The Role of Neutral Hydrogen in Setting the Abundances of Molecular Species in the Milky Way’s Diffuse Interstellar Medium. II. Comparison between Observations and Theoretical Models

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Abstract

We compare observations of H1 from the Very Large Array (VLA) and the Arecibo Observatory and observations of HCO+ from the Atacama Large Millimeter/submillimeter Array (ALMA) and the Northern Extended Millimeter Array (NOEMA) in the diffuse (AV < 1) interstellar medium (ISM) to predictions from a photodissociation region (PDR) chemical model and multiphase ISM simulations. Using a coarse grid of PDR models, we estimate the density, FUV radiation field, and cosmic-ray ionization rate (CRIR) for each structure identified in HCO+ and H1 absorption. These structures fall into two categories. Structures with AV < 40 K, mostly with N(HCO+) ≲ 1012 cm−2, are consistent with modest density, FUV radiation field, and CRIR models, typical of the diffuse molecular ISM. Structures with spin temperature T < 40 K, mostly with N(HCO+) ≳ 1012 cm−2, are consistent with high density, FUV radiation field, and CRIR models, characteristic of environments close to massive star formation. The latter are also found in directions with a significant fraction of thermally unstable H1. In at least one case, we rule out the PDR model parameters, suggesting that alternative mechanisms (e.g., nonequilibrium processes like turbulent dissipation and/or shocks) are required to explain the observed HCO+ in this direction. Similarly, while our observations and simulations of the turbulent, multiphase ISM agree that HCO+ formation occurs along sight lines with N(H1) ≳ 1021 cm−2, the simulated data fail to explain HCO+ column densities > few × 1012 cm−2. Because a majority of our sight lines with HCO+ had such high column densities, this likely indicates that nonequilibrium chemistry is important for these lines of sight.

Unified Astronomy Thesaurus concepts: Photodissociation regions (1223); Interstellar absorption (831); Interstellar phases (850); Interstellar atomic gas (833); Diffuse molecular clouds (381); Molecule formation (2076)

1. Introduction

Many molecular species have been detected in the diffuse interstellar medium (ISM), revealing important chemistry even at AV < 1 (Marscher et al. 1991; Lucas & Liszt 1996, 2000a, 2000b; Liszt & Lucas 2001; Liszt et al. 2014; Snow & McCall 2006 and references therein). HCO+ is one of the most commonly detected molecules in the diffuse ISM (e.g., Lucas & Liszt 1996) and has been shown to be an excellent tracer of molecular hydrogen, H2 (Liszt & Lucas 2000; Liszt et al. 2010). However, an outstanding problem for the last few decades has been that the observed HCO+ column densities in the diffuse ISM are often one to two orders of magnitude higher than what is expected theoretically from UV-dominated chemical models (Lucas & Liszt 1996), with large column density variations observed across interstellar clouds of similar total hydrogen column density (see, e.g., Figure 3 of Rybarczyk et al. 2021, hereafter Paper I). HCO+ has been observed in absorption in the direction of extragalactic point sources (e.g., Lucas & Liszt 1996; Godard et al. 2010; Liszt & Gerin 2018; Liszt et al. 2018b; Gerin et al. 2019; Luo et al. 2020) as well as Galactic H II regions (e.g., Nyman 1983; Maxia et al. 2001; Churchwell et al. 2010; Gerin et al. 2019). The range of the observed HCO+ column densities spans a few × 1010 cm−2 to ∼ 1014 cm−2, with an essentially continuous distribution sampling a range of interstellar environments, from more diffuse molecular gas to dense dark clouds. More diffuse environments (AV ≲ 1) typically have HCO+ column densities < 1012 cm−2 and often show weak CO emission (Liszt & Lucas 1998), while clouds in the Galactic Center or prominent local clouds such as Taurus or California have column densities > 1012 cm−2 and tend to have more pronounced CO emission.

Several previous studies have modeled HCO+ observations using photodissociation region (PDR) chemical models, where FUV photons are attenuated by dust and molecules as AV increases, allowing molecular species to form in shielded regions, and where molecular abundances are calculated under the steady-state approximation (e.g., Hollenbach & Tielens 1999). Such models have often been able to explain the column densities observed in denser environments but have routinely failed to explain the high HCO+ column densities observed in the diffuse ISM (e.g., Godard et al. 2009). This suggests that some key elements, likely involving dynamical effects, are still not accounted for in our conventional understanding of the formation and evolution of molecules in the
explain the enhanced column densities of species such as $\text{HCO}^+$ in the diffuse ISM, for example, the turbulent mixing between the cold neutral medium (CNM) and warm neutral medium (WNM) (Lesaffre et al. 2007), or turbulent dissipation in shocks or velocity shear (Flower & Pineau des Forêts 2003; Falgarone et al. 2006; Godard et al. 2009; Lehmann et al. 2020). In particular, the turbulent dissipation region (TDR) model has had success in explaining high HCO$^+$ column densities in the diffuse ISM (Godard et al. 2009). In this model, the release of suprathermal energy by turbulent dissipation enhances the formation of various molecular species along the line of sight. The model predictions were strongly dependent on the gas density and the turbulent rate of strain, but for a wide range of values, the TDR model was able to explain the high HCO$^+$ and CH$^+$ column densities observed in the diffuse ISM. Although several species were still underpredicted by an order of magnitude and the results are also dependent on the chemistry, this nevertheless demonstrates that attention to dynamical processes can significantly reduce the disparity between model predictions and observational results. More recently, intermittent turbulent dissipation—which occurs on timescales much shorter than the $10^5$–$10^7$ yr required for H$_2$ to reach steady state in the diffuse ISM (Goldsmith & Li 2005)—has been proposed to explain the CH$^+$ column densities in the diffuse ISM that far exceed PDR model predictions (e.g., Valdivia et al. 2017; Lesaffre et al. 2020). As CH$^+$ contributes to HCO$^+$ formation, this may suggest that the high HCO$^+$ column densities observed in the diffuse ISM reflect a large supply of CH$^+$ from dynamical events.

These alternative chemical models couple the chemical evolution of gas with the turbulent dynamical evolution of the environment. Therefore, to distinguish between these different models, we need to trace the underlying dynamical processes that influence molecule formation. With the goal of diagnosing the underlying properties of atomic gas, which is the main ingredient for the formation and survival of molecules, we recently conducted a survey of HCN, C$_2$H, HCO$^+$, and HNC in the direction of 20 background radio continuum sources where the 21-SPONGE project (21 cm Spectral Line Observations of Neutral Gas with the Karl G. Jansky Very Large Array; Murray et al. 2015, 2018) previously observed atomic hydrogen (H$_1$) in emission and absorption (Paper I). With the characterization of the line-of-sight environments from 21-SPONGE, we can highlight the interstellar conditions where models typically fail to match observed molecular column densities. This approach has not been used previously, yet it can differentiate the environments where UV-dominated chemical models are sufficient to explain the observed molecular column densities from those where alternative chemical models are needed. Specifically, in this work we test whether the Gong et al. (2017) PDR model can reproduce the observed HCO$^+$ column densities given the environmental constraints from 21-SPONGE for absorption features detected in Paper I. We use a set of models with a broader range of far-ultraviolet (FUV) interstellar radiation field (ISRF) strengths and cosmic-ray ionization rates (CRIR) than have previously been employed in comparisons of PDR model predictions to HCO$^+$ abundances in the diffuse ISM (Godard et al. 2010). We do not seek a precise model fit to the data, but rather a rough estimate of the density, FUV radiation field, and CRIR needed by the PDR model to explain observations. We then compare these estimates to existing observational probes of these environmental parameters along the observed lines of sight. Sight lines where the PDR estimates differ from observationally constrained estimates by an order of magnitude or more likely mark sites of nonequilibrium chemistry, where the PDR models fail to explain HCO$^+$ abundances due to the role of dynamical processes in molecule formation and survival. Alternative chemical models are likely required to explain the HCO$^+$ column densities in such cases, although, as we discuss in Sections 4 and 5, it may also be possible to understand high HCO$^+$ column densities for PDRs near H II regions. We discuss further in Section 6 whether this explanation is plausible for our lines of sight.

Furthermore, despite the power of PDR models to explain observed molecular abundances in some (denser) interstellar environments, the PDR model remains a very crude representation of the ISM—the realistic ISM is turbulent and multiphase, with complex dynamical, thermal, and chemical structures. This situation can be improved somewhat by pairing chemical modeling with magnetohydrodynamical (MHD) simulations, which provide a more realistic description of density structures in the turbulent, multiphase ISM. For example, postprocessing PDR chemistry on lines of sight from MHD simulations rather than uniform-density cloud models can change the column density estimates by a factor of at least a few for key species in the diffuse ISM and bring theoretical predictions closer to observational results (Levrier et al. 2012). Such work often relies on simplified networks that reliably reproduce PDR model results at a lower computational cost than a full chemical network. More complex chemical modeling is also possible with MHD simulations (e.g., Glover et al. 2010), but this can be very computationally costly. A variety of different chemical models have emphasized that more realistic models of ISM density structures from MHD simulations significantly impact molecular abundances and are important for understanding the observed molecular column densities in the ISM (e.g., Levrier et al. 2012; Gong et al. 2018). Thus, in this work, we also compare the HCO$^+$ (Paper I) and multiphase H I (Murray et al. 2018) column densities to predictions from chemically postprocessed MHD simulations (Gong et al. 2020).

In Paper I, we presented a summary of new observations of C$_2$H, HCN, HCO$^+$, and HNC in absorption obtained using the Atacama Large Millimeter/submillimeter Array (ALMA) and the Northern Extended Millimeter Array (NOEMA). We also discussed methods for extracting HCO$^+$ column densities and decomposing absorption spectra into Gaussian components. We used complementary observations of atomic and molecular gas to investigate the atomic gas conditions necessary for molecule formation in the diffuse ISM. We demonstrated that HCO$^+$ (as well as C$_2$H, HCN, and HNC) forms along sight lines where the visual extinction is $\gtrsim 0.25$ and the column density of cold H I is $\sim 10^{20}$ cm$^{-2}$, similar to the observed conditions required for the H I-to-H$_2$ transition in the Galactic ISM (e.g., Savage et al. 1977; Shull et al. 2021). Moreover, we found that these molecular species were associated only with structures with a H I optical depth $\gtrsim 0.1$, spin temperature $<80$ K, and turbulent Mach number $\gtrsim 2$. We note that the spin temperature is approximately equal to the kinetic temperature in these environments. Also, the higher turbulent Mach numbers, which are consistent with previous results (e.g., Burkhardt et al. 2015), reflect the colder gas temperature rather than...
than higher turbulent velocities in most cases. The turbulent Mach number is not used as a constraint in this work.

In this second paper, we compare the results from Paper I with predictions from the Gong et al. (2017) PDR chemical model and the Gong et al. (2020) ISM simulations. In Section 2, we briefly introduce the data and methods presented in Paper I, including observations of H I emission and absorption from the 21-SPONGE project (Murray et al. 2015, 2018), new observations of HCO\(^+\) absorption from ALMA and NOEMA, and supplementary archival measurements of dust extinction and dust temperature from the Planck satellite (Planck Collaboration et al. 2014). We then discuss the PDR model from Gong et al. (2017) and the ISM simulations from Gong et al. (2020) in Section 3. In Section 4, we find the PDR models that best reproduce the observed HCO\(^+\) and H I gas properties from a grid of models with varying densities, FUV fields, and CRIRs. In Section 5, we compare the observed line-of-sight column densities to predictions derived from the multiphase ISM simulations in Gong et al. (2020). We then discuss our results in Section 6. We compare the PDR model results in Section 4 (constraints on the local density, FUV field, and CRIR) to previous observations in these directions to test whether the PDR model results are plausible. Our conclusions are then presented in Section 7.

2. Data

Here we provide a brief summary of new and existing observations used in this study. A full description of these observations was presented in Paper I.

2.1. Observations of H I with 21-SPONGE

The 21-SPONGE project (Murray et al. 2015, 2018) observed Galactic H I absorption and emission with the Very Large Array (VLA) and the Arecibo Observatory in the direction of 57 bright background radio continuum sources with Galactic latitude \(3\leq |b| \leq 81^\circ\). The H I absorption and emission spectra were decomposed into Gaussian components.

The optical depth, \(\tau\), spin temperature, \(T_s\), and column density, \(N(HI)\), of each H I component was estimated using the equations of radiative transfer. From the spin temperatures, Murray et al. (2018) also determined the fraction of H I in each of the three atomic gas phases in the neutral ISM: the cold neutral medium (CNM, \(T_s < 250\) K), the unstable neutral medium (UNM, 250 K < \(T_s < 1000\) K), and the warm neutral medium (WNM, \(T_s < 1000\) K). We use the H I properties constrained by 21-SPONGE for comparison with the PDR model and MHD simulations.

2.2. Observations of HCO\(^+\) Absorption with ALMA and NOEMA

We observed C2H, HCN, HCO\(^+\), and HNC in absorption with ALMA during observing cycles 6 and 7 (ALMA-SPONGE) in the direction of 19 bright background radio continuum sources previously observed by the 21-SPONGE project. We observed an additional three sources (two overlapping with ALMA-SPONGE) in HCO\(^+\) and HCN absorption with NOEMA (NOEMA-SPONGE). Here we consider only the HCO\(^+\) absorption spectra, as C2H, HCN, and HNC are not included in the Gong et al. (2017) chemical model.

We decomposed the HCO\(^+\) absorption spectra into Gaussian components. The HCO\(^+\) column density was calculated from the optical depth integral, \(N(HCO^+) = 1.11 \times 10^{15} \text{ cm}^{-2} \int \tau(HCO^+) \text{ d}v\), for individual components and for the total line of sight. This conversion assumes an excitation temperature equal to the temperature of the CMB, 2.725 K (Godard et al. 2010; Luo et al. 2020). We test and discuss this assumption in Section 5.

2.2.1. Identifying the Corresponding H I Spectral Features

In total, nine sight lines in Paper I showed HCO\(^+\) absorption at a level \(\geq 3\sigma\), comprising 23 Gaussian components. Murray et al. (2018) identified H I absorption in all 20 sight lines, comprising 101 Gaussian components. Using a radial-velocity-matching criterion, we identified the H I structures with a molecular component (i.e., those that were coincident in velocity with HCO\(^+\) absorption). In some cases, a single H I feature was associated with multiple HCO\(^+\) features. In these cases, we consider the total HCO\(^+\) column density (the sum of the individual HCO\(^+\) column densities). We also ignore five features for which Murray et al. (2018) were unable to fit a physically meaningful \(T_s\), because \(T_s\) is an important constraint in our fitting.

We find 11 features with detailed H I properties from 21-SPONGE and well-constrained HCO\(^+\) column densities from Paper I. Table 1 lists the observed parameters we use for PDR modeling for these structures—the HCO\(^+\) column density, the
H I optical depth, and the H I spin temperature (see Equation (2)). These parameters are also plotted in Figure 1. Figure 1 also includes the remaining 85 components where Murray et al. (2018) detected H I in absorption but we detected no HCO$^+$; upper limits to the HCO$^+$ column densities for these features are shown in gray.

2.3. E(B - V) and $T_d$ from Planck

We estimate the total hydrogen column density, $N_{\text{H}} = N(\text{H}) + 2N(\text{H}_2)$, from the interstellar reddening, $E(B - V)$,

$$N_{\text{H}} = 2.08 \times 10^{21} \times 3.1E(B - V) \text{ cm}^{-2} \text{ mag}^{-1}$$  (1)  

(Zhu et al. 2017). Here, $3.1E(B - V)$ is used as an estimate of the visual extinction, $A_V$. For each sight line, we extract $E(B - V)$, derived from the dust radiance measured by the Planck satellite (Planck Collaboration et al. 2014), from the nearest pixel using the dustmaps Python package (Green 2018). We also extract the dust temperature, $T_d$, from the maps derived by Planck Collaboration et al. (2016) based on a modified blackbody spectral model of Planck temperature maps at 353, 545, 857, and 3000 GHz. Because the dust temperature is set in part by the strength of the interstellar radiation field (ISRF), it can be used to estimate the strength of the radiation field, $\propto T_d^{\beta - 4}$, where $\beta$ (also measured by Planck) is the power-law index that describes the dust emissivity cross section as a function of frequency (e.g., Equation (7.15) of Lequeux 2005). However, the dust temperature also depends on the grain size distribution, grain composition, and structure, which results in a more complex relationship between $T_d$ and the strength of the ISRF. Moreover, the resolution of the Planck dust maps is $S'$, so the values of $E(B - V)$, $T_d$, and $\beta$ are only considered as very rough estimates to the local properties of the gas sampled by our H I and molecular pencil-beam absorption spectra. We also note that the estimates of $T_d$, $\beta$, and the ISRF strength derived from Planck observations are not included in our modeling; they are only discussed in Section 6 for context.

3. Descriptions of Theoretical Models

We now briefly describe the PDR chemical model from Gong et al. (2017) and the ISM simulations from Gong et al. (2020). In Sections 4 and 5, we compare the HCO$^+$ and H I observations from Paper I and Murray et al. (2018) to the predictions from these models.

3.1. PDR Models

We use the PDR code developed by Gong et al. (2017), which is publicly available. The simplified chemical network in the PDR code has been tested against a much larger network and proved to produce accurate abundances of all modeled chemical species such as HCO$^+$, CO, H$_2$, H$_3^+$, etc. (Gong et al. 2017). We adapt a 1D slab model of uniform density, with a CRIR. The incident FUV radiation field comes from one side of the slab, which is then attenuated by both dust and molecular shielding. The code uses a simplified chemical network that solves the evolution of chemical species such as HCO$^+$, CO, and H$_2$, HCN, HNC, and C$_2$H—which were also observed in Paper I—are not yet included in the chemical network, so we focus only on the properties of HCO$^+$ and H I. The heating and cooling of the gas are solved simultaneously with the chemical evolution. The solar-neighborhood condition assumes a primary CRIR per H atom of $\xi = \xi_0$, where $\xi_0 = 2 \times 10^{-16}$ s$^{-1}$ is the measured local CRIR (Indriolo et al. 2007), and the FUV radiation field of $G' = 1$, where $G'$ is the radiation field strength relative to the standard Draine (1978) field. For each PDR model, we use a fixed value of $\xi$ and $G'$, run the
chemistry, temperature, and radiation transfer up to a total column (in units of H atoms) of \(N_H = 5 \times 10^{23} \text{ cm}^{-2}\),\(^{10}\) and iterate until steady state. We vary the density of the PDR (in the unit of H atoms) between \(n = 10^{-6} \text{ cm}^{-3}\). To explore the effect of the environment, we vary the FUV radiation field \(G' = 0.1 - 100\) and \(\xi/\xi_0 = 0.1 - 10\), with a very coarse grid, spacing the values of \(G'\) and \(\xi\) by factors of 10.

For each component of the Gaussian decomposition where HCO\(^+\) is detected, there are three values constrained by the observations in Paper I: the HCO\(^+\) column density \(N_{\text{HCO}^+}\), the HI optical depth \(\tau_{\text{HI}}\), and the H I spin temperature \(T_s\). We attempt to find the PDR model that minimizes the residual \(\chi^2\) between the model and observations by investigating a coarse grid of model parameters, where \(\chi^2\) is defined as

\[
\chi^2 = \left( \frac{N_{\text{HCO}^+ \text{obs}} - N_{\text{HCO}^+ \text{PDR}}}{\epsilon^2_{\text{HCO}^+ \text{obs}}} \right)^2 + \left( \frac{\tau_{\text{HI} \text{obs}} - \tau_{\text{HI} \text{PDR}}}{\epsilon^2_{\tau_{\text{HI}}}} \right)^2
\]

\[
+ \left( \frac{T_s \text{obs} - T_s \text{PDR}}{\epsilon^2_{T_s}} \right)^2
\]

(2)

This fitting process is not looking for the best-fit model but a rough estimate of the parameters needed to explain observations. The uncertainties in the denominators are calculated from

\[
\epsilon^2 = \epsilon^2_{\text{obs}} + \epsilon^2_{\text{sys}}
\]

(3)

where \(\epsilon^2_{\text{obs}}\) is the observational uncertainty directly obtained from the Gaussian decomposition (Paper I) and \(\epsilon^2_{\text{sys}}\) is the systematic uncertainty. For each slab model at a given \(N_H\), \(N_{\text{HCO}^+ \text{PDR}}\) is obtained directly from the chemical abundances; \(\tau_{\text{HI} \text{PDR}}\) is the integrated peak optical depth of H I assuming a constant velocity dispersion derived from the observed Gaussian component; and \(T_s \text{PDR}\) is calculated from the average \(T_s\) weighted by the H I mass. The systematic uncertainty \(\epsilon^2_{\text{sys}}\) is difficult to estimate. One source of systematic uncertainty is the changes in HCO\(^+\) excitation temperatures, which affect the calculation of \(N_{\text{HCO}^+}\) (see Section 5). Another source of systematic uncertainty lies in the intrinsic assumption of Gaussian decomposition, which presumes that the different parts of the ISM can be represented by uniform structures well separated in velocity space. Murray et al. (2017) compared the H I observations from 21-SPONGE to numerical simulations and found a good agreement for H I column density and spin temperature within a factor of \(\sim 2\). Here we simply assume a systematic error of 50% of each observed value. Although \(\chi^2\) changes when we vary systematic error fraction, we experimented with varying \(\epsilon^2_{\text{sys}}\) and found that the resulting parameters derived from the PDR models are insensitive to the choice of systematic error fraction. For each Gaussian component, we put an upper limit on the total column density \(N_H\) of the slab models to be the \(N_H\) derived from Planck dust emission (Equation (1)). For sight lines in the direction of 3C 123B and 3C 120 where two Gaussian components with HCO\(^+\) detection are identified, the upper limit of column density for each component is simply set to be half of the \(N_H\) derived from dust, as there is no constraint on how much each Gaussian component contributes to the dust column.\(^{11}\)

### 3.2. ISM Simulations

While the PDR model provides constraints on the underlying physical processes by using a one-dimensional view of the ISM, numerical simulations provide complementary information by enabling a more direct representation of interstellar turbulence taking place in the multiphase medium. We use here ISM simulations from Gong et al. (2018) and briefly describe the key numerical methods. For more detailed descriptions, we refer readers to Gong et al. (2018, 2020).

The simulations are taken from the result of the R8-Z1 models in Gong et al. (2020), which represent the solar-neighborhood ISM environment. The simulation resolution is 2 pc and the box size is 1 kpc in the \(x\) and \(y\) directions in the galactic disk plane and 7 kpc in the \(z\) direction perpendicular to the galactic disk. The 3D magnetohydrodynamic simulations are run within the TIGRESS framework (Kim & Ostriker 2017; Kim et al. 2020), which models the self-consistent star formation feedback in the three-phase turbulent ISM. In the simulations, the gravitational collapse of dense gas leads to the formation of star clusters. Supernova and FUV feedback from the star clusters are calculated from a population synthesis model (Leitherer et al. 1999). The simulations reach a quasi-steady state after about 200 Myr. The TIGRESS simulations have been widely used for comparison with a large range of ISM observations, such as H I (Murray et al. 2017, 2020), CO (Gong et al. 2018, 2020), dust polarization (Kim et al. 2019), and H\(_\alpha\) (Kado-Fong et al. 2020). We postprocess the outputs to obtain the steady-state chemical abundances and gas temperature. Finally, we use the RADMC-3D code (Dullemond et al. 2012) to perform radiation transfer calculations to obtain the HCO\(^+\)(1-0) line excitation temperature, adopting the large velocity gradient (LVG) approximation.

Because it is nontrivial to match the structures along the line of sight in simulations to Gaussian components in observed spectra, we simply compare the simulations to the observed total line-of-sight column densities of HCO\(^+\) and H I presented in Paper I. In the future, we plan to generate synthetic spectra of H I and HCO\(^+\) directly from the simulations, which can be directly compared to observations.

### 4. Comparisons with PDR Models

The parameters for the most reasonable PDR models estimated for each Gaussian feature detected in HCO\(^+\) and H I absorption are given in Table 1. Even with a very coarse grid of \(G'\) and \(\xi\), the PDR model can fit the observed Gaussian components reasonably well, with the residual \(\chi^2 \lesssim 1\) (Equation (2)).

Table 1 is arranged with descending values of \(T_s\) and one can immediately see that there are two distinct groups in the parameters derived from PDR models. When \(T_s \gtrsim 40\) K, the data points are best reproduced with high density, \(n \approx 500 - 10^4 \text{ cm}^{-3}\), and higher values of \(G' \gtrsim 1\) and \(\xi/\xi_0 \gtrsim 1\). These dense PDRs exposed to strong FUV and CR radiation are indicative of environments close to the formation of

\(^{11}\) When fitted without any upper limits on \(N_H\), the column densities derived from the two Gaussian components in the direction of 3C 123B or 3C 120 are similar. Therefore, without better knowledge, we choose to simply use half of the dust-based \(N_H\) as the upper limit of the column density for each component.
massive stars, such as the edge of H II regions (Hollenbach & Tielens 1999; see Section 6.1 for more discussion). All sight lines in this group also have a significant fraction of thermally unstable H I (UNM; see Paper I, for details). In contrast, when $T_s \lesssim 40$ K, the data points are best reproduced by models with lower density, $n \approx 60$–700 cm$^{-3}$, and lower values of $G' \lesssim 1$ and $\xi/\xi_0 \lesssim 1$. Based on Paper I, three out of five of these components are in directions with negligible thermally unstable H I. These environments are consistent with classic diffuse molecular gas in the solar neighborhood (Draine 2011; Tielens 2013).

We note that our grid of models is very coarse, and there are significant uncertainties with regard to each parameter. For example, the parameters derived from PDR models change somewhat when we use two-sided instead of one-sided slab models, when we increase $\xi$ somewhat when we use two-sided instead of one-sided slab models. All sight points in these two distinct groups of data points separated by $T_s$ is robust. This clearly demonstrates the power of using H I to characterize the underlying physical conditions where molecules form and reside.

Figure 1 further demonstrates the behavior of these two groups. In order to achieve higher $T_s$, stronger FUV radiation and higher CRIR are needed to heat up the gas. However, FUV radiation and CRs also lead to the destruction of molecular gas, and thus higher densities are needed to form the observed column of HCO$^+$. We note that the fractional abundance of HCO$^+$ does not saturate until $\tau_{HI} \gtrsim 1$. Therefore, in the bottom panel of Figure 1, the curves show that $N$(HCO$^+$/H$^+$) steeply increases with $\tau_{HI}$ as the HCO$^+$ abundance increases. In the top panel, the $N$(HCO$^+$/H$^+$) relation is close to linear at $\tau_{HI} \gtrsim 1$, as the HCO$^+$ abundance approaches a constant value.

Previously, Godard et al. (2010) found that PDR models underpredicted the observed HCO$^+$ column densities by an order of magnitude for many diffuse lines of sight. They used the Meudon PDR code (Le Petit et al. 2006) with $n = 10^2$–10$^4$ cm$^{-3}$, $G'$ = 1–3, and $\xi/\xi_0 = 0.15$. Here we show that PDR models can reproduce the high observed HCO$^+$ abundances in the diffuse ISM (as well as environmental constraints provided by H I), but only when a much broader range of FUV radiation fields and CRIRs is allowed. In particular, the CRIR is significantly different between our models and those used in Godard et al. (2010). They used $\zeta_0 = 3 \times 10^{-17}$ s$^{-1}$, i.e., $\xi/\xi_0 = 0.15$, for all models. Observations of H$^+_1$, which due to its simple chemistry is one of the most direct tracers of the CR, have indicated a mean CRIR of a few times 10$^{-16}$ s$^{-1}$ in the Milky Way’s diffuse ISM (McCall et al. 2003; Indriolo et al. 2007), with measurements spanning an order of magnitude, from $\sim 0.5 \times 10^{-16}$ s$^{-1}$ to $\sim 5 \times 10^{-15}$ s$^{-1}$ (van der Tak et al. 2006; Indriolo et al. 2007; Indriolo & McCall 2012). These observationally derived CRIRs tend to be much higher than the canonical value used in Godard et al. (2010). The models used in this work range from $\xi = 0.1\xi_0$ (similar to the value used in Godard et al. 2010) to $\xi \approx 10\xi_0$. As discussed in Godard et al. (2010), the CR ionization rate has a strong influence on the HCO$^+$ column density, independent of density.

In Section 6.1 we further discuss whether the broad ranges in $n$, $G'$, and $\xi_0$ required by the PDR to approximate the observed HCO$^+$ and H I gas properties (Table 1) are plausible. We argue that environments where the PDR model requirements are incompatible with observations likely represent sites of nonequilibrium chemistry not represented in the PDR models.

5. Comparisons with Multiphase ISM Simulations

The MHD simulations allow us to investigate a common assumption used in calculating the HCO$^+$ column density. In Section 2.2, we assumed, like many previous studies, that the excitation temperature is equal to the CMB temperature (e.g., Godard et al. 2010; Luo et al. 2020). However, we can check this assumption using the simulated data. In the ISM simulation, the level population of HCO$^+$ is calculated by RADMC-3D code using the LVG approximation, where the escape probability of the photon is determined by the local velocity gradient. A background blackbody radiation field of 2.725 K is included, as well as collisional excitation by the H$_2$ molecule. The level population is solved iteratively, from which we derive the excitation temperature.

The excitation temperature of HCO$^+$ versus gas density is shown in Figure 2. At density $n \gtrsim 300$ cm$^{-3}$, the excitation temperature $T_{exc}(\text{HCO}^+)$ rises above the CMB temperature. This clearly shows that the observed $N$(HCO$^+$) can be underestimated in the higher-density regions. For example, if the excitation temperature of HCO$^+$ were 5 K (Figure 2), then the estimated HCO$^+$ column densities would be a factor of 2.2 too low. There are also significant variations in $T_{exc}(\text{HCO}^+)$ across snapshots in the simulations, where gas structure, FUV radiation field strength, and CRIR differ. This indicates that directions with higher $T_s$ in Table 1 likely have underestimated HCO$^+$ column densities. This will affect the comparison with the PDR model in Figure 1.

In Figure 3 we compare the total line-of-sight column densities of HCO$^+$ and H I, both from the simulation and from the observations. The total H I column density is shown in the
upper left panel. We can track in the simulation H I in different phases. The CNM column density (the column density of H I with \(T_s < 250 \text{ K}\)) is shown in the upper right panel. The UNM column density (the column density of H I with \(250 \text{ K} < T_s < 1000 \text{ K}\)) is shown in the lower-left panel. This is similar to Figure 3 of Paper I. We plot one representative time snapshot in the simulation, as we did not find a large variation with time. The line-of-sight column density in the simulations is calculated along the \(z\)-axis (face-on), and we found that viewing along the \(x\)- or \(y\)-axis (edge on) gives similar results. We note that only pixels with \(N(\text{HCO}^+) > 10^{10} \text{ cm}^{-2}\) are shown in Figure 3. In fact, most of the sight lines in the simulations only have the WNM component with a negligible amount of HCO\(^+\).

Both the simulation and observations show a transition from an atomic to a molecular region at \(N(\text{HI}) \approx 10^{21} \text{ cm}^{-2}\). This is mainly due to the H\(_2\) self-shielding (with a small contribution from dust-shielding) at \(A_v < 1\), which attenuates the FUV radiation and allows molecules to form in the absence of fast photodissociation.

Similarly, both the observations and simulation show that HCO\(^+\) is detected only where the column density of H I in the CNM is \(\gtrsim 10^{20} \text{ cm}^{-2}\). The lower-right panel further shows that the total amount of cold H I (CNM plus UNM) is correlated with the HCO\(^+\) column density for \(N(\text{HI})_{\text{CNM+UNM}} \gtrsim 2 \times 10^{20} \text{ cm}^{-2}\), below which no HCO\(^+\) is detected.

There are a few features that indicate potential tension between the observations and simulation, though. First, there are two distinct groups in the observations with low \(N(\text{HCO}^+) \approx 10^{11} \text{ cm}^{-3}\) and high \(N(\text{HCO}^+) > 10^{12} \text{ cm}^{-3}\), while the simulation shows a continuous distribution with most sight lines having intermediate values of \(N(\text{HCO}^+)\). Second, a couple of observed sight lines show a very high value of \(N(\text{HCO}^+) \approx 2 \times 10^{12} \text{ cm}^{-3}\), which is very rare in the simulations. One possible cause is the fact that we did not include H II regions in the simulations, which can produce ionization fronts with high gas density and incident radiation (Hollenbach & Tielens 1999) As discussed in Section 4, dense PDRs close to H II regions can be the site for HCO\(^+\) formation. In fact, sightlines in the direction of 3C 111A, 3C 123A, and 3C 123B have both total \(N(\text{HCO}^+) \gtrsim 2 \times 10^{12} \text{ cm}^{-3}\) as well as Gaussian decomposition components of high HI spin temperature and HCO\(^+\) column. It will be very interesting to investigate if the formation of HCO\(^+\) near H II regions can explain such high values of \(N(\text{HCO}^+)\). Finally, almost all simulated data have a significant fraction of UNM, and the lower-left panel of Figure 3 suggests that a UNM column density threshold of \(10^{20} \text{ cm}^{-2}\) is required for HCO\(^+\) formation. As we discussed in Paper I, though, 40% of observed directions in our sample have

![Figure 3. Comparison between the numerical simulation in Gong et al. (2020) (contours) and the observed HCO\(^+\) and H I column densities (scattered points). The contours show the 10%, 50%, and 90% density levels of the pixels with \(N(\text{HCO}^+) > 10^{10} \text{ cm}^{-2}\), viewing along the \(z\)-axis of the simulation (face on). Two sight lines (3C 120 and 3C 454.3) have no H I in the UNM, so only six points appear in the lower-left panel.](image-url)
no detectable UNM, including two of the nine sight lines that showed HCO$^+$ absorption (3C 120 and 3C 454.3).

Currently, we are working on a new set of numerical simulations with radiation feedback and H II regions from massive stars, as well as more accurate modeling of gas heating and cooling. In the future, direct comparisons between the observed spectra and simulated synthetic spectra, as well as more observational data, will put better constraints on the formation of molecules in the ISM.

6. Discussion

6.1. Are the PDR Parameters Realistic?

While results in Section 4 suggest that the HCO$^+$ column densities reported in Paper I may be underestimated in a few directions by a factor of a few due to the assumption of a constant (CMB) excitation temperature (and an even larger factor in the direction of 3C 111A, 3C 111B, and 3C 123B due to absorption-line saturation), we investigate here whether environmental estimates given in Table 1 are reasonable.

We can provide a rough estimate of the mean UV radiation field along a line of sight using the dust temperature $T_d$ and power-law index $\beta$, namely $G' \propto T_d^{\beta+4}$ (Section 2.3). Taking $T_d$ and $\beta$ from Planck (Planck Collaboration et al. 2014, 2016), we find that $G' \approx 0.52$ toward 3C 123, $G' \approx 0.44$ toward 3C 111, $G' \approx 0.90$ toward 3C 78, and $G' \approx 0.90$ toward BL Lac. These values are essentially similar to the solar-neighborhood ambient radiation field and are in agreement with PDR predictions in the direction of 3C 123B, BL Lac, 3C 120, 3C 454.3, and 3C 154, but are much lower than PDR predictions for 3C 111A, 3C 123A, 3C 78, and 3C 111B. There is no systematic difference in $T_d$ or the estimated FUV radiation field in the direction of the sources with high-$T_d$ structures in Table 1 from those with low-$T_d$ structures. We note that the Planck maps provide only line-of-sight integrated properties, while from $\mathrm{H}_I$ we know that there are multiple absorption structures along each line of sight listed in Table 1, as well as multiple molecular absorption structures along all but 3C 78. It is also known that $G'$ can vary on very small spatial scales, especially near O stars (e.g., Marconi et al. 1998). Nevertheless, the star formation rates in California and Taurus are modest (Lada et al. 2010), and neither 3C 111, 3C 123, nor 3C 78 are particularly close to any known $\mathrm{H}_II$ regions or protostellar objects (Lada et al. 2017). While it is difficult to definitively rule out the values of $G'$ given in Table 1 based on the above discussion, it is likely that PDR model parameters in the direction of 3C 111A, 3C 123A, 3C 78, and 3C 111B—an order of magnitude greater than the local mean—are too high.

Estimates of the local density in the diffuse ISM along our exact lines of sight are also difficult to obtain. In general, estimates of the densities of diffuse molecular gas structures are modest (∼a few $\times 10^4$ cm$^{-3}$ to a few $\times 10^5$ cm$^{-3}$; Goldsmith 2013), consistent with estimates from the PDR model for structures with $T_d < 40$ K. 3C 111 is behind the California molecular cloud, and 3C 111 and 3C 123 both probe gas from the Taurus molecular cloud, so we can compare the estimates in Table 1 to estimates of the densities in these well-studied structures. Previous works have estimated the densities of cores ($\sim 10^3$ cm$^{-3}$, assuming $G \sim 0.1$–1; Pineda et al. 2010) and filaments ($10^3$–$10^4$ cm$^{-3}$; Rodríguez-Baras et al. 2021) in Taurus and clumps in the direction of California ($10^3$–$10^3$ cm$^{-3}$; Herbst et al. 1991). The maximum densities toward 3C 123 and 3C 111 in Table 1 are $10^3$–$10^4$ cm$^{-3}$, which are similar in magnitude to those of cores and filaments in Taurus and California. However, extinction maps derived from Planck (full sky, 5′ resolution; Planck Collaboration et al. 2014), from point sources in the Two Micron All Sky Survey (Taurus and California, 2′ resolution; Lombardi et al. 2010), and from Herschel (California, 1′3 resolution; Lada et al. 2017) do not show exceptionally high extinction toward 3C 111 or 3C 123 (observations of cores, clumps, and filaments had higher resolution, 12″–47″). Nevertheless, Araya et al. (2014) established rough limits on the gas densities in the direction of 3C 111 (for gas structures between $-5$ km s$^{-1}$ and $+2$ km s$^{-1}$; the same as those listed in Table 1) in the range of $10^2$–$10^3$ cm$^{-3}$ from observations of H$_2$CO. The lower limit was established by comparison of CO and HCO$^+$ line profiles and the upper limit was established by the low observed excitation temperatures of H$_2$CO. A wide variety of other molecular lines has also been detected in absorption in the direction of 3C 111, including HCO, H$^{13}$CO$^+$, c-C$_3$H (Liszt et al. 2014), OH (Liszt & Lucas 1996), $^{12}$CO, $^{13}$CO, $^{15}$O (Liszt & Lucas 1998), CH, C$_2$H (Liszt & Liszt 2000), CN, HCN, HNC (Liszt & Lucas 2001), CS, SO, H$_2$S, HCS$^+$ (Liszt & Liszt 2002), CH (Liszt & Lucas 2002), l-C$_3$H, HC$_3$N, and CH$_3$CN (Liszt et al. 2018a). The rich diversity of molecular species identified in this direction testifies to a complex chemistry and likely implies high density. Observations toward 3C 123 have been rarer, although Nguyen et al. (2018) recently identified three OH absorption components in the direction of 3C 123, all consistent with the features we find at $\sim 3.3$ km s$^{-1}$, $\sim 4.3$ km s$^{-1}$, and $\sim 5.3$ km s$^{-1}$. OH is a diffuse molecular gas tracer (Li et al. 2018), so it is not clear based on existing observations if a density of $10^3$ cm$^{-3}$ (Table 1) is plausible.

The two highest-density estimates are in the direction of 3C 78 and BL Lac, with $n \sim 10^4$ cm$^{-3}$. The sight line toward 3C 78 probes the outer layers of the starless molecular cloud MBM 16 (Magnani et al. 1985) and may be directly probing a separate molecular cloud identified by LaRosa et al. (1999). H$_2$CO observations in the direction of MBM 16 suggest a density of $\lesssim 10^3$ cm$^{-3}$ (Magnani et al. 1993), but the 3C 78 sight line only probes the outermost layers of MBM 16. The density of the second molecular cloud is not known. LaRosa et al. (1999) detected CO in this direction, but we do not detect significant CO emission from Dame et al. (2001) in the pixels nearest 3C 78, nor do we see C$_2$H, HCN, or HNC absorption in this direction, probably indicating that a density of $10^4$ cm$^{-3}$ is not plausible. Meanwhile, BL Lac probes the Lacerta molecular cloud. As with 3C 111, Araya et al. (2014) inferred a density of $\sim 10^2$–$10^3$ cm$^{-3}$ in this direction from the properties of H$_2$CO absorption. The result in Table 1, $n \approx 10^4$ cm$^{-3}$, is consistent with these bounds.

The CRIR is not observationally well constrained along our lines of sight. It is known that the CRIR does vary between different lines of sight by as much as an order of magnitude, even in the diffuse ISM (van der Tak et al. 2006; Indriolo et al. 2007; Indriolo & McCall 2012). If low-energy cosmic rays are accelerated in localized shocks, it is expected that sight lines near more energetic regions, such as regions of massive star formation, will have higher CRIRs (Indriolo & McCall 2012), although this has not been tested observationally. CRIRs measured from observations of diffuse molecular gas have been...
as high as $\xi \approx 10\xi_0$ (Shaw et al. 2008), which is consistent with the higher estimates in Table 1.

In summary, the HCO$^+$ column densities of structures with $T_s < 40$ K are well explained by PDR models with modest densities, FUV fields, and CRIRs, consistent with what is expected for local diffuse molecular gas. On the other hand, the HCO$^+$ column densities of structures with $T_s > 40$ K are only explained by PDR models with systematically higher densities, FUV fields, and CRIRs. Previous observations in the direction of these structures suggest that the high densities in Table 1 may be plausible for some structures (in the direction of 3C 111 and BL Lac), but are very likely too high in at least one case (in the direction of 3C 78). We also do not find evidence for extremely strong FUV fields in any direction, nor are the star formation rates particularly high for molecular clouds in these directions like California or Taurus. This suggests that the estimates of the FUV field in Table 1 may also be too high for some of these structures.

6.2. Equilibrium versus Nonequilibrium Chemistry in the Diffuse ISM

The Gong et al. (2017) PDR (UV-dominated, equilibrium) chemical models appear sufficient to explain the observed HCO$^+$ column densities for the structures with $T_s < 40$ K along lines of sight that tend to have lower fractions of thermally unstable H I, without the need for nonequilibrium chemistry or nearby H II regions. While the densities ($\sim 60–700$ cm$^{-3}$) and FUV field strengths ($G^\prime \approx 0.1$) for these features were moderate, we note that in most cases the CRIR was $\xi \approx 0.5$. This is consistent with the observationally derived CRIR from H II (van der Tak et al. 2006; Indriolo et al. 2007; Indriolo & McCaill 2012), but about an order of magnitude higher than the CRIR used in the PDR models in Godard et al. (2010) (3 $\times 10^{-17}$ s$^{-1}$; Dalgarno 2006). As noted by Godard et al. (2010), increasing $\xi$ by an order of magnitude increases the column density of HCO$^+$ by an order of magnitude, regardless of gas density. This suggests that the CRIR may be partly responsible for the discrepancy between their PDR model predictions and HCO$^+$ observations (although we note that this is not the case for all species).

Meanwhile, structures with $T_s > 40$ K that were found along sight lines with high fractions of thermally unstable H I were most consistent with PDR models that had a very high density, FUV field, and CRIR. Based on the discussion in the previous section, the enhancement of HCO$^+$ near H II regions is probably not responsible for the high HCO$^+$ column densities along these lines of sight. In at least one case (toward 3C 78), we can definitively reject several of the parameters in Table 1, likely indicating that nonequilibrium effects play a role in producing HCO$^+$ in this direction. In Paper I, we showed that several of these structures had higher turbulent velocities ($v_t \gtrsim 1$ km s$^{-1}$ for the structures with $T_s > 40$ K and $v_t \lesssim 1$ km s$^{-1}$ for the structures with $T_s < 40$ K), suggesting they probe more turbulent environments than the low-$T_s$ structures. Moreover, the sight lines with high-$T_s$ structures in Table 1 also tend to have a high fraction of thermally unstable H I. Interestingly, the UNM is thought to be enhanced by the turbulent mixing of the CNM and UNM (e.g., Audit & Hennebelle 2005; Saury et al. 2014)—a process also thought to enhance molecular abundances (Lesaffre et al. 2007). The extent to which the UNM is a tracer of turbulent mixing or turbulent dissipation, though, depends on assumptions about the fraction of turbulent energy injected into each atomic gas phase. Nevertheless, the incompatibility of the PDR model parameters and existing observations in at least one case (and perhaps several cases), coupled with the large quantity of thermally unstable gas along these sight lines, argues in favor of alternative, nonequilibrium chemical models in these directions.

6.3. Future Work

In the future, observations of multiple molecular transitions can be used to more tightly constrain the environment of molecular clouds along these lines of sight. Observations of a wider range of chemical species may also be used as a probe for nonequilibrium chemistry to elucidate the role of turbulent dissipation, shocks, and other dynamical processes in diffuse interstellar chemistry. For example, Nguyen et al. (2018) measured three OH absorption features in the direction of 3C 154 at $-2.32$ km s$^{-1}$, $-1.39$ km s$^{-1}$, and $2.23$ km s$^{-1}$. In Paper I, we detected strong absorption for C$_2$H, HCN, HCO$^+$, and C$_2$H at $-2$ km s$^{-1}$ and $-1.3$ km s$^{-1}$. Additional, somewhat broader components were also identified in the HCO$^+$, C$_2$H, and HCN absorption spectra at $2.3$ km s$^{-1}$ and $-4$ km s$^{-1}$. The latter component was not detected in OH absorption by Nguyen et al. (2018), possibly suggesting that HCO$^+$, C$_2$H, and HCN are enhanced relative to OH in this particular structure. The TDR model predicts that at high HCO$^+$ column density, these species are enhanced relative to PDR predictions, while OH abundances are depressed (Godard et al. 2009). This feature is not included in Table 1 because $T_s$ is unknown for the H I structure (Murray et al. 2018). Nevertheless, this hints at nonequilibrium chemistry and emphasizes the importance of observing multiple species to disentangle PDR and TDR predictions. Species like CH$^+$ are also enhanced in TDRs, and SiO and HNCO are shock tracers. A comparison of observed absorption-line profiles to simulated synthetic spectra may also help identify regions where chemistry is out of equilibrium—it remains unclear, for example, if the broad component of HCO$^+$ identified in the ALMA-SPONGE and NOEMA-SPONGE spectra (see Paper I) can be explained by PDR models or if this spectral signature is indicative of turbulent dissipation (e.g., Falgarone et al. 2006).

7. Conclusion

We compare predictions from the Gong et al. (2017) PDR chemical model and the Gong et al. (2020) ISM simulations with HCO$^+$ observations from Paper I and H I observations from 21-SPONGE (Murray et al. 2015, 2018). It has previously been observed that HCO$^+$ column densities are generally higher than predicted from PDR models with solar-neighborhood conditions (e.g., Godard et al. 2010). Here, by using H I observations, we are able to diagnose interstellar conditions in which high column densities of HCO$^+$ are found. Using a coarse grid of PDR models, we estimate the density, FUV radiation field, and CRIR for each structure we identify in HCO$^+$ absorption. We find that absorbing structures fall into two categories—warmer features ($T_s \gtrsim 40$ K) mostly with high HCO$^+$ column densities ($\gtrsim 10^{12}$ cm$^{-2}$) that are best reproduced with high density, FUV radiation field, and CRIR models ($n \sim 10^3$–$10^4$ cm$^{-3}$, $G^\prime \gtrsim 1$, $\xi/\xi_0 \gtrsim 1$), and cooler features ($T_s \lesssim 40$ K) mostly with low HCO$^+$ column densities ($\lesssim 10^{12}$ cm$^{-2}$) that are best reproduced by low density, FUV radiation
The latter are typical of the diffuse molecular ISM in the solar neighborhood, whereas the former are more characteristic of environments close to the formation of massive stars. The important diagnostics provided by H1 observations demonstrated that high HCO⁺ column density features have systematically higher T* than the features with lower HCO⁺ column densities, and they are also found along lines of sight with higher fractions of thermally unstable HI (30%–70% Murray et al. 2018) than the lower-column-density features, a majority of which have negligible amounts of thermally unstable H1.

In at least one case, the parameters derived from PDR models for a structure with T* > 40 K is at odds with existing observations. Toward 3C 78, the estimated density of 10⁸ cm⁻³ and FUV field of G ~ 10 are implausible given that C₂H, HCN, and HNC are not detected in this direction and that there are no nearby sites of massive star formation. The densities and FUV fields required by the PDR model for several other structures, all with T* > 40 K, are also likely too high. A likely alternative explanation for the high HCO⁺ column density in these environments is HCO⁺ production through dynamical processes such as shocks or turbulent dissipation (Godard et al. 2009, 2010; Valdivia et al. 2017). Future observations (including, e.g., direct observations of shock tracers, isotopologues of CO and HCO⁺ that are not saturated, and species whose predicted line ratios are highly model dependent) are needed to distinguish between different nonequilibrium chemical models.

Finally, we show that observations and simulations of the turbulent, multiphase ISM (Gong et al. 2020) agree that HCO⁺ formation occurs when the total hydrogen column density reaches ~10²¹ cm⁻². However, the simulated data fail to explain HCO⁺ column densities ~10² cm⁻². Because six of the nine sight lines with detected HCO⁺ absorption from Paper I had such high column densities, this may again indicate that nonequilibrium chemistry is important for these lines of sight.

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Software: PDR code (Gong et al. 2017), RADMC-3D (Dullemond et al. 2012), dustmaps (Green 2018), CASA (McMullin et al. 2007).

References

Araya, E. D., Dieter-Conklin, N., Goss, W. M., & Andreev, N. 2014, ApJ, 784, 129
Audit, E., & Hennebelle, P. 2005, A&A, 433, 1
Bachiller, R., Lee, M.-Y., Murray, C. E., & Stanimirović, S. 2015, ApJL, 811, L28
Churchwell, E., Sievers, A., & Thum, C. 2010, A&A, 513, A9
Dalgarno, A. 2006, PNAS, 103, 12269
Dame, T. M., Hartmann, D., & Thaddeus, P. 2001, ApJ, 547, 792
Draine, B. T. 1978, ApJS, 36, 595
Draine, B. T. 2011, Physics of the Interstellar and Intergalactic Medium (Princeton, NJ: Princeton Univ. Press)
Dullemond, C. P., Juhász, A., Pohl, A., et al. 2012, RADMC-3D: A multi-purpose radiative transfer tool, Astrophysics Source Code Library, ascl:1202.015
Falgarone, E., Pineau Des Forêts, G., Hily-Blant, P., & Schilke, P. 2006, A&A, 452, 511
Flower, D. R., & Pineau des Forêts, G. 2003, MNRAS, 343, 390
Gerin, M., Liszt, H., Neufeld, D., et al. 2019, A&A, 622, A26
Glover, S. C. O., Federrath, C., Mac Low, M. M., & Klessen, R. S. 2010, MNRAS, 404, 2
Godard, B., Falgarone, E., Gerin, M., Hily-Blant, P., & de Luca, M. 2010, A&A, 520, A20
Godard, B., Falgarone, E., & Pineau Des Forêts, G. 2009, A&A, 495, 847
Goldsmith, P. F. 2013, ApJ, 774, 134
Goldsmith, P. F., & Li, D. 2005, ApJ, 622, 938
Gong, M., Ostriker, E. C., & Kim, C.-G. 2018, ApJ, 858, 16
Gong, M., Ostriker, E. C., Kim, C.-G., & Kim, J.-G. 2020, ApJ, 903, 142
Gong, M., Ostriker, E. C., & Wolfire, M. G. 2017, ApJ, 843, 38
Green, G. 2018, JOSS, 3, 695
Herbertz, R., Ungerechts, H., & Winnewisser, G. 1991, A&A, 249, 483
Hollenbach, D. J., & Tielens, A. G. G. M. 1999, RVMP, 71, 173
Indriolo, N., Geballe, T. R., Oka, T., & McCaill, B. J. 2007, ApJ, 671, 1736
Indriolo, N., & McCaill, B. J. 2012, ApJ, 745, 91
Kado-Fong, E., Kim, J.-G., Ostriker, E. C., & Kim, C.-G. 2020, ApJ, 897, 143
Kim, C.-G., Choi, S. K., & Flauger, R. 2019, ApJ, 880, 106
Kim, C.-G., & Ostriker, E. C. 2017, ApJ, 846, 133
Kim, C.-G., Ostriker, E. C., Somerville, R. S., et al. 2020, ApJ, 900, 61
Lada, C. J., Lewis, J. A., Lombardi, M., & Alves, J. 2017, A&A, 606, A100
Lada, C. J., Lombardi, M., & Alves, J. F. 2010, ApJ, 724, 687
LaRossa, T. N., Shore, S. N., & Magnani, L. 1999, ApJ, 512, 761
Le Petit, F., Nehmé, C., Le Bourlot, J., & Roueff, E. 2006, ApJS, 164, 506
Lehmann, A., Godard, B., Pineau des Forêts, G., & Falgarone, E. 2020, A&A, 643, A101
Leitherer, C., Schaerer, D., Goldader, J. D., et al. 1999, ApJS, 123, 3
Lequeux, J. 2005, The Interstellar Medium (Berlin: Springer)
Lesaffre, P., Todorov, P., Le Petit, F., et al. 2012, A&A, 544, A22
Li, D., Tang, N., Nguyen, H., et al. 2018, ApJS, 235, 1
Liszt, H., & Gerin, M. 2018, A&A, 610, A49
Liszt, H., Gerin, M., Beasley, A., & Pety, J. 2018a, ApJ, 856, 151
Liszt, H., Gerin, M., & Grenier, I. 2018b, A&A, 617, A54
Liszt, H., & Lucas, R. 1996, A&A, 314, 917
Liszt, H., & Lucas, R. 2000, A&A, 355, 333
Liszt, H., & Lucas, R. 2001, A&A, 370, 576
Liszt, H., & Lucas, R. 2002, A&A, 391, 693
Liszt, H., Lucas, R., & Pety, J. 2005, in IAU Symp. 231, Astrochemistry: Recent Successes and Current Challenges, ed. D. C. Lis, G. A. Blake, & E. Herbst (Cambridge: Cambridge Univ. Press), 187
Liszt, H. S., & Lucas, R. 1998, A&A, 339, 561

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