, we refer to induced photodissociation with the label “crxp”. Thus,

\[
\text{O}_2 + \text{crxp} \rightarrow \text{O} + \text{O} \quad \text{(R53)}
\]

At low metallicity, the \text{O}_2 is removed by protons in the sequence

\[
\begin{align*}
\text{O}_2 + \text{H}^+ & \rightarrow \text{O}_2^+ + \text{H} \quad \text{(R54)} \\
\text{O}_2^+ + \text{e} & \rightarrow \text{O} + \text{O} \quad \text{(R55)}
\end{align*}
\]

rather than by reactions with metal atoms and ions.

When any penetrating FUV radiation is present direct photodissociation and photoionization can become important in reducing the \text{OH}, \text{H}_2\text{O}, and \text{O}_2 abundances. We discuss the FUV photo-processes further in \text{[2,4]}.

### 2.3 Carbon: CH and CO

Our carbon-oxygen network is shown in Figure 3. It includes \text{C}, \text{C}^+, \text{CH}^+, \text{CH}_2^+, \text{CH}_3^+, \text{CH}, \text{CH}_2, \text{CO}^+, \text{HCO}^+, and \text{CO}. We are mainly interested in the formation and destruction of CH and CO.
The production of CH is initiated by the formation of CH\textsuperscript{+} via proton transfer and abstraction
\[
\text{C} + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}_2 \quad \text{(R56)} \\
\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H} \quad \text{(R57)}
\]
or by direct radiative association
\[
\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \nu \quad \text{(R58)}
\]
The relative efficiencies of [R56]-[R57] versus [R58] depend on the C\textsuperscript{+}/C ratio. The formation of CH\textsubscript{2}\textsuperscript{+} is followed by
\[
\text{CH}_2^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H} \quad \text{(R59)}
\]
and then dissociative-recombination
\[
\text{CH}_3^+ + \text{e} \rightarrow \text{CH}_2 + \text{H} \quad \text{(R60)} \\
\rightarrow \text{CH} + \text{H}_2 \quad \text{(R61)} \\
\rightarrow \text{CH} + \text{H} + \text{H} \quad \text{(R62)}
\]
terminating in the production of CH (and CH\textsubscript{2}). When the fractional ionization is large the abstraction sequence is moderated by
\[
\text{CH}^+ + \text{e} \rightarrow \text{C} + \text{H}_2 \quad \text{(R63)} \\
\text{CH}_2^+ + \text{e} \rightarrow \text{CH} + \text{H} + \text{H} \quad \text{(R64)} \\
\rightarrow \text{C} + \text{H} + \text{H} \quad \text{(R65)} \\
\rightarrow \text{C} + \text{H}_2 \quad \text{(R66)}
\]
and
\[
\text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2 \quad \text{(R67)}
\]
Reaction [R65] is an additional source of CH, but overall these moderating reactions tend to reduce the CH formation efficiency. When the e/H ratio is small
\[
\text{CH}_2 + \text{H} \rightarrow \text{CH} + \text{H}_2 \quad \text{(R68)}
\]
also contributes to CH formation.

In most of our parameter space, the dominant CH destruction reaction is
\[
\text{CH} + \text{H} \rightarrow \text{C} + \text{H}_2 \quad \text{(R69)}
\]
This, in contrast with OH, which is not removed by H atoms,\textsuperscript{3} the destruction efficiency increases with the atomic hydrogen fraction, and CH therefore disappears as the metallicity is reduced. We discuss this further in \[5\] where we show that CH vanishes compared to OH as the metallicity is reduced.

We now consider CO, which is produced via several channels. First is via OH,
\[
\text{C} + \text{OH} \rightarrow \text{CO} + \text{H} \quad \text{(R70)}
\]
or
\[
\text{C}^+ + \text{OH} \rightarrow \text{CO}^+ + \text{H} \quad \text{(R71)} \\
\text{CO}^+ + \text{H} \rightarrow \text{CO} + \text{H}^+ \quad \text{(R72)}
\]
Reactions [R70]-[R74] are the CO production pathways via the “OH-intermediary”. For a given OH abundance, the relative efficiencies of these reactions depend on the C\textsuperscript{+}/C and H/H\textsubscript{2} density ratios. As we will discuss below, CO production via OH always dominates in the low Z’ limit.

At sufficiently high Z’, the CH/OH ratio may become large (see \[5.1\]), and CO is then also produced by
\[
\text{O} + \text{CH} \rightarrow \text{CO} + \text{H} \quad \text{(R75)} \\
\text{O} + \text{CH}_2 \rightarrow \text{CO} + \text{H}_2 \rightarrow \text{CO} + \text{H} + \text{H} \quad \text{(R76)(R77)}
\]
Another route is via chemionization
\[
\text{O} + \text{CH} \rightarrow \text{HCO}^+ + \text{e} \quad \text{(R78)} \\
\text{HCO}^+ + \text{e} \rightarrow \text{CO} + \text{H} \quad \text{(R74)}
\]
Reactions [R74]-[R78] are the CO production pathways via the “CH intermediary”. At sufficiently high metallicity (but mostly outside our parameter space) these reactions also contribute to the removal of the CH in addition to removal by H atoms.

CO formation can also proceed via
\[
\text{O}_2 + \text{C} \rightarrow \text{CO} + \text{O} \quad \text{(R49)} \\
\text{O}_2 + \text{C}^+ \rightarrow \text{CO} + \text{O}^+ \rightarrow \text{CO}^+ + \text{O} \quad \text{(R50)(R51)}
\]
followed by [R72]-[R74]. These reactions are the CO production pathways via the “O\textsubscript{2} intermediate”. As we discuss below, CO

\footnote{The binding energies of H\textsubscript{2}, OH, and CH are 4.48, 4.41 and 3.49 eV respectively. The reaction OH + H → O + H\textsubscript{2} is endothermic, but it has a large barrier (Balakrishnan 2004, van Dishoeck, Herbst & Neufeld 2013) and is ineffective in cold gas. CH + H → C + H\textsubscript{2} is much more energetically favorable, and is rapid at low temperatures (Grebe & Homann 1992, Harding, Guadaoanni & Schatz 1995).}
formation via O_2 becomes important at low ζ/n in the molecular regime where the O_2/OH abundance ratio can become large.

In the absence of FUV photodissociation, CO is destroyed mainly by dissociative charge transfer with He^+,
\[ \text{He}^+ + \text{CO} \rightarrow \text{He} + \text{O} + \text{C}^+ . \]  \text{(R19)}

This is the primary CO removal mechanism at all metallicities.

Reaction \text{(R19)} is a major source of C^+ when much of the carbon is locked in CO, as occurs at high-metallicity. An additional source of C^+, at all metallicities, is via crxp-ionization of any free carbon atoms
\[ \text{C} + \text{crxp} \rightarrow \text{C}^+ + e^- . \]  \text{(R79)}

The C^+ ions are removed by radiative recombination
\[ \text{C}^+ + e^- \rightarrow \text{C} + \nu , \]  \text{(R80)}

charge transfer
\[ \text{C}^+ + \text{S} \rightarrow \text{C} + \text{S}^+ , \]  \text{(R81)}

radiative association (reaction \text{(R55)}), and via the CO-forming reactions with OH or O_2 (reaction \text{(R71)} and \text{(R50)}-\text{(R51)}).

At high metallicity reactions \text{(R51)}, \text{(R82)}, and induced photodissociation
\[ \text{CO} + \text{crxp} \rightarrow \text{C} + \text{O} , \]  \text{(R83)}

dominate the production of free atomic carbon. The carbon atoms are removed by induced ionization (reaction \text{(R79)}), by
\[ \text{C} + \text{H}^+_3 \rightarrow \text{CH}^+ + \text{H}_2 , \]  \text{(R50)}

and also by the CO-forming reactions with OH and O_2 (reactions \text{(R70)} and \text{(R79)}).

At low metallicity the C^+/C ratio is set by the balance between induced photoionization \text{(R79)} and radiative-recombination \text{(R80)}.

\subsection{2.4 Photoprocesses}

We also present computations including the effects of photodissociation and photoionization by externally incident FUV radiation. At very low metallicities, dust shielding may be ineffective, and photoprocesses will become significant in the presence of FUV. However, we assume that even at low Z', the gas parcels are always shielded by H_2 gas columns \(\geq 10^{22} \text{cm}^{-2}\) that completely block the 918-1108 Å LW band via fully overlapping H_2 absorption lines (e.g. Sternberg et al. 2014).

For such conditions, species such as C or CO with photodestruction thresholds within the LW band are fully shielded against the FUV. But for species with thresholds longward of 1108 Å, removal by FUV radiation can become important. This includes photodissociation
\[ \text{OH} + \nu \rightarrow \text{O} + \text{H} \]  \text{(R84)}
\[ \text{H}_2\text{O} + \nu \rightarrow \text{OH} + \text{H} \]  \text{(R85)}
\[ \rightarrow \text{O} + \text{H}_2 \]  \text{(R86)}
\[ \text{O}_2 + \nu \rightarrow \text{O} + \text{O} \]  \text{(R87)}
\[ \text{CH} + \nu \rightarrow \text{C} + \text{H} \]  \text{(R88)}

\section{3 RATE EQUATIONS}

In our chemical computations we examine how the steady state abundances of atomic and molecular hydrogen, H and H_2, and heavy metal-bearing species, especially OH, H_2O, O_2, CH and CO, depend on the overall heavy element abundances as parameterized by the metallicity scaling factor Z', and on the ionization parameter ζ/n. Here ζ is the total (primary plus secondary) H_2 ionization rate (s^{-1}), and n \approx n_{\text{H}1} + 2n_{\text{H}2} is the total volume density (cm^{-3}) of hydrogen nuclei in the gas parcels, where n_{\text{H}1} and n_{\text{H}2} are the atomic and molecular densities respectively. We assume that the parcels are exposed to steady sources of crxp-ionization. We write the ionization rate as ζ = 10^{-16}ζ_{-16} s^{-1} where ζ_{-16} \approx 1 is the characteristic Galactic value as inferred via

\url{http://home.strw.leidenuniv.nl/~ewine/photo/}

\copyright 0000 RAS, MNRAS 000, 000–000
Table 2. Photodissociation rates for $I_{UV} = 1$

| Reaction                  | Threshold (eV) | Draine Photonrate $\Gamma$ ($10^{-10}$ s$^{-1}$) |
|---------------------------|---------------|--------------------------------------------------|
|                          |               | Draine thick LW-blocked | Draine thin LW-blocked | Diluted $10^5$ K |
| OH $+$ $\nu$ $\rightarrow$ O $+$ H$_2$ | 6.4 | 3.8 | 2.8 | 4.7 | 2.5 |
| H$_2$O $+$ $\nu$ $\rightarrow$ O $+$ H$_2$ | 9.5 | 0.49 | 0.28 | 1.1 | 0.32 |
| H$_2$O $+$ $\nu$ $\rightarrow$ OH $+$ H | 6.0 | 7.5 | 5.5 | 11.7 | 4.8 |
| O$_2$ $+$ $\nu$ $\rightarrow$ O $+$ O | 7.0 | 7.9 | 7.0 | 9.4 | 5.1 |
| CH $+$ $\nu$ $\rightarrow$ C $+$ H | 3.4 | 9.0 | 8.8 | 5.5 | 4.7 |
| CO $+$ $\nu$ $\rightarrow$ C $+$ O | 11.5$^a$ | 2.6 | 0.0 | 14.2 | 0.0 |
| C $+$ $\nu$ $\rightarrow$ C$^+$ $+$ e | 11.3 | 3.2 | 0.0 | 10.1 | 0.0 |
| CH $+$ $\nu$ $\rightarrow$ CH$^+$ $+$ e | 3.4 | 7.7 | 0.97 | 21.3 | 1.4 |
| H$^-$ $+$ $\nu$ $\rightarrow$ H $+$ e | 0.75$^a$ | 145.2 | 145.1 | 23.1 | 20.7 |

$^a$ CO photodissociation occurs via absorption-line predissociation (Visser, van Dishoeck & Black 2009) and 11.5 eV is the lowest photon energy in this multilane process.

$^b$ In computing the photodeattachment rate we adopt the normalized Draine and diluted $10^5$ K photon intensities from 13.6 eV all the way to the H$^-$ electron detachment threshold of 0.75 eV.

H$^+$ observations of clouds with H$_2$ column densities $\geq 10^{21}$ cm$^{-2}$ (McCall et al. 2003, Indriolo & McCall 2012, Tielens 2013). We write the density $n = 10^3 n_3$ cm$^{-3}$, where $n_3 \approx 1$ is the characteristic density for star-forming molecular clouds in the Milky Way (McKee & Ostriker 2007). We adopt the chemical networks described in [2] We employ the reaction rate coefficients used by Boger & Sternberg (2005), which are based mainly on the UMIST99 database (Le Teuff, Millar & Markwick 2000) with some updates. The data compiled in UMIST12 (McElroy et al. 2013) or KIDA (Wakelam et al. 2012) do not differ significantly for our reaction networks, and we have verified by explicit computation that our results are insensitive to the data set used$^4$.

For H$_2$ formation on grains we assume a rate coefficient per hydrogen nucleus (Hollenbach, Werner & Salpeter 1971; Jura 1974; Cazaux & Tielens 2002; Sternberg et al. 2014)

$$R = 3 \times 10^{-17} \left( \frac{T}{100 \text{K}} \right)^{0.5} Z_i^3 \text{ cm}^3 \text{ s}^{-1} .$$

The rate coefficient depends on the dust-to-gas ratio, and we assume that this varies as a power law, $Z_i^3$, of the metallicity. We also assume that even for $Z' \equiv 1$ only a small fraction of the heavy elements are locked in grains. For the gas phase elemental abundances, we adopt the Asplund et al. (2009) solar photospheric values (Table I), multiplied by the overall metallicity factor $Z'$, with no grain depletion factors at any $Z'$.

3.1 FUV off

In the absence of externally incident FUV radiation, the steady state densities, $n_i$ (cm$^{-3}$), of the atomic and molecular species are determined by the set of formation-destruction rate equations,

$$\sum_{il} k_{ijl}(T) n_j n_l + \zeta \left[ \sum_{j} a_{ij}^D n_j + x_{H_2} \sum_{j} a_{ij}^P n_j \right]$$

$$= n_i \left[ \sum_{jl} k_{ijl}(T) n_l + \zeta \left[ \sum_{j} a_{ij}^D + x_{H_2} \sum_{j} a_{ij}^P \right] \right] . \quad (2)$$

The $k_{ijl}(T)$ 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 $i$. The $a_{ij}^D$ are constants that multiply the total H$_2$ ionization rate $\zeta$, and are divided into two parts. The $a_{ij}^P$ are for direct removal of species $j$ by the energetic (ionizing) particles, leading to the production of $i$. The $a_{ij}^D$ are for induced photodestruction (crxp) by the internal UV photons produced by secondary-electron excitations of the H$_2$. The rates of the crxp processes are proportional to the H$_2$ gas density, and the $a_{ij}^P$ are therefore multiplied by the H$_2$ fraction, $x_{H_2} \equiv n_{H_2}/n$.

The set of formation-destruction equations are augmented by mass and charge conservation. Thus,

$$\sum_i \alpha_{im} n_i = X_m n$$

where $\alpha_{im}$ is the number of atoms of element $m$ contained in species $i$, and $X_m$ is the total gas-phase abundance of element $m$ relative to the hydrogen density $n$ of nucleons. For the metals

$$X_m = A_m Z' ,$$

where $A_m$ is the solar abundance of element $m$ as given by Table[1]. For helium we assume a constant cosmological abundance $A_{He} = 0.1$. Charge conservation is,

$$\sum_i q_i n_i = 0$$

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

$^5$ An exception is the position of the LIP/HIP boundary (see below) which can be sensitive to small rate-coefficient variations.
Dividing the rate equations by \( n^2 \) gives
\[
\sum_{j l} k_{ijl}(T) x_j x_l + \frac{\zeta}{n} \left[ \sum_j a_{ij}^D x_j + x_{H_2} \sum_j a_{ij}^P x_j \right] = x_l \left\{ \sum_{j l} k_{ijl}(T) x_i + \frac{\zeta}{n} \left[ \sum_j a_{ij}^D + x_{H_2} \sum_j a_{ij}^P \right] \right\},
\]
where \( x_i \equiv n_i/n \) are the fractional abundances of species \( i \) relative to the total hydrogen gas density. This shows that for a given \( Z' \) (and with \( X_{\text{HI}} = A_m Z' \) for the metals) and for a given gas temperature, the fractional abundances depend only on the ionization parameter \( \zeta/n \) (e.g., Lepp & Dalgarno 1996; Boger & Sternberg 2009). We consider isothermal gas, and thus the two basic parameters in our study are \( \zeta/n \) and the metallicity \( Z' \).

The rate equations are non-linear, and we solve them iteratively using Newton’s method.

### 3.2 FUV on

In the presence of externally incident FUV radiation (\( \lambda < 24 \AA \)), photodissociation and photoionization processes must be added to the formation-destruction equations. These are then,
\[
\sum_{j l} k_{ijl}(T) x_j n_l + \zeta \left[ \sum_j a_{ij}^D x_j + x_{H_2} \sum_j a_{ij}^P x_j \right] + \frac{I_{\text{UV}}}{n} \sum_j b_{ij} x_j \left\{ \sum_{j l} k_{ijl}(T) n_l \right\} + \zeta \left[ \sum_j a_{ij}^D + x_{H_2} \sum_j a_{ij}^P \right] + \frac{I_{\text{UV}}}{n} \sum_j b_{ij} \right\} .
\]

The \( b_{ij} I_{\text{UV}} \) in the additional terms are the photodissociation or photoionization rates \( \left( \text{s}^{-1} \right) \) of species \( j \) that produce \( i \) (Table 2).

Dividing by \( n^2 \) we have,
\[
\sum_{j l} k_{ijl}(T) x_j x_l + \frac{\zeta}{n} \left[ \sum_j a_{ij}^D x_j + x_{H_2} \sum_j a_{ij}^P x_j \right] + \frac{I_{\text{UV}}}{n} \sum_j b_{ij} x_j = x_l \left\{ \sum_{j l} k_{ijl}(T) x_i \right\} + \zeta \left[ \sum_j a_{ij}^D + x_{H_2} \sum_j a_{ij}^P \right] + \frac{I_{\text{UV}}}{n} \sum_j b_{ij} \right\} .
\]

When FUV radiation is present a third parameter enters, \( I_{\text{UV}}/n \), the ratio of the FUV intensity to the gas density. Here \( I_{\text{UV}}/n \) refers to the local FUV intensity inside the gas parcel, after accounting for any shielding by an outer dust-absorption layer.

We assume that the LW band is always fully blocked by a shielding H2 gas column of at least \( 10^{22} \) cm\(^{-2} \). For an LW H2 blocking column \( N_{\text{H}_2}^{\text{block}} = 10^{22} \) cm\(^{-2} \) the associated 1000 Å dust opacity is \( \tau_{1000} = 2 \sigma_g N_{\text{H}_2}^{\text{block}} \approx 38 Z'^2 \), where \( \sigma_g = 1.9 \times 10^{-21} \) cm\(^2\) is the dust cross-section per hydrogen nucleon (Draine 2003; Sternberg et al. 2014). Thus when turning on the FUV field in Equations 2 and 3,
\[
I_{\text{UV}} = I_{\text{UV}}^0 e^{-\tau_{1000}} = I_{\text{UV}}^0 e^{-38 Z'^2 / \theta},
\]
where \( I_{\text{UV}}^0 \) is the unshielded free space intensity factor. In this expression we are assuming that the dust opacity associated with any HI in the shielding layer is negligible. This is a valid assumption provided \( I_{\text{UV}}^0/n_3 \lesssim 10^{12} \).\(^{6}\)

Our expression for \( I_{\text{UV}} \) allows the local field intensity inside the parcels to vary smoothly as we vary \( Z' \), and as the effects of dust shielding are altered. For simplicity, and because we are assuming an arbitrary shielding column, we ignore the wavelength dependence of the dust attenuation for the individual species in our set. For high enough \( Z' \), the dust opacity becomes large and all of the photorates vanish due to significant dust shielding. When the metallicity is low, \( \tau_{1000} \) is small, but the LW band remains blocked. Species that are removed by \( \lambda > 1108 \) Å photons are only partially shielded, or not at all for sufficiently small \( Z' \).

### 4 H/H2 BALANCE ANALYTIC TREATMENT, AND TIME SCALES

Before presenting our detailed chemical computations (in §5 and 6) we consider just H2 formation-destruction and the behavior of the H/H2 density ratio, in a simplified analytic treatment, showing the dependence on \( \zeta/n \) and \( Z' \). Our analysis generalizes previous discussions (e.g., Jee 1972; Glover 2008). We also consider the dependences of the H2 formation time-scales on \( Z' \) and \( \zeta/n \). The H2 formation time-scales determine the overall conditions required for chemical equilibrium.

#### 4.1 Steady State H/H2

As discussed in §2.1 the two primary H2 formation channels are grain catalysis (reaction [R1]) and gas phase production via H+ (R2) and (R3). In the absence of FUV photodissociation, the H2 is removed by crx-ionization (reactions [R6] and [R7]) leading mainly to the formation of H+ (reaction [R9]). However, when the gas is atomic the net H2 removal rate is reduced by electron charge transfer from H to H+ (reaction [R6]).

Thus, the H/H2 formation-destruction equation for steady state conditions is
\[
\zeta x_f \times f d x_{H_2} = [R n + k_2 n_e] x_{H_2} ,
\]
with
\[
2 n_{H_2} + n_{H} = n ,
\]
or
\[
\left( \frac{\zeta}{n} \right) x_f \times f d x_{H_2} = [R + k_2 x_e] x_{H_2} ,
\]
with
\[
2 x_{H_2} + x_{H} = 1 .
\]

\(^6\) This follows from the Sternberg et al. (2014) expression for the photodissociated HI column in the “weak field” limit (\( I_{\text{UV}}/n_3 \lesssim 10 \)) and at low metallicity (\( \omega = 1 \)) for which the HI column

\[
N_{\text{HI}} = \frac{1}{\sigma_g} \ln[0.1 \sigma_g n F_0/(2 R n)] + 0.1 \frac{F_0}{(2 R n)} \approx 4 \times 10^{18} Z'^{2/3} (I_{\text{UV}}/n_3) \text{ cm}^{-2} ,
\]
where \( F_0 = 2.07 \times 10^{7} I_{\text{UV}} \text{ cm}^{-2} \) is the photon flux integrated over the LW band.
Here \( n_{H1} \) and \( n_{H2} \), and \( x_{H1} \) and \( x_{H2} \), are the atomic and molecular hydrogen densities and fractions, \( \zeta \) is the crx-ionization rate, and \( R \) is the grain-surface H2 formation rate coefficient. The rate coefficient \( k_2 \approx 2 \times 10^{-16} T_2^{0.67} \) cm\(^3\) s\(^{-1}\) (independent of \( Z' \)) is for radiative association of hydrogen atoms with electrons (reaction [2]) which is the rate limiting step for gas-phase H2 formation. On the left-hand side, the factor \( y \approx 2 \) in the molecular regime \((2x_{H2} \approx 1)\) where the H2 destruction rate is enhanced by the further reactions with \( H_2^+ \). In the atomic regime \((x_{H1} \approx 1)\) the parameter \( y \approx 1 \). The factor \( f_d \) is the fraction \( f_d \equiv \frac{\beta_{H2} \rho_{H2}}{\beta_{H2} \rho_{H2} + \beta_{H1} \rho_{H1}} \), \( \text{(14)} \)
of all H2 ionizations that are not followed by charge-transfer back to H2. In the molecular regime \( f_d \approx 1 \). In the atomic regime \( f_d \approx 3.3 x_{H1}/x_{H2} \).

In this analysis we assume that the dust-to-gas ratio varies as a power \( \beta \) of the metallicity as given by Equation [1], and write
\[
R = R_0 Z'^\beta, \quad \text{(15)}
\]
where \( R_0 \approx 3 \times 10^{-17} T_2^{1/2} \) cm\(^3\) s\(^{-1}\) is the rate coefficient for solar \((Z'=1)\) metallicity. (In our full chemical computations in \[5\] and \[6\] we set \( \beta = 1 \).)

In Equation [12], the gas phase formation term, \( k_2 x_e \), can become important only when the hydrogen is primarily atomic since then a relatively large H\(^-\) abundance can be maintained by electron attachment. We estimate \( x_e \) in the atomic-regime via the condition of ionization-recombination equilibrium
\[
0.46 \zeta n_{H1} \approx 0.46 \zeta n = \alpha_B n_{H1} + x_e \approx \alpha_B n_e^2, \quad \text{(16)}
\]
or
\[
x_e \equiv \frac{n_e}{n} = 0.68 \left( \frac{\zeta}{\alpha_B n} \right)^{0.5} = 7.6 \times 10^{-5} \left( \frac{\zeta_{-16}}{n_3} \right)^{0.5} T_2^{0.38}. \quad \text{(17)}
\]
Here we have assumed \( \alpha_B = 7.98 \times 10^{-12} T_2^{-0.75} \) cm\(^3\) s\(^{-1}\) for case B radiative recombination.

Given expressions [15] and [17] for \( R \) and \( x_e \), and setting \( x_{H1} = x_{H2} \) in Equation [12], we obtain the relation between \( \zeta/n \) and \( Z' \) for which the atomic and molecular densities are equal. These are the solid curves in Figure 5 for \( \beta = 1, 2, 3 \), and 4, and assuming \( T = 100 \) K. For any \( \beta \), the curves flatten when \( Z' \) is sufficiently small and gas-phase H2 formation dominates. In this limit \( R_{H1} \) is negligible in Equation [12], and for \( x_{H1} = x_{H2} \)
\[
f_d \times y \times \frac{\zeta}{n} = k_2 x_e. \quad \text{(18)}
\]
Assuming \( y = 2 \), \( f_d = 1 \) at the H-to-H2 transition point (justified by the results of our detailed numerical solutions), and assuming Equation [17] for the fractional ionization, the ionization parameter for which \( x_{H1} = x_{H2} \) is given by
\[
\frac{\zeta}{n} = 0.12 \frac{k_2^2}{\alpha_B}. \quad \text{(19)}
\]
Thus for gas-phase H2 formation (low \( Z' \) limit), the atomic-to-molecular transition occurs at
\[
\frac{\zeta_{-16}}{n_3} \approx 5.7 \times 10^{-3} T_2^{1/2} Z'^{\beta}, \quad \text{(20)}
\]
as seen in Figure 5 for very low \( Z' \).

At sufficiently high \( Z' \), grain H2 catalysis dominates, the H2 formation efficiency increases as \( Z'^{\beta} \), and the H2/H transition curves turn upward. Then, neglecting the gas phase formation term \( k_2 n_e \) in Equation [12], and again setting \( y = 2 \) and \( f_d = 1 \) we have
\[
\frac{\zeta_{-16}}{n_3} = 0.5 R_0 Z'^{\beta}. \quad \text{(21)}
\]
This gives
\[
\frac{\zeta_{-16}}{n_3} \approx 1.5 \times 10^2 T_2^{1/2} Z'^{2\beta} \quad \text{(22)}
\]
for the H2 transition curves for H2 grain catalysis. For example, for \( \beta = 2 \), the H-to-H2 transition occurs at \( \zeta_{-16}/n_3 \approx 1.5 \) for \( Z' = 1 \), or at \( \zeta_{-16}/n_3 \approx 1.5 \times 10^2 \) for \( Z' = 1 \).

In Figure 5 the dashed lines delineate the zones where gas-phase production (to the left) versus grain catalysis (to the right) dominates H2 formation in the atomic regimes \((x_H \approx 1)\) above the solid curves. We draw these by equating the two formation rates
\[
R_0 Z'^{\beta} = x_e k_2 \quad \text{(23)}
\]
and using Equation [17] for \( x_e \). This gives
\[
\frac{\zeta}{n} = 2.2 \left( \frac{R_0 Z'^{\beta}}{k_2} \right)^2 \alpha_B, \quad \text{(24)}
\]
or
\[
\frac{\zeta_{-16}}{n_3} = 4 \times 10^6 T_2^{-1.1} Z'^{2\beta}, \quad \text{(25)}
\]
for the dashed lines in Figure 5. For example, for \( \beta = 2 \) the gas phase and grain H2 formation rates are equal for \( \zeta_{-16}/n_3 \approx 4 \times 10^{-2} \) for \( Z' = 1 \), or \( \zeta_{-16}/n_3 \approx 4 \times 10^2 \) for \( Z' = 0.1 \).

We may now define the critical metallicity \( Z'_{\text{crit}} \) at which the gas-phase and dust-grain formation rates are equal at the H-to-H2 transition point. For \( Z' < Z'_{\text{crit}} \) the H-to-H2 transition is controlled.
by the gas-phase formation. For $Z' > Z'_{\text{crit}}$, dust-formation dominates the transition. The critical metallicities occur at the intersections of the dashed and solid curves in Figure 5. These intersections may be estimated by equating Equations (20) and (22). This gives

$$Z_{\text{crit}}^{-3} \approx 0.46 \frac{k_2^3}{2 \times \alpha_B R_0} \approx 3.8 \times 10^{-5} \frac{T_2^{1.6}}{T_2}.$$  

(26)

As shown in Figure 5 for $\beta$ increasing from 1 to 4, $Z_{\text{crit}}^{-3}$ ranges from $8 \times 10^{-3}$ to 1.

Finally, using Equations (13)–(17), expressions for the H$_2$ fraction in the atomic regime ($x_H \approx 1$) may now be written down. For gas-phase formation

$$x_{H_2} \approx \frac{x_{H_2}}{x_H} = k_2 x_e \frac{1}{f_d} \frac{1\, \text{g}}{y} \left(\frac{\zeta}{n}\right)^{-1} = 0.2 \left(\frac{\zeta}{n}\right)^{-1/4} T_2^{1.5}.  \quad (27)$$

For dust catalysis

$$x_{H_2} \approx \frac{x_{H_2}}{x_H} = R_0 Z^{-3/2} \frac{1}{f_d} \frac{1\, \text{g}}{y} \left(\frac{\zeta}{n}\right)^{-1} = 0.96 T_2^{1/4} \left(\frac{\zeta}{n}\right)^{-1/2} \left(\frac{Z}{10^{-2}}\right)^{\beta/2}.  \quad (28)$$

In Equations (27) and (28) we set $y = 1$ and $f_d \approx 3.25 x_{H_2}/x_H$ as appropriate for the atomic regime.

4.2 Time Scales

In the analysis above and in our computations in Figures 1 and 2 we are assuming that the systems are in a steady state. Overall equilibrium is set by the relatively long time-scale for H$_2$ formation. For grain catalysis the H$_2$ formation time scale is

$$t_{\text{dust}}^{\text{H}_2} \approx \frac{1}{R_n} \approx 10^6 T_2^{1/2} \frac{1}{n_3} \frac{Z_{\text{crit}}^{-3}}{T_2}\text{ yr } \quad (29)$$

For the gas phase formation via H$^-$ the time scale is

$$t_{\text{gas}}^{\text{H}_2} = k_{2} n x_e \approx 2 \times 10^9 \left(\frac{\zeta}{n_3}\right)^{-1/2} T_2^{-1}\text{ yr } \quad (30)$$

where we used Equation (17) for $x_e$. The ratio of these time scales is

$$k_{2} n x_e \approx 5 \times 10^{-4} T_2^{3/2} \zeta^{-1/2} \frac{1}{n_3} \frac{1}{Z_{\text{crit}}^{-3}}.  \quad (31)$$

At solar ($Z' = 1$) metallicity, H$_2$ formation on dust is much faster than in the gas-phase unless the gas density is unusually low, or the ionization parameter is extremely large. At low $Z'$ and low dust-to-gas ratios, the gas phase formation route may become faster even at characteristic densities. Both time-scales are generally short compared to the present day age of the universe (13.8 Gyr), and the typical ages of galaxies, and H$_2$ formation is rapid for shielded gas. However, at the early reionization epoch ($z \approx 10$, or 0.48 Gyr, Hinshaw et al. 2013), the H$_2$ formation time-scale may become long. For example, at reionization, and an early metal abundance $Z' \approx 10^{-3}$ but for a Galactic $\zeta_{16}/n_3 = 1$, the dust and gas-phase H$_2$ formation time-scales are comparable even for $\beta = 1$. A large cloud density, $n \gtrsim 2 \times 10^3 \text{ cm}^{-3}$, is then required to achieve a chemical steady state, for complete conversion of H to H$_2$. For most of our parameter space the H$_2$ formation time is the longest chemical time-scale.

5 ILLUSTRATIVE 1D MODEL SEQUENCES

With the above analytic results for the steady-state H/H$_2$ balance and time scales, we now show full chemical computations for several illustrative model sequences, as one-dimensional (1D) cuts through our parameter space. We first present models for varying $Z'$ at fixed $\zeta/n$, and second for varying $\zeta/n$ at fixed $Z'$. In all of these computations we assume that the H$_2$ formation rate coefficient varies linearly with $Z'$ (i.e., we set $\beta = 1$ in Equation (1)).

We also show the proton fraction $x$ and the metallicity $Z'$. In the “low-ionization-phase” (LIP) and “ionization-phase” (HIP) for the equilibrium ionization states, depending on $Z'$. In the “high-ionization-phase” (HIP) the electrons are removed by a combination of H$^+$ dissociative recombination and radiative recombination of the atomic metal ions. In the “low-ionization-phase” (LIP) the electrons are removed mainly by dissociative recombination with molecular metal ions. In purely gas-phase systems the HIP to LIP transition can be abrupt due to instabilities in the chemical networks (e.g. Boger & Sternberg 2006). The model sequence in Figure 6 is for fixed $\zeta/n_3 = 1$, and varies $Z'$ from 1 to $10^{-4}$.

5.1 Dependence on $Z'$ for fixed $\zeta/n_3$

In Figure 6, we display the steady-state abundances, $x_i \equiv n_i/n$, for H, H$_2$, H$^-$, e, C, O, OH, H$_2$O, O$_2$, CH and CO. In these computations we set $\zeta_{16}/n_3 = 1$, and vary $Z'$ from 1 to $10^{-4}$. Again, we are assuming that the LW band is always blocked so that H$_2$ and CO photodissociation is always excluded whether or not an FUV background field is present.

The upper left panel shows the behavior for H and H$_2$. For $Z' \gtrsim 10^{-2}$, H$_2$ formation by dust-grain catalysis is rapid compared to H$_2$ removal by crx-ionization, and the gas is fully molecular. The atomic hydrogen fraction increases as grain H$_2$ formation becomes less efficient with decreasing $Z'$ according to Equation (1). The H-to-H$_2$ transition occurs at $Z' \approx 10^{-2}$, and is consistent with Equation (23) for $\zeta_{16}/n_3 = 1$. The H$_2$ abundance continues to drop as $Z'$ is reduced and as the molecular formation efficiency decreases. The curve for $x_{H_2}$ flattens as $Z'$ becomes very small and gas-phase formation starts contributing. As given by our Equation (25), gas-phase formation dominates for $Z' \lesssim 5 \times 10^{-4}$. In this limit we find that $x_{H_2}$ approaches 0.13, consistent with Equation (29).

The upper-right panel of Figure 6 shows the electron fraction $x_e$. It also shows the summed fractions of the metal positive charge carriers. For our assumed $\zeta_{16}/n_3 = 1$, these are mainly the atomic ions C$^+$, Si$^+$, and S$^+$. The metal positive charge carriers are collectively labeled “metal-ions” in Figure 6. This panel also shows the proton fraction $x_{H_+}$. In general, the interstellar gas-phase chemical sequences yield two types of solutions (HIP and LIP) for the equilibrium ionization states, depending on $\zeta/n_3$ and the gas-phase elemental abundances (Oppenheimer & Dalgarno 1974; Pineau des Forêts, Roueff & Flower 1992; Lee et al. 1998; Boger & Sternberg 2006; Wakelam et al. 2006). In the “high-ionization-phase” (HIP) the electrons are removed by a combination of H$^+$ dissociative recombination and radiative recombination of the atomic metal ions. In the “low-ionization-phase” (LIP) the electrons are removed mainly by dissociative recombination with molecular metal ions. In purely gas-phase systems the HIP to LIP transition can be abrupt due to instabilities in the chemical networks (e.g. Boger & Sternberg 2006). The model sequence in Figure 6 is for fixed $\zeta_{16}/n_3 = 1$. At $Z' = 1$, $x_e \approx 5 \times 10^{-5}$ and the positive charge is carried by the metal ions. As $Z'$ is reduced the total metal ion fraction drops linearly, and $x_e$ decreases accordingly. Meanwhile, the proton fraction rises with the increasing abundance of free hydrogen atoms available for direct crx-ionization (reaction (1)). The decreasing metal-ion densities together with the increasing abundance of protons leads to the minimum $x_e \approx 6 \times 10^{-6}$ at $Z' \approx 4 \times 10^{-2}$. At
very low $Z'$, H$^+$ becomes the dominant positive charge carrier, and $x_e$ increases until the gas becomes fully atomic. He$^+$ does not contribute significantly because it is rapidly removed by charge transfer (reactions $[R19]$–$[R22]$). In the fully atomic regime the electron fraction reaches a plateau of $x_e \approx 7 \times 10^{-5}$, consistent with Equation (17) for the balance between hydrogen ionization and electron-proton radiative recombination.

The middle-left panels of Figure 6 show the abundance fractions $x_i$ versus $Z'$, for C, O, OH, H$_2$O, O$_2$, CH, and CO, for FUV off. These fractions are relative to the total hydrogen gas density. In the lower-left panels we normalize relative to the total available oxygen or carbon at each $Z'$, and plot curves for C/C$_{tot}$, CH/C$_{tot}$, CO/C$_{tot}$, O/0$_{tot}$, OH/0$_{tot}$, H$_2$O/0$_{tot}$, and O$_2$/0$_{tot}$.

Several important features and trends can be seen. First, at high $Z'$, the dominant metal-bearing molecule is CO. For example for $Z' \approx 1$, $x_{CO} \approx 8 \times 10^{-5}$ and CO/C$_{tot} \approx 0.3$. When the hydrogen is molecular ($Z' \gtrsim 10^{-2}$), at least 30% of the available carbon is locked in CO with the remaining carbon in atomic form. Because O$_{tot}$/C$_{tot} > 1$ in our models a large fraction of the oxygen always remains atomic. The large CO abundance is the familiar chemical state for standard interstellar molecular clouds. Figure 6 shows that CO production is efficient at all $Z'$ so long as the hydrogen is molecular. In the absence of selective photodissociation the CO then serves as a good proxy for the $H_2$ (e.g. Bolatto, Wolfire & Leroy 2013). We refer to this limit as the “CO-dominated regime”. When the hydrogen is atomic ($Z' \lesssim 10^{-2}$ for $\zeta_{-16}/n_3 = 1$) the CO abundance drops sharply and then OH becomes the most abundant molecule containing a heavy element. We refer to this limit as the “OH-dominated” regime. Figure 6 shows that the transition from the OH to CO dominated regimes occurs close to the H-to-$H_2$ transition point. As we discuss further below this is generally true for any $\zeta/n$. A large atomic carbon abundance is generally maintained when $\zeta/n$ is sufficiently large for a given $Z'$, and the C/CO density ratio is then of order of unity. At low $\zeta/n$ the C/CO ratio always becomes small. In Figure 6 we are in the large $\zeta/n$ regime.

Second, the OH, H$_2$O, O$_2$, and CH abundances are all comparable for large $Z'$. For our assumed $\zeta_{-16}/n_3=1$, $x_{OH}$, $x_{H_2O}$, $x_{O_2}$, and $x_{CH}$ are $\approx 10^{-3}$ at $Z' = 1$, as seen in Figure 6. However, the abundance curves for these four species diverge sharply as $Z'$ becomes small.

The behavior for OH is of particular interest. As $Z'$ is reduced, the OH abundance first increases, and reaches a maximum near the H/$H_2$ transition. At this point, $x_{OH} = 6 \times 10^{-7}$, and OH/0$_{tot}$ = 0.16, and a significant fraction of the gas phase oxygen is locked in OH molecules. In particular, the OH/CO abundance ratio $\approx 1$ at this point. At still lower $Z'$ the OH abundance decreases, but once the hydrogen becomes predominantly atomic OH/0$_{tot}$ approaches a constant value of 2%. In contrast, CO/C$_{tot}$ decreases linearly with $Z'$, and OH/CO becomes large.

The variation of $x_{OH}$ with $Z'$ and $\zeta/n$ is essential and can be understood via an approximate analytic scaling relation, as follows. We show numerical results for $x_{OH}$ versus $\zeta/n$ at fixed $Z'$ in §5.2. At high $Z'$, and in the molecular regime ($2Z_{H_2} \approx 1$), crx-ionization of $H_2$ leads to the formation of $H^+$ or $H_2^+$ that then react with atomic oxygen (reactions $[R14]$ and $[R28]$) initiating the abstraction sequence leading to OH. The $H^+$ density is limited by charge transfer with atomic oxygen (reaction $[R14]$) but the $O^+$ ions are removed by reactions with the $H_2$. Thus the OH formation rate via $H^+$ is equal to the dissociative $H_2$ ionization rate, and independent of metallicity. For the HIP conditions in Figure 6 the $H^+$ density is limited by dissociative recombination ($[R10]$ and $[R11]$). The relative rates of the $H^+$ versus $H_2^+$ routes therefore depends on the atomic oxygen to electron ratio. The OH is removed mainly by atomic oxygen (reaction $[R39]$) hence the removal rate is proportional to $Z'$, and independent of $\zeta/n$. To a good approximation we then have

$$x_{OH} \propto \frac{\zeta}{n} \left[ 1 + \frac{0.93 k_{R28} \rho_{H_2}}{0.021 k_{R10} + 1.1 k_{R11}} \frac{x_O}{x_e} \right] \frac{1}{Z'}$$

where $k_{R28}$, $k_{R10}$, and $k_{R11}$ (evaluated for $T = 100$ K), and the term in brackets accounts for the $H^+$ and $H_2^+$ formation channels. To first-order, $x_{OH}$ is proportional to $\zeta/n$, and for a given hydrogen gas density the OH abundance is a measure of the ionization rate (e.g. Black & Dalgarno 1973; van Dishoeck & Black 1986). The $H^+$ formation channel dominates when the oxygen-to-electron ratio, $x_O/x_e$, is small. The oxygen-to-electron ratio is independent of $Z'$ when the positive charge is carried by metal species as is the case for high $Z'$, but it does vary inversely with $\zeta/n$ and this moderates the sensitivity of $x_{OH}$ to $\zeta/n$ (as discussed further in §5.2). To first order the OH formation rate is independent of metallicity.

The $1/Z'$ term in Equation (32) accounts for the removal of the OH...
by atomic oxygen. Figure 6 shows the approximately linear rise in $x_{\text{OH}}$ as the metallicity is reduced.

In Figure 7, atomic regime ($x_{\text{H}} \approx 1$), and for gas-phase H$_2$ production, OH formation proceeds via reactions of O$^+$ ions with the trace H$_2$ available (reaction $(R27)$). But now the O$^+$ density is set by charge transfer equilibrium with atomic hydrogen (reaction $(R44)$), and the H$^+$ is removed by electron recombination. Thus, in this limit the OH formation rate is linearly proportional to the oxygen abundance and metallicity. Removal of the OH is via reactions with H$^+$ $(R43)$ rather than by hydrogen and other metals. In this limit

$$x_{\text{OH}} \propto x_{\text{H}_2} \frac{1}{f} \frac{x_{\text{O}}^+}{x_{\text{H}^+}} \propto x_{\text{H}_2} \frac{1}{f} \frac{x_{\text{O}}}{x_{\text{H}}} \propto x_{\text{H}_2} \frac{1}{f} \frac{Z'}{Z}. \quad (33)$$

Here $f \propto x_{e}/x_{\text{H}_2}$ is the fraction of OH$^+$ productions (via $(R43)$) that do not loop back to OH via the abstraction sequence $(R29)$–$(R32)$. In Equation $(33)$, $x_{\text{O}}^+/x_{\text{H}^+} \propto x_{\text{O}}/x_{\text{H}}$ as set by forward and backward charge-transfer equilibrium. Furthermore, from Equations $(13)$ and $(17)$, we have $x_e \propto (\zeta/n)^{1/2}$ and $x_{\text{H}_2} \propto (\zeta/n)^{-1/4}$. Thus at low $Z'$, $x_{\text{OH}}$ is proportional to $Z'$, and

$$x_{\text{OH}} \simeq 0.02 A_O Z' \left(\frac{\zeta_{16}}{n_3} \right)^{-1}, \quad (34)$$

where $A_O = 4.9 \times 10^{-4}$ is the oxygen abundance at solar metallicity. In expression $(34)$ the prefactor of $2\%$ is obtained from our numerical results, as shown in Figure 6. Importantly, the OH fraction varies inversely with $\zeta/n$ in the low $Z'$ limit. This is due to (a) the reduced H$_2$ fraction with increasing ionization parameter, and (b) the increased electron to H$_2$ ratio that enhances the efficiency of OH destruction by protons.

The behavior for H$_2$O and O$_2$ differs due to the variety in removal processes with metal atoms and ions, $(R44)$–$(R47)$ for H$_2$O, and $(R39)$–$(R33)$ for O$_2$. At high $Z'$, the H$_2$O and O$_2$ removal rates are weakly dependent on $Z'$ as the relative fractions of C, C$^+$, Si, and Si$^+$ vary. The overall abundances of these atoms and ions increase with $\zeta/n$ and therefore so do the H$_2$O and O$_2$ removal rates. The H$_2$O formation rate is independent of $Z'$ to first order, as for OH. For O$_2$ the formation rate is proportional to the product of the OH and O densities, and this is also independent of $Z'$. However, the formation rates increase with $\zeta/n$. Thus, in the high $Z'$ regime we expect that $x_{\text{H}_2O}$ and $x_{\text{O}_2}$ will be insensitive to both $Z'$ and $\zeta/n$. As seen in Figure 6, $x_{\text{H}_2O}$ and $x_{\text{O}_2}$ are indeed roughly constant from $Z' = 1$ down to 0.05. We show results as functions of $\zeta/n$ in Figures 7 and 8 below.

At lower $Z'$, and into the atomic regime, the H$_2$O and O$_2$ are both removed by H$^+$. In the low $Z'$ atomic limit,

$$x_{\text{H}_2O} \simeq 2 \times 10^{-3} A_O Z' \left(\frac{\zeta_{16}}{n_3} \right)^{-1}, \quad (35)$$

and

$$x_{\text{O}_2} \simeq 3 \times 10^{-3} A_O Z'^2 \left(\frac{\zeta_{16}}{n_3} \right)^{-1.5}. \quad (36)$$

The H$_2$O fraction depends on the ionization parameter in the same way as OH does, and for identical reasons. For $x_{\text{O}_2}$, the dependence is steeper, with one power of $\zeta/n$ entering due to the formation via OH, and an additional $(\zeta/n)^{1/2}$ term for the proton fraction that controls the removal rate.

In the low $Z'$ limit $x_{\text{OH}}$ and $x_{\text{H}_2O}$ are proportional to $Z'$ because both OH and H$_2$O contain just one heavy element. However, $x_{\text{O}_2}$ is $Z'^2$ because O$_2$ consists of two heavy elements. These simple metallicity scalings are inevitable when the heavy molecules are removed only by hydrogen-helium species and once the hydrogen-helium chemistry and the electron fraction are no longer affected by metals (or dust), as occurs at sufficiently low $Z'$ for any $\zeta/n$ (or for sufficiently high $\zeta/n$ for any $Z'$). In this limit, and for any network of two-body reactions, the abundances of any trace species containing $n$ heavy elements must always vary as $Z'^n$. Our numerical calculations are consistent with this general principle. Thus O$_2$ vanishes compared to OH in the low $Z'$ limit, as does CO compared to OH as we discuss further below.

In the molecular regime the H$_2$O/OH abundance ratio is variable and can become large. In the atomic regime, H$_2$O/OH is always small, $\sim 0.1$, (and constant) because the H$_2$O removal rate by H$^+$ is larger than for OH, and because most H$_2$O$^+$ ions dissociatively recombine to OH rather than to H$_2$O (e.g., Vejby-Christensen et al. 1997).

Figure 6 shows that OH/CH is a strongly decreasing function of $Z'$, even though the total oxygen to carbon abundance ratio, $O_{\text{tot}}/C_{\text{tot}}$, is independent of $Z'$ in our models. In particular, CH vanishes with decreasing $Z'$. This occurs because for all $Z' \lesssim 1$, and for our assumed $\zeta_{16}/n_3 = 1$, CH is always removed by H atoms (reaction $(R69)$) rather than by metal species or protons. To a good approximation

$$x_{\text{CH}} = \frac{x_{\text{OH}}}{x_{\text{CO}}} \left(\frac{\zeta_{16}/n_3}{x_{\text{H}}} \right)^{2.5}. \quad (37)$$

The numerator in this expression accounts for CH production initiated via the formation of CH$^+$ by either radiative association (reaction $(R58)$) or proton transfer (reactions $(R55)$–$(R57)$) involving C or C$^+$. The denominator accounts for removal by hydrogen atoms. As $Z'$ is reduced and $x_{\text{H}}$ increases, CH is rapidly removed, as seen in Figure 6. In general CH is a negligible hydride compared to OH or H$_2$O at low metallicity.

Finally, in the middle- and lower-right panels of Figure 6 we illustrate the effects of turning on a background FUV radiation field assuming $I_{\text{UV}}/n_3 = 1$. We solve Equations $(8)$, and as $Z'$ is reduced we vary the field intensity inside the parcels according to our dust-shielding formula Equation $(9)$. Because we are assuming that the LW band is blocked for any $Z'$, the H and H$_2$ curves are unaffected when the FUV field is turned on. However, for $Z' \lesssim 0.1$ the OH, H$_2$O, and O$_2$ are removed by photodissociation as the dust opacity vanishes. CO is fully shielded by the blocked LW band and continues to be removed by He$^+$ throughout. Nevertheless, the CO abundance is reduced when the FUV is turned on because of the suppression of the OH intermediary. Importantly, because the CO removal rate is not altered, the OH/CO abundance ratio is unaffected when the FUV is turned on, and the transition from the CO-dominated to the OH-dominated regimes still occurs near the H-to-H$_2$ transition. We discuss OH/CO further in 5.5.

### 5.2 Dependence on $\zeta/n$ for fixed $Z'$

We now consider the behavior as a function of $\zeta_{16}/n_3$, for two values of $Z'$. In Figure 7, $Z' = 10^{-2}$ and $\zeta_{16}/n_3$ ranges from $10^{-2}$ to $10^2$. In Figure 8, $Z' = 1$ and $\zeta_{16}/n_3$ ranges from $10^{-2}$ to $10^3$. Our results for $Z' = 1$ are similar to those found by Lepp & Dalgarno (1996) in their study of X-ray driven chemistry
at solar metallicity, where \( \zeta \) is the X-ray ionization rate (see their Figures 1 and 2). See also Bayet et al. (2011), their Figure 3.

As seen in Figures 7 and 8 when \( \zeta/n \) is small \( H_2 \) destruction by crx-ionization is ineffective and the hydrogen is fully molecular (upper-left panels of Figures 7 and 8). The \( H/H_2 \) ratio increases with \( \zeta/n \), and for \( Z' = 10^{-2} \), the \( H-\text{to-}H_2 \) transition occurs at \( \zeta_{16}/n_3 \approx 1 \). For \( Z' = 1 \) it occurs at \( \zeta_{16}/n_3 \approx 10^2 \). This behavior is consistent with our Equation (32) for the location of the \( H-\text{to-}H_2 \) transition (for \( \beta = 1 \)).

The ionization fraction \( x_e \) is shown in the upper-right panels. It also increases with \( \zeta/n \). For example, for \( Z' = 1 \), \( x_e \) ranges from \( 2 \times 10^{-6} \) to \( 2 \times 10^{-4} \) for \( \zeta_{16}/n_3 \) ranging from \( 10^{-2} \) to \( 10^2 \) (see also Lepp & Dalgarno 1994, their Figure 1). At low \( \zeta/n \), and in the \( H_2 \) regime, the positive charge is carried by metals. This includes molecular ions, e.g., \( H_3^+ \), HCO\(^+\), HCO\(^3\), in addition to the atomic ions. At high \( \zeta/n \), and in the atomic regime, the positive charge is carried by protons, and \( x_e \approx x_{H^+} \).

The lower-left panels in Figures 7 and 8 show the C, O, OH, H\(_2\)O, O\(_2\), CH, and CO abundance fractions \( x_i \). The steepening rise of \( x_{OH} \) toward the \( H-\text{to-}H_2 \) transition point and then the decline with \( \zeta/n \), is consistent with our approximate \( OH \) abundance scaling Equations (32) and (34). For example, for \( Z' = 1 \), and for \( \zeta_{16}/n_3 \) between \( \sim 1 \) and \( 10^2 \), \( x_{OH} \) increases linearly with \( \zeta/n \) as given by Equation (33) for small \( x_O/x_e \). For \( \zeta_{16}/n_3 \lesssim 1 \), the oxygen to electron ratio becomes large and the variation of \( x_{OH} \) with \( \zeta/n \) is moderated. For \( \zeta_{16}/n_3 \gtrsim 10^2 \) the hydrogen becomes atomic and \( x_{OH} \) then decreases with the ionization rate and varies approximately as \( (\zeta/n)^{-1} \) as given by Equation (34).

Similar behavior was found by Bayet et al. (2011) in their study of molecular chemistry at high cosmic-ray ionization rates (for models with fixed gas density). Their numerical results also show an \( OH \) abundance peak close to the \( H-\text{to-}H_2 \) transition point, but they did not discuss this connection.

At low \( \zeta/n \), and in the molecular regime, \( O_2 \) becomes abundant compared to \( OH \), but as \( \zeta/n \) increases the \( O_2/OH \) ratio decreases. Correspondingly, at low \( \zeta/n \) in the \( H_2 \) regime, most of gas-phase carbon is locked in CO, and the C/CO ratio is small. The free atomic carbon increases with \( \zeta/n \) and C/CO reaches a local maximum just before the \( H-\text{to-}H_2 \) transition point, and the subsequent sharp drop in the CO abundance. The slight rise in the CO abundance near the \( H-\text{to-}H_2 \) transition in Figure 8 is due to the OH maximum and the resulting enhanced CO production rate at this point.

The lower right panel of Figure 7 shows the effect of FUV radiation, for our assumed \( Z' = 0.01 \) models for \( I_{FUV}/n_3 = 1 \). Photodissociation suppresses the \( OH \), H\(_2\)O and \( O_2 \). At high \( \zeta/n \), and well inside the atomic regime, \( H^+ \) dominates the OH removal and the abundance curve is unaffected by photodissociation. Similarly \( H_2O \) and \( CH \) are suppressed by photodissociation when \( \zeta/n \) is not too large. \( CO \) is shielded but is indirectly reduced by the photodissociation of the \( OH \) intermediary.

For \( Z' = 1 \) (Figure 8), dust-shielding is operative for all wavelengths, so that the photo-processes are ineffective for all \( \zeta/n \), and we do not include an FUV panel for this model sequence.

### 5.3 Abundance Ratios: \( OH/O_2 \), C/CO and OH/CO

The C/CO, OH/O\(_2\), and OH/CO abundance ratios are of particular interest. We plot them in Figure 9 as functions of \( Z' \) for \( \zeta_{16}/n_3 = 1 \), and as functions of \( \zeta_{16}/n_3 \) for \( Z' = 10^{-2} \), given our results presented in Figures 5-8. The solid curves are for FUV off, and the dashed cues are for FUV on with \( I_{FUV}/n_3 = 1 \). The vertical dashed lines in Figure 9 indicate the positions of the \( H-\text{to-}H_2 \) transitions. For fixed \( \zeta_{16}/n_3 = 1 \) the \( H-\text{to-}H_2 \) transition occurs at \( Z' \sim 10^{-2} \), and the gas is atomic (molecular) to the left (right) of the dashed line. For fixed \( Z' = 0.01 \), the transition occurs at \( \zeta_{16}/n_3 \approx 1 \), and the gas is atomic (molecular) to the right (left) of the dashed line. We consider the behavior of the C/CO, OH/O\(_2\), and OH/CO abundance ratios in both the molecular and atomic regimes.

We begin with a discussion of C/CO and OH/O\(_2\). These ratios are coupled in an important way in the molecular regime (Boger & Sternberg 2006; Wakelam et al. 2006). To see this we first write

\[
\frac{x_{OH}}{x_{O_2}} \propto \left( \frac{\zeta_{16}}{n_3} \right) \frac{1}{Z'}.
\]  

(38)
This follows because the $O_2$ formation rate is proportional to the atomic oxygen abundance which is proportional to $Z'$, and because the $O_2$ removal rate (via reactions [R49]-[R53]) is approximately proportional $\zeta/n$. Alternatively, this is just the first-order scaling for $x_{O_2}$ with $x_{O_2}$ approximately constant. Equation (38) accounts for the fact that OH/O$_2$ can be large or small depending on $Z'$ and $\zeta-1/n_3$ as seen in Figure 9 (and Figures 6-8).

As discussed in §2.3 there are two primary CO formation pathways, involving either OH as the main intermediary, via reactions [R70]-[R71] with C and C$^+$, or involving O$_2$ via [R49]-[R53], again with C and C$^+$. In general $C^+$/C $\ll 1$ in the molecular regime, but CO formation via C$^+$ can still contribute due to the large rate coefficients of the ion-molecule reactions. The C/CO ratio can now be understood qualitatively by considering a simplified formation-destruction equation for the CO,

$$ (k_{OH}x_{OH} + k_{O_2}x_{O_2})x_{CO} = k_{OH}x_{He^+}x_{CO} = 0.5 \left(\frac{\zeta-16}{n_3}\right) x_{He^+}. \quad (39) $$

The left-hand side of this expression encapsulates CO formation, where $k_{OH} \equiv 10^{-9}$ cm$^3$ s$^{-1}$ is the effective total rate coefficient for formation via OH (involving both C and C$^+$), and $k_{O_2} \equiv 3 \times 10^{-10}$ cm$^3$ s$^{-1}$ is the effective rate coefficient for formation via O$_2$. We assume that C$^+$/C is small so that the abundance of carbon species not locked in CO is represented just by the free atomic carbon abundance $x_C$. The middle term of Equation (39) is the CO destruction rate via dissociative charge transfer with He$^+$ (reaction [R19]). So long as this is also the dominant He$^+$ neutralization process, the rate equals the helium ionization rate on the right hand side. Because the helium is predominantly neutral we set $x_{He} = A_{He} = 0.1$.

At high $\zeta/n$ and/or low $Z'$ (but still in the molecular regime), OH/O$_2$ becomes large, according to Equation (38), and we then have

$$ x_C \approx \frac{0.5}{\kappa_{OH}x_{O_2}} \left(\frac{\zeta}{n}\right) A_{He} \approx 0.4A_C Z'. \quad (40) $$

Here we use our first order expression for the OH abundance in the molecular regime

$$ x_{OH} \approx 4 \times 10^{-8} \left(\frac{\zeta-16}{n_3}\right) \frac{1}{Z'}. \quad (41) $$

The prefactor of $4 \times 10^{-8}$ is obtained from our numerical calculations for $\zeta-10/n_3 = 1$ and $Z' = 1$ (see Figure 6). Importantly, Equation (40) shows that when OH/O$_2 \gg 1$, $x_C$ is independent of the ionization parameter $\zeta/n$. Furthermore, $x_C$ approaches saturation and becomes comparable to the total carbon abundance $A_C Z'$. In this limit the analysis shows that C/CO becomes large, but numerically we find that it remains of order unity in the H$_2$ regime.

When OH/O$_2 \ll 1$, as occurs at low $\zeta/n$ and/or high $Z'$ (again in the molecular regime) we have

$$ x_C = \frac{0.5}{k_{O_2}x_{O_2}} \left(\frac{\zeta}{n}\right) A_{He} \approx 10^{-6} \left(\frac{\zeta-16}{n_3}\right) \ll A_C Z'. \quad (42) $$

Here we have assumed $x_{O_2} \approx 10^{-7}$, and to first-order independent of $Z'$ and $\zeta/n$ (as found for the HIP in our full 2D computations in §6). In this limit the free atomic carbon abundance is proportional to $\zeta/n$, but C/CO remains small.

The above discussion for OH/O$_2$ and C/CO is for the H$_2$ regime. In the atomic regime, $x_{OH}$ and $x_{O_2}$ are given by Equations (34) and (36), and

$$ \frac{x_{OH}}{x_{O_2}} \approx 6.7 \left(\frac{\zeta-16}{n_3}\right)^{0.5} \frac{1}{Z'}. \quad (43) $$

As $Z'$ becomes small OH/O$_2 \gg 1$, as expected.

In the atomic regime, the CO is formed mainly via the C+OH channel, and continues to be removed by He$^+$. Crucially however, the He$^+$ is no longer removed by CO but by charge transfer with atomic and molecular hydrogen, so that

$$ x_{He^+} = \left(\frac{\kappa_{R19}}{\kappa_{R21} + \kappa_{R22}}\right) x_{He^+} + \frac{0.5}{k_{O_2}x_{O_2}} \left(\frac{\zeta}{n}\right) A_{He}. \quad (44) $$

independent of $Z'$. In this limit

$$ \frac{x_C}{x_{CO}} = \frac{k_{R19}x_{He^+}}{k_{R19}x_{O_2} + k_{R20}x_{O_2}} \approx 0.5 \left(\frac{\zeta-16}{n_3}\right)^{1.5} \frac{1}{Z'}, \quad (45) $$

c and C/CO grows without limit. As indicated by Equations (43) and (45), in the atomic regime the OH/O$_2$ and C/CO ratios are decoupled.

We now consider OH/CO. Well inside the molecular regime where a large fraction of the carbon is locked in CO, the OH/CO ratio is small. In the atomic regime OH/CO $\gg 1$. In general the transition from the “OH-dominated” to “CO-dominated” regimes occurs close to the H-to-H$_2$ transition point. This is seen in Figure 2. We can write down approximate expressions for $x_{OH}/x_{CO}$ as follows. At high $Z'$, and assuming most of the carbon is locked in CO, $x_{CO} \propto Z'$ so that

$$ \frac{x_{OH}}{x_{CO}} \propto \frac{1}{Z'} \frac{x_{OH}}{x_{CO}} \propto \frac{1}{Z'} \left[1 + 0.27 \frac{x_{OH}}{x_{CO}} \right] \frac{1}{Z'}. \quad (46) $$
where here we have used Equation \(32\) for \(x_{OH}\). In this limit \(OH/CO\) varies as \(1/Z^2\), and sublinearly with \(\zeta/n\).

In the atomic regime \(CO\) is formed via the \(OH+C\) channel, and is still removed by \(He^+\), so that

\[
\frac{x_{OH}}{x_{CO}} = \frac{n_{He^+}}{n_{CO}} \approx 10^{-2} \left( \frac{\zeta_{16}}{n_3} \right) \frac{1}{Z^2}, \tag{47}
\]

where \(x_C = A_C Z^2\), and \(x_{He^+}\) is given by Equation \(44\). Once again, because \(OH\) contains one heavy element and \(CO\) consists of two, \(OH/CO\) varies as \(1/Z^2\) in the low \(Z'\) limit. The linear dependence on \(\zeta/n\) enters via \(x_{He^+}\) as given by Equation \(44\).

The dashed curves in Figure 9 are for FUV on with \(I_{\text{UV}}^0/n_3 = 1\). The \(OH/CO\) ratio is now inversely proportional to the \(O_2\) photodestruction rate and is independent of \(\zeta/n\), but the dependence on \(Z'\) is unaffected. \(CO\) is enhanced due to the indirect reduction of \(CO\) via photodissociation of the \(OH\) and the \(O_2\). Importantly, so long as \(CO\) is mainly formed via the \(OH\) intermediary, \(OH/CO\) is unaffected by photodissociation of the \(OH\). This is seen in the lower panels of Figure 9 in which the dashed (FUV on) and solid (FUV off) curves coincide. The CO/He curves do diverge for very low \(\zeta/n\) at fixed \(Z'\), because when FUV is on the \(OH\) and \(O_2\) abundances become so small that residual processes start contributing to the CO production. However in the (atomic) “OH-dominated” regime photodissociation of the \(OH\) never affects the \(OH/CO\) ratio. In particular, photodissociation does not affect the transition points from the CO-dominated to OH-dominated regimes.

6 2D RESULTS: \(Z'\) VERSUS \(\zeta/n\)

Given our description in \(44\) and \(5\) of the basic chemical behavior and regimes, we now present computations that span our full two-dimensional (2D) \(Z'\) versus \(\zeta/n\) parameter space. For our 2D computations we vary \(Z'\) from \(10^{-3}\) to 1 and \(\zeta_{16}/n_3\) from \(10^{-3}\) to \(10^2\). We again assume that the grain \(H_2\) formation rate coefficient varies linearly with \(Z'\) (\(\beta = 1\) in Equation \(1\)), and we show results for FUV off (\(\delta = 1\) and \(\delta = 2\)) and on (\(\delta = 4\), according to Equations \(1\) and \(2\)). We again assume \(T = 100\) K gas. We present the atomic and molecular abundances in the \(Z'\) versus \(\zeta_{16}/n_3\) plane as color-contour plots, in which the color varies with \(\log x_i\), from large (red) to small (blue). The displayed dynamic-ranges for the \(\log x_i\) differ for different species \(i\), and are indicated for each panel.

6.1 \(H, H_2, H^+, \) and \(e\)

In Figure 10 we show the atomic and molecular hydrogen fractions \(x_{H}\) and \(x_{H_2}\), and the electron and proton fractions, \(x_e\) and \(x_{H^+}\), in the \(Z'\) versus \(\zeta_{16}/n_3\) plane assuming FUV off \(I_{\text{UV}}^0 = 0\), as given by the solutions to Equations \(3\) to \(5\).

The upper left panel shows \(x_{H_2}\) for the range \(10^{-1.5}\) to 1. The upper right panel shows \(x_{H}\) from \(10^{-6}\) to 1. The solid diagonal line shows the H-to-H\(_2\) transition where \(x_{H_2} = x_{H}\). Its slope, \((\zeta/n) \propto Z'\), and position is consistent with our Equation \(22\). We draw the H-to-H\(_2\) transition line in all of our parameter-space plots to delineate the atomic and molecular hydrogen regimes. As seen in Figure 10 the gas becomes atomic at a \(Z'\) for sufficiently large \(\zeta/n\), or at sufficiently low \(Z'\) for a given \(\zeta/n\). In the panel for \(x_{H_2}\), we also draw a dashed line where the \(H_2\) formation rates in the gas-phase and on grains are equal. The position of this line is in good agreement with our Equation \(25\) for \(\beta = 1\). Grain \(H_2\) formation is dominant in most of our parameter space including in the atomic regime, except in the upper-left corner where \(Z'\) is very low and \(\zeta_{16}/n_3\) is large.

The lower left and right panels of Figure 10 shows \(x_e\) and \(H^+\) ranging from \(10^{-10}\) to \(10^{-3}\). Several zones may be identified for the fractional ionization \(x_e\). The solid line again divides the parameter-space into the atomic and molecular regimes. The abrupt switch from LIP to HIP conditions can be seen at \(\zeta_{16}/n_3 \approx 10^{-2}\) to \(10^{-4}\). The dashed curve is where gas phase and dust grain \(H_2\) formation rates equal. (b) Upper right panel is \(x_{H^+}\), from 6 to 0. (c) Lower left panel is \(x_{e}\), from -10 to -3. The abrupt switch from HIP to LIP is indicated. (d) Lower right panel is \(x_{H^+}\), from -10 to -3. In both lower panels, the dashed curves are where \(x_{H^+} = 0.25x_e\).

6.2 \(CO, C, C^+, OH, O_2\) and \(O_3\)

Our 2D results for the C, CO, OH, \(O_2\) and \(O_3\) abundances, with FUV off, are shown in Figures 11 and 12. In the left hand panels we show the \(x_i\). In the right hand panels we normalize to the total carbon or oxygen abundances, \(C_{\text{tot}} = A_C Z'\) and \(O_{\text{tot}} = A_O Z'\). In Figure 11 we show \(CO/C_{\text{tot}}\), \(C/C_{\text{tot}}\) and \(C^+/C_{\text{tot}}\), and in Figure 12 we show \(OH/O_{\text{tot}}\), \(H_2O/O_{\text{tot}}\), and \(O_3/O_{\text{tot}}\).

The upper panels of Figure 11 display the CO abundances, with \(x_{CO}\) ranging from \(10^{-4}\) to \(10^{-1}\) in the molecular regime (below the solid line) and down to less than \(10^{-9}\) in the atomic regime. These plots show that in the \(H_2\) regime a large fraction, 30-...
100%, the available carbon is always locked in CO. This is true even at very low Z', so long as \( \zeta/n \) is small enough for the hydrogen to be molecular. The general result is that gas-phase CO formation is efficient at all metallicities so long as the hydrogen is molecular. Thus, in the H₂ regime \( x_{\text{CO}} \) varies approximately linearly with \( Z' \) and very weakly with \( \zeta/n \). However, in the atomic regime \( x_{\text{CO}} \) drops very sharply with decreasing \( Z' \) or increasing \( \zeta/n \), and CO becomes a trace species. In this regime \( x_{\text{CO}} \propto (\zeta/n)^{-1.5} Z'^2 \) as seen in Figure 11 and consistent with Equation 45.

The middle and lower panels of Figure 11 show the free atomic and ionized carbon abundances. Even in the H₂ regime, a significant fraction (\( \sim 50\% \)) of the carbon remains atomic as long as \( \zeta/n \) is not too low, especially in the HIP. But at sufficiently low \( \zeta/n \) for any \( Z' \) the atomic carbon vanishes and is fully absorbed into CO. This is the behavior we discussed in 3.3. In the atomic regime where CO vanishes most of the carbon remains atomic as long as the ionization parameter is not too large, with \( C^+ / C \ll 1 \) for \( \zeta_{16}/n_{\text{H}_2} \lesssim 50 \). For higher ionization parameters most of the carbon is ionized.

The upper panels of Figure 12 show the behavior for OH. To first order, \( x_{\text{OH}} \propto (\zeta/n)/Z' \) in the molecular regime (see Equation 12) and the color contours for \( x_{\text{OH}} \) run approximately parallel to the H-to-H₂ transition line. As we have discussed, for any \( Z' \) we expect the OH abundance to be maximal near the H-to-H₂ transition. This is indeed seen in Figure 12. Along the transition line, \( x_{\text{OH}} \) ranges from \( \approx 3 \times 10^{-6} \) at \( Z' = 1 \) to \( \approx 10^{-7} \) at \( Z' = 10^{-3} \). The reduction of \( x_{\text{OH}} \) along the transition line is due to H⁺ removal of the OH (reaction [R43]) in addition to removal by atomic oxygen and other metals. Along the transition line the OH is formed mainly via the charge-transfer route with H⁺ (reaction [R14]). Well within the molecular regime where H⁺ becomes small the H₂⁺ proton transfer route predominates (reaction [R28]). The jump in \( x_{\text{OH}} \) at the HIP-to-LIP boundary is due, in part, to the sudden change in the H₂⁺ abundance at the phase transition. In the atomic regime the OH abundance decreases, and \( x_{\text{OH}} \propto (\zeta/n)^{-1} Z' \) (see Equation 41), but the relative fraction \( \text{OH}/\text{tot} \) is relatively large in this regime, as seen in the upper-right panel.

The middle panels of Figure 12 show that \( x_{\text{H}_2\text{O}} \) is weakly dependent on \( Z' \) and \( \zeta/n \) in the H₂ regime. We find \( x_{\text{H}_2\text{O}} \approx 10^{-8} \) to \( 10^{-7} \) in the HIP and \( \approx 3 \times 10^{-6} \) in the HIP. In the atomic regime the \( \text{H}_2\text{O} \) abundance decreases, and \( x_{\text{H}_2\text{O}} \propto (\zeta/n)^{-1} Z' \) (see Equation 45). The lower panels of Figure 12 show that as expected \( x_{\text{O}_2} \) is also weakly dependent on \( Z' \) and \( \zeta/n \) in much of the H₂ regime. In the HIP \( x_{\text{O}_2} \approx 2 \times 10^{-7} \) is a characteristic value. For the HIP \( x_{\text{O}_2} \approx 2 \times 10^{-6} \). At sufficiently low \( Z' \) removal of the O₂ by H⁺ rather than metals takes over, and \( x_{\text{O}_2} \) drops. In the atomic regime the \( \text{O}_2 \) rapidly vanishes as \( (\zeta/n)^{-1.5} Z'^2 \) (see Equation 48). Figure 13 shows the abundance ratios for OH/O₂, CO/O₂, OH/H₂O, and OH/CO, in our \( Z' \) versus \( \zeta/n \) parameter space. In these plots we limit the dynamic ranges of the displayed ratios from \( 10^{-5} \) to \( 10^3 \).

Most of the variation in OH/O₂ is due to the variation in \( x_{\text{OH}} \). At low \( \zeta/n \) and/or at high \( Z' \), in the molecular regime, OH/O₂ becomes small (see Equation 38). Still in the molecular regime,
OH/O₂ approaches unity as Z’ is decreased or as ζ/n is increased. For example, OH/O₂ ≈ 1 at Z’ = 3 × 10^{-3} for ζ_{16}/n_{3} = 10^{-3} or at Z’ = 1 for ζ_{16}/n_{3} = 20. At still lower Z’, or higher ζ/n, OH begins to dominate over O₂. In the atomic regime OH always strongly exceeds O₂ as it must, due to the Z’ versus Z² metallicity scalings for the OH and O₂ abundances in the low Z’ limit.

As discussed in [5,3] the C/CO and OH/O₂ abundance ratios are strongly coupled in the molecular regime. So long as OH/O₂ is not too low C/CO remains of order unity. At very low ζ/n, OH/O₂ becomes small and consequently C/CO strongly decreases (approximately as ζ/n) as all of the carbon is driven to CO. For example, at solar metallicity, C/CO ≈ 0.1 for ζ_{16}/n_{3} = 10^{-1}, but C/CO ≈ 6 × 10^{-3} for ζ_{16}/n_{3} = 10^{-2}. In the atomic regime, C/CO rapidly increases as the CO vanishes.

The lower-left panel of Figure 13 shows OH/H₂O. In the atomic regime OH/H₂O ≈ 10 and is approximately constant, as set by the branching ratios of H₂O⁺ dissociative recombination, and the preferential removal of H₂O by protons. In the molecular regime, OH/H₂O varies and can become small as x_{OH} decreases more rapidly at high Z’ and low ζ/n.

The OH/CO ratio for ζ/n versus Z’ is shown in the lower-right panel of Figure 13. As expected, OH/CO is small inside the H₂ regime. In the atomic regime OH/CO ≫ 1. The switch from the OH- to CO-dominated regimes occurs close to the H-to-H₂ transition line.

Finally in Figure 14 we show the CH/OH abundance ratio within our Z’ versus ζ/n parameter space. The CH/OH ratio approaches unity at high Z’ within the HIP. As expected, CH vanishes and CH/OH becomes small at low Z’ and into the atomic regime. OH is the dominant heavy molecule at low Z’ and/or high ζ/n.

6.3 FUV on

In Figures 15, 16 and 17 we show 2D model results for FUV on. We again assume P_{UV}/n_3 = 1, and vary I_{UV} inside the parcels according to our dust shielding formula (Equation 9). As before, we assume that the LW band is always completely blocked so that the H₂ and CO are shielded from direct photodissociation at all Z’. However OH, H₂O, and O₂ are photodissociated when Z’ is small and the dust shielding vanishes. For our assumed P_{UV}/n_3 = 1 photodissociation dominates over chemical removal for Z’ ≤ 0.1 for the HIP, and for Z’ ≤ 0.4 for the LIP. Figure 15 shows the CH, H₂O, and O₂ abundances with FUV on. For ζ_{16}/n_{3} ≥ 1, chemical removal remains dominant at all Z’.

For lower ionization parameters, photodissociation becomes rapid once the parcels become unshielded at Z’ ≤ 0.1, and OH, H₂O, and O₂ abundances are reduced. Reduction of O₂ by FUV is very effective because the OH intermediary required for O₂ formation is removed and because the O₂ is itself directly photodissociated.

The upper panel of Figure 16 shows that the CO vanishes within the H₂ regime as the OH (and O₂) are photodissociated, even though the CO itself is fully shielded. CO then becomes a trace species as Z’ is reduced, and most of the carbon remains atomic or ionized as shown in the middle panels.
Figure 16. The same as Figure 11 but with $I_{UV}^0/n_3 = 1$.

Figure 17. The same as Figure 13 but with $I_{UV}^0/n_3 = 1$.

Figure 17 shows the OH/O$_2$, C/CO, OH/H$_2$O, and OH/CO abundance ratios for the computations with FUV on. The OH/O$_2$ ratio becomes very high in most of the parameter space. When photodissociation is effective we find OH/H$_2$O $\approx$ 10, now also in the H$_2$ regime, not just in the atomic regime. This is now due to preferential formation of OH in the dissociative recombination of H$_2$O$^+$, and the higher H$_2$O photodissociation rate compared to OH. Once photodissociation becomes effective the OH/O$_2$ and C/CO ratios decouple, and the C/CO ratio becomes large as the CO vanishes.

Importantly, the OH/CO ratio is unaffected by the FUV, because only the OH, that is required for the formation of the CO, is reduced by the FUV. Thus the transition from the CO to OH dominated regimes still occurs close to the H-to-H$_2$ transition line (as given by Equation 22), whether or not FUV is off or on. Inevitably, OH becomes the dominant heavy molecule in the limit of low metallicity.

7 SUMMARY

In this paper we have presented a theoretical study of interstellar molecule production via ionization-driven gas-phase chemistry, for a wide range of overall heavy-element abundances or metallicities, $Z^*$, and cloud ionization parameters $\zeta/n$. Here $\zeta$ is the total ionization rate, and $n$ is the hydrogen gas volume density. Our main motivation is analysis of the chemical behavior down to the very low but non-vanishing metallicities ($Z^* \lesssim 10^{-3} \times$ solar) associated with the early cosmic transition from Pop-III to Pop-II stars and early enrichment at the reionization epoch.

We have focused on the steady-state behavior and trends for H$_2$, CO, CH, OH, H$_2$O, and O$_2$, and the associated diagnostic abundance ratios CO/H$_2$, C/CO, OH/CO, and OH/O$_2$. In [2] we present a detailed discussion of the hydrogen-carbon-oxygen chemical networks and the varying molecule formation-destruction pathways, from Milky Way conditions to the low metallicity PopIII/PopII regime.

We have considered idealized shielded or partially shielded “one-zone” isothermal gas parcels, for which the steady-state abundances of the atomic and molecular species are fully determined by the assumed metallicity and ionization parameter, as discussed in [5]. We imagine that the (hydrogen) ionization rate $\zeta$ is provided by penetrating cosmic-rays or X-rays, and the associated secondary electrons. When FUV photo(destruction) processes are included a third parameter enters, the ratio $I_{UV}/n$ of the FUV intensity to the gas density. We have then considered two types of models. First are sequences for which irradiation by external FUV is fully excluded. Second are models for which FUV is turned on, but the H$_2$ Lyman-Werner photodissociation band remains fully blocked even when the parcels are optically thin to longer wavelength radiation. Our overall parameter space is, $10^{-3} \leq Z^* \leq 1$ and $10^{-3} \leq \zeta/n_3 \leq 10^2$. We assume a solar relative abundance pattern for the heavy elements, with absolute total abundances proportional to $Z^*$. For models with FUV-on we set $I_{UV}/n_3 = 1$. We adopt relative photoion rates appropriate for a diluted $10^7$ K blackbody field as representative of pop-III star spectra. Our computed atomic and molecular photodissociation and photoionization rates for such spectra are presented in Table 2.

The H/H$_2$ balance is critical to the overall chemical behavior since the ion-molecule sequences for the metal-bearing species all require at least some H$_2$. In [4] we present general purpose analytic results for the H-to-H$_2$ transition points and H$_2$ fractional abundances for optically thick conditions (i.e. no LW photodissociation) in which the H$_2$ is destroyed by ionization (by cosmic-rays or X-rays) and is formed on dust-grains or in the gas phase via the H$^-$ negative ion. We assume that the dust-to-gas ratio and H$_2$ grain formation efficiency vary as a simple power-law of the metallicity. The ionization parameters at the H-to-H$_2$ transition points in the limits of grain versus gas-phase H$_2$ formation are given by our Equations 20 and 22. The H$_2$ abundances (in the atomic regime) are given by Equations 24 and 25. We have verified our H/H$_2$ analysis with our detailed full chemistry computations in [5] and [6].

For our chemical study we have first considered 1D cuts, for varying $Z^*$ and fixed $\zeta/n$, and second for varying $\zeta/n$ at fixed $Z^*$.
with and without FUV. These computations are presented in §5 and enable our development of abundance scaling formulae, mainly for OH, O$_2$ and CO, in both the molecular and atomic hydrogen regimes, from high to low metallicity. The division between these regimes in our full $Z'$ versus $\zeta/n$ parameter space depends on how the dust-to-gas ratio varies with metallicity (§4). In our numerical calculations (§5 and 6) we have assumed a linear variation.

In §6 we present the results of our chemical computations as color-contour plots in our 2D, $Z'$ versus $\zeta/n$ parameter space. Our primary results, all for steady state conditions, are as follows. First, in the absence of photodissociation CO molecules always form efficiently even at very low $Z'$ provided $\zeta/n$ is small enough for the hydrogen to become molecular. (The time-scale for such conversion may be long at early cosmic times as we have estimated in §4.2.) The C/CO abundance ratio grows to ~1 at high $\zeta/n$ but not much larger, again so long as the conversion to H$_2$ is complete.

Second, we find that the OH abundances are maximal near the critical H-to-H$_2$ transition points. This is a very general trend also encapsulated in our analytic expressions for the OH abundance in the atomic and molecular regimes (Equations 32 and 34). A large fraction of the available gas-phase oxygen is driven to OH at low $Z'$, and the OH persists within the atomic regime (e.g., Figure 12). To first-order, the OH abundance is proportional to $\zeta/n$ in the molecular regime, but inversely proportional to $\zeta/n$ in the atomic regime.

Third, the OH/O$_2$ abundance ratio approaches unity near the critical H-to-H$_2$ transition points, and increases without limit, as $1/Z'$, into the (low-metallicity) atomic regime. The behavior of the OH/O$_2$ ratio is not affected by FUV photodissociation of the OH so long as the CO is shielded by H$_2$.

Fourth, the O$_2$/OH ratio becomes large within the molecular regime at sufficiently low $\zeta/n$ and increasing metallicity. In the molecular regime C/CO and O$_2$/OH are anticorrelated. However, OH is always the dominant oxygen-bearing molecule at sufficiently low $Z'$. Furthermore, even for comparable carbon and oxygen elemental abundances, OH/CH $\gg$ 1 at low metallicities, and OH becomes the dominant heavy-bearing molecule at low $Z'$.

Dense cold star-forming clouds at the PopIII/PopII transition and the epoch of reionization may have been atomic and OH-dominated rather than molecular and CO dominated.

ACKNOWLEDGMENTS

We thank Alex Dalgarno and Avi Loeb for helpful conversations during the course of this work. S.B. acknowledges support from the Raymond and Beverly Sackler Tel Aviv University – Harvard Astronomy Program. This work was also supported in part by the DFG via German-Israeli Project Cooperation grant STE1869/1-1/GE625/15-1, and by a PBC Israel Science Foundation I-CORE Program grant 1829/12.

REFERENCES

Asplund M., Grevesse N., Sauval A. J., Scott P., 2009, ARAA, 47, 481

Balakrishnan N., 2004, Geophys. Res. Lett., 31, L04106

Bayer E., Williams D. A., Hartquist T. W., Viti S., 2011, MNRAS, 414, 1583

Beers T. C., Christlieb N., 2005, ARAA, 43, 531

Black J. H., Dalgarno A., 1973, ApJ, 184, L101

Boger G. I., Sternberg A., 2005, ApJ, 632, 302

Boger G. I., Sternberg A., 2006, ApJ, 645, 314

Bolatto A. D., Wolfire M., Leroy A. K., 2013, ARAA, 51, 207

Bromm V., Loeb A., 2003, Nature, 425, 812

Caffau E. et al., 2011, Nature, 477, 67

Carollo D., Freeman K., Beers T. C., Placco V. M., Tumlinson J., Martell S. L., 2014, ApJ, 788, 180

Cazaux S., Tielens A. G. G. M., 2002, ApJ, 575, L29

Chen P., Wise J. H., Norman M. L., Xu H., O’Shea B. W., 2014, eprint [arXiv:1408.2523]

Dalgarno A., 2006, PNAS, 103, 12269

Dalgarno A., Black J. H., 1976, a, 39, 573

Dalgarno A., McCray R. A., 1973, ApJ, 181, 95

de Jong T., 1972, AA, 20, 263

Draine B. T., 1978, ApJS, 36, 595

Draine B. T., 2003, ApJ, 598, 1017

Draine B. T., 2011, Physics of the Interstellar and Intergalactic Medium (Princeton, NJ: Princeton Univ. Press)

Förster Schreiber N. M. et al., 2009, ApJ, 706, 1364

Freedel A., Simon J. D., Kirby E. N., 2014, ApJ, 786, 74

Glover S. C. O., 2003, ApJ, 584, 331

Glover S. C. O., Clark P. C., 2013, MNRAS, 437, 9

Graedel T. E., Langer W. D., Freking M. A., 1982, ApJS, 48, 321

Grebe J., Homann K. H., 1982, Berichte der Bunsengesellschaft für Phys. Chemie, 86, 587

Gredel R., Lepp S., Dalgarno A., Herbst E., 1989, ApJ, 347, 289

Hailey-Dunsheath S. et al., 2012, ApJ, 755, 57

Harding L. B., Guadagnini R., Schatz G. C., 1993, J. Phys. Chem., 97, 5472

Harwit M., Spans M., 2003, ApJ, 589, 53

Heays A. N., Visser R., Gredel R., Ubachs W., Lewis B. R., Gibson S. T., van Dishoeck E. F., 2014, AA, 562, A61

Heger A., Woosley S. E., 2010, ApJ, 724, 341

Herbst E., Klemperer W., 1973, ApJ, 185, 505

Hinshaw G. et al., 2013, ApJS, 208, 19

Hollenbach D. J., Werner M. W., Salpeter E. E., 1971, ApJ, 165

Igea J., Glassgold A. E., 1999, ApJ, 518, 848

Indriolo N., McCall B. J., 2012, ApJ, 745, 91

Jura M., 1974, ApJ, 191, 375

Le Teuff Y. H., Millar T. J., Markwick A. J., 2000, AAS, 146, 157

Lee H.-H., Roueff E., Pineau des Forets G., Shalabiea O. M., Terzieva R., Herbst E., 1998, AA, 334, 1047

Lepp S., Dalgarno A., 1996, AA, 306, L21

Lepp S., Tiné S., 1998, in The Molecular Astrophysics of Stars and Galaxies, ed., T.W. Hartquist and D.A. Williams. Clarendon Press, Oxford, p. 489.

Maloney P. R., Hollenbach D. J., Tielens A. G. G. M., 1996, ApJ, 466, 561

Mannucci F., Cresci G., Maiolino R., Marconi A., Gnerucci A., 2010, MNRAS, 408, 2115

Mashian N., Sternberg A., Loeb A., 2013, MNRAS, 435, 2407

McCall B. J. et al., 2003, Nature, 422, 500

McElroy D., Walsh C., Markwick A. J., Cordiner M. A., Smith K., Millar T. J., 2013, AA, 550, A36

McKee C. F., Ostriker E. C., 2007, ARAA, 45, 565

Meijerink R., Spaans M., 2005, AA, 436, 397

© 0000 RAS, MNRAS 000, 000–000
