Water shielding in the terrestrial planet-forming zone: Implication for inner disk organics

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ABSTRACT

The chemical composition of the inner region of protoplanetary disks can trace the composition of planetary building material. The exact elemental composition of the inner disk has not yet been measured and tensions between models and observations still exist. Recent advancements have shown UV-shielding to be able to increase emission of organics. Here, we expand on these models and investigate how UV-shielding may impact chemical composition in the inner 5 au. In this work, we use the model from Bosman et al. (2022a) and expand it with a larger chemical network. We focus on the chemical abundances in the upper disk atmosphere where the effects of water UV-shielding are most prominent and molecular lines originate. We find rich carbon and nitrogen chemistry with enhanced abundances of C$_2$H$_2$, CH$_4$, HCN, CH$_3$CN, and NH$_3$ by > 3 orders of magnitude. This is caused by the self-shielding of H$_2$O, which locks oxygen in water. This subsequently results in a suppression of oxygen-containing species like CO and CO$_2$. The increase in C$_2$H$_2$ seen in the model with the inclusion of water UV-shielding allows us to explain the observed C$_2$H$_2$ abundance without resorting to elevated C/O ratios as water UV-shielding induced an effectively oxygen-poor environment in oxygen-rich gas. Thus, water UV-shielding is important for reproducing the observed abundances of hydrocarbons and nitriles. From our model result, species like CH$_4$, NH$_3$, and NO are expected to be observable with the James Webb Space Telescope (JWST).

Keywords: protoplanetary disks – astrochemistry – chemical abundances

1. INTRODUCTION

Within protoplanetary disks, the inner 2 to 3 au is a critical location in which much of the process of planet formation is believed to occur, referred to as the planet-forming zone (e.g. Pierrehumbert & Gaidos 2011; Morbidelli et al. 2012; Raymond et al. 2014; Morbidelli & Raymond 2016). Most directly, this region corresponds to radii at which terrestrial planets are formed (Mulders et al. 2015; Madhusudhan et al. 2021). Observations have shown that many stars are expected to have a planet within 1 au (Johnson et al. 2010; Mulders et al. 2018). The inner 1 au is inside or contains the H$_2$O iceline and water plays a large role in the evolution of life (e.g. Brown et al. 2013; Cockell et al. 2016; Lingam & Loeb 2019). Furthermore, inside the water iceline the elemental C/O ratio is predicted to be ~ stellar, which becomes inherited by giant planets (Öberg et al. 2011; Ida et al. 2019; Öberg et al. 2021). Thus, the location of formation impacts chemical composition (e.g. Lahuis et al. 2006; Öberg et al. 2011; Pontoppidan et al. 2011; Walsh et al. 2012; Madhusudhan 2019).

The inner disk is dust-rich leading to high optical depths. This makes it difficult to determine chemical content of the disk midplane. However, the radiation from the star, which is in close proximity, leads to a heated disk surface (i.e. T$_{gas}$ > T$_{dust}$), which produces a rich spectrum of emission from volatile molecules, particularly at infrared wavelengths.
(e.g. Carr & Najita 2008; Brown et al. 2013). Water vibrational lines at 3 µm, HCN vibrational at 3.3 µm, and CO vibrational at 4.7 µm have been observed with both Keck Near Infrared Spectrograph (NIRSPEC) and VLT-CRIRES (e.g. Salyk et al. 2011a; Brown et al. 2013; Mandell et al. 2013; Carr et al. 2018). Further lines of H₂O, OH, HCN, C₂H₂, and CO₂ have been detected by the Spitzer Space Telescope Infrared Spectrograph (IRS) which ranges from 10-37 µm (e.g. Carr & Najita 2008; Salyk et al. 2008, 2011b; Pontoppidan et al. 2010). All these lines are thought to originate in the inner 2 to 3 au, which allows us to trace the gas composition. These observations show that a diverse chemistry is present in the inner planet-forming zone.

Najita et al. (2013) and Najita et al. (2018) investigate the ratio of HCN/H₂O line flux and find it is related to disk dust mass. They argue that this relation is due to the formation of planetesimals which decouple from the dust and lock up water in distant regions. This effectively increases the C/O ratio in the inner disk directly impacting disk dust mass. They argue that this relation is due to the formation of planetesimals which decouple from the dust chemistry is present in the inner planet-forming zone.

To distinguish these scenarios we need to understand the C/O ratio of inner disk gas.

One way to determine the inner disk chemical content and C/O ratio is to use detailed thermo-chemical models. Models such as Dust and Lines (DALI) (Bruderer et al. 2012; Bruderer 2013), RAC2D (Du & Bergin 2014), and Protoplanetary Disk Model (ProDiMo) (Woitke et al. 2009), solve for both the gas thermal physics and the chemical equilibrium, given stellar parameters, the dust properties and mass distribution, and an overall gas-to-dust mass ratio. Based on these models, Woitke et al. (2018) and Anderson et al. (2021) find that altering the C/O ratio changes the predicted emission of molecules arising from inner disk gas. In their models, they have matched emission from multiple organics, but underproduced C₂ which unless an elevated C/O ratio is invoked.

Bethell & Bergin (2009) showed that strong formation rates of water vapor in hot (>400 K) surface gas can compete with ultraviolet (UV) photodestruction, allowing water to self-shield. Since water has a broad UV photoabsorption cross-section (Yoshino et al. 1996), this can also shield other molecules downstream, a process called water UV-shielding. Bosman et al. (2022a) (hereafter, Paper I), Calahan et al. (2022) (Paper II), and Bosman et al. (2022b) (Paper III) have shown that water UV-shielding lowers the UV flux deeper into the disk and is important in understanding H₂O, H₂O, and CO₂ emission.

Additional species beyond H₂O such as: H₂, CO, CI, HI and N₂ are also abundant in the surface layers to potentially impact the UV field. H₂, CO, atomic carbon, and N₂ all absorb wavelengths less than 110 nm, while most other species dissociate at wavelengths > 110 nm and most of the UV photons are also in this wavelength range (e.g. Herczeg et al. 2004; Heays et al. 2017). Thus, while the UV attenuation of these species greatly impacts each other, they do not greatly impact the dissociation of other species, in contrast to H₂O. Shielding by atomic H, specifically scattering of Ly-α does not seem to have a big impact of the chemistry of the inner disk (Paper II).

This naturally raises the question as to whether water UV-shielding affects the rest of the chemistry in the inner disk. This is what we investigate in this paper: the impact of water UV-shielding on chemistry in the inner disk, with the goal of reconciling current models with observations and making predictions for observations with the James Webb Space Telescope.

2. METHODS

2.1. Model setup

We use the DALI models from Paper I. These models include modification from standard DALI (Bruderer et al. 2012; Bruderer 2013) to better represent the inner disk regions. These include more efficient H₂ formation at high temperature, more efficient heating following photo-dissociation (following Glassgold & Najita 2015) and water UV-shielding (Bethell & Bergin 2009, Paper I). The models have an AS 209 like input spectrum with most of the UV in Ly-α taken from Zhang et al. (2021). Model setup details are in Paper I and model parameters are reiterated in Table 1. For this Letter we will only focus on one of the four structures discussed in Paper I, the flat ($h_c = 0.08$) model with a gas-to-dust ratio of $10^5$ as this model is best able to reproduce both the water and CO₂ emission (Paper III). The elemental abundances assumed in the chemistry are found in Table 1 and are based on Jonkheid et al. (2006), with reduced Mg, Si, S and Fe. Finally, as the chemical time-scale in the region of interest are short, we solve for statistical equilibrium (Anderson et al. 2021).
Table 1. Disk model parameters

| Parameter                        | Value                                      |
|----------------------------------|--------------------------------------------|
| Stellar Luminosity               | $1 \, L_\odot$                             |
| Stellar Spectrum                 | AS 209 $^a$                                |
| Stellar Mass                     | $1.0 \, M_\odot$                           |
| X-ray luminosity                 | $10^{30} \, \text{erg s}^{-1}$             |
| Cosmic ray ionization rate       | $10^{-17} \, \text{s}^{-1}$                |
| Sublimation radius               | 0.08 AU                                    |
| Critical radius                  | 46 AU                                      |
| Disk outer radius                | 100.0 AU                                   |
| Gas surf. dens. at $R_c$          | 21.32 g cm$^{-2}$                          |
| Surf. dens. powerlaw slope       | 0.9                                        |
| Disk opening angle               | 0.08                                       |
| Disk flaring angle               | 0.11                                       |
| Large dust fraction              | 0.999                                      |
| Large dust settling              | 0.2                                        |

| Element                  | Abundance w.r.t. H          |
|--------------------------|-----------------------------|
| H                        | 1.0                         |
| He                       | $7.59 \times 10^{-2}$       |
| C                        | $1.35 \times 10^{-4}$       |
| N                        | $2.14 \times 10^{-5}$       |
| O                        | $2.88 \times 10^{-4}$       |
| Mg                       | $4.17 \times 10^{-9}$       |
| Si                       | $7.94 \times 10^{-8}$       |
| S                        | $1.91 \times 10^{-8}$       |
| Fe                       | $4.27 \times 10^{-9}$       |

The DALI models use a simplified chemical network, which is sufficient for species such as CO, H$_2$O and CO$_2$. However, it does not include the reactions for realistic abundances of the organics, including C$_2$H$_2$ and HCN, which have been commonly observed with Spitzer-IRS (Carr & Najita 2008; Pontoppidan et al. 2010). To correct this, we use an expanded chemical network. This network is based on the network from Walsh et al. (2015) and includes modifications as denoted in Bosman et al. (2021). Furthermore, we made sure that the adaptations made to the simplified network, such as the H$_2$ formation reactions, 3-body reaction, and the collisional dissociation reactions are correctly incorporated into the bigger chemical network. This chemical network is then used to calculate the chemical composition with the gas-temperature and UV field from the standard DALI model. We adopt the H$_2$O abundances from the full chemical calculation to calculate the shielding of UV photons for the chemistry, but we do not update the gas temperature. More details on the model setup can be seen in Appendix A. Figure 4 contains information about the disk structure for our UV-shielding model. In Fig. 5, we show that the water abundances between the simplified and full network are very similar in the surface layers where water UV shielding is most important.

2.2. Determination of emitting layer

In Paper I, hot (>300–400 K) water vapor is found in high abundance in a thin surface layer that is radially confined within 1 au. In this region, the water vapor column exceeds $10^{20} \, \text{cm}^{-2}$ and with a gas-to-dust ratio of $10^5$, dust UV absorption is negligible compared to water UV shielding. Thus, including water shielding alters the UV transfer in the surface of the disk which should lead to large differences in our models. In the disk surface, UV photons heat the gas, creating $T_{\text{gas}} > T_{\text{dust}}$, a condition necessary for the emission of molecular lines. Inclusion of UV shielding thus is expected to lower the gas temperature and decrease emission deeper in the disk. This provides a boundary from below which we do not expect emission. In Papers I - III, we found that the emission comes from gas of $T_{\text{gas}} \gtrapprox 300\text{-}400 \, \text{K}$ and a hydrogen nuclei column of $\lesssim 10^{24} \, \text{cm}^{-2}$. This paper does not explore the radiation transfer, so we consider
Figure 1. The molecular abundance of various species over the inner 5 au, determined from the IR emitting layer, for the standard and water shielding models. The locations of the water and CO$_2$ icelines are at 0.27 au and 0.94 au, respectively. The drops in abundance near 0.9 au are a result of drops in the gas temperature in the surface layer (Sec. 4).

the top $10^{24}$ cm$^{-2}$ as our “infrared (IR) emitting layer”, corresponding to a $z/r \gtrsim 0.15$, and focus our analysis on the chemical composition of this layer.

3. RESULTS

Figure 1 shows the abundance in the emitting layer for two models, with and without water UV shielding (water shielding and standard, respectively). For H$_2$O, the predicted abundance remains relatively similar at radii within the CO$_2$ iceline, where the model with UV-shielding has more abundant water. In the case of CO, there is a clear depletion in abundance for the model with water UV-shielding. In the disk surface, CO can be destroyed by two pathways. In the highest reaches where CO is not fully shielded, it can be directly dissociated by UV radiation or through reactions with He$^+$, which requires ionization by X-rays. Both pathways create free oxygen which is stolen to make H$_2$O before CO can reform. In summary, the important reaction pathway is:

$$
\begin{align*}
\text{CO} + h\nu &\longrightarrow \text{C} + \text{O} \\
\text{He}^+ + \text{CO} &\longrightarrow \text{C}^+ + \text{O} + \text{He} \\
\text{O} + \text{H}_2 &\longrightarrow \text{OH} + \text{H} \\
\text{OH} + \text{H}_2 &\longrightarrow \text{H}_2\text{O} + \text{H}.
\end{align*}
$$

(1)
Figure 2. The 2D abundance distributions of the 6 species for the standard and water shielding models in the inner 5 au. The red line signifies the location of our estimate of the IR emitting layer above \( z/r \sim 0.15 \). It is clear that with the inclusion of water UV-shielding, these species reach higher abundances at locations higher up in the disk atmosphere.

which leaves carbon without any oxygen to reform CO. This excess carbon is sequestered in large (hydro)carbon-chain species, which will be discussed in Sec. 4.1.

The behavior of CO\(_2\) varies with radius. In the inner 1 au, the progressively lower temperature at increasing radius increases the CO\(_2\) formation rate relative to the water formation rate (e.g. Bosman et al. 2018). Outside of the CO\(_2\) midplane iceline, the temperatures of the surface layers become too low for efficient formation of OH, the main precursor of CO\(_2\), causing a strong CO\(_2\) abundance drop. H\(_2\)O, C\(_2\)H\(_2\), HCN, NO, CH\(_4\), CH\(_3\)CN, and NH\(_3\) all experience a similar temperature-driven drop in abundance around 0.9 au.

We have selected a number of species that have a many order of magnitude difference in abundance, between the standard model and including water UV-shielding, out to the CO\(_2\) iceline: C\(_2\)H\(_2\), HCN, CH\(_4\), CH\(_3\)CN, and NH\(_3\). For these species, water UV shielding has a significant effect, enhancing these abundances by \( > 3 \) orders of magnitude, in disks with high gas-to-dust mass ratios, where there is significant dust settling and growth. We expect that the species with an enhanced abundance due to water UV-shielding will be able to be observed more prominently at heights further up in the disk atmosphere. Figure 3 shows the emitting columns for these species at 0.3 au and 0.6 au along with the other abundant species that are present in our UV-shielded model. It can be seen that the impact of UV-shielding on molecular abundance yields significant results, impacting abundance at radii less than 0.9 au.

Figure 2 shows the 2D abundance distributions for the standard model and the water shielding model over the inner 5 au for C\(_2\)H\(_2\), CH\(_4\), NO, HCN, CH\(_3\)CN, and NH\(_3\). Looking in the IR emitting layer, the area above the red line at \( z/r \sim 0.15 \), it is clear that this region is most affected by the inclusion of water UV-shielding. We see that C\(_2\)H\(_2\), CH\(_4\), CH\(_3\)CN, and NH\(_3\) are found in the IR emitting layer only if water UV-shielding is included, while NO becomes depleted relative to the standard model, as was found in the average abundances in Fig. 1. At deeper layers, below the IR emitting layer, practically identical results are seen for both models, reflecting that the differences in abundance are limited to the surface layers. Thus, Fig. 1 includes the entire vertical column of gas that is impacted by UV-shielding.

4. DISCUSSION

4.1. Carbon

In Fig. 1, the CO abundance is reduced within the CO\(_2\) iceline when water UV-shielding is included. The self-shielding of water lowers the abundance of water photo-products, such as atomic oxygen and OH, in the gas. These species are critical in the formation of CO, so its formation is slowed. This effect combined with dissociation reactions with He\(^+\) in the upper atmosphere as discussed in Section 3 reduces the abundance of CO. Thus, more carbon is available for the formation of other species.

Similarly to CO, we can also see that the abundance of CO\(_2\) is reduced when water self-shielding is included due to the atomic oxygen and OH-poor environment (Bosman et al. 2022b); both are crucial to its formation. In contrast, we see increases in abundance for HCN, C\(_2\)H\(_2\), CH\(_4\), and CH\(_3\)CN.

Figure 3 shows that at 0.3 au, most of the carbon is incorporated into long carbon chains, such as C\(_6\)H\(_2\) and C\(_8\)H\(_2\) for the UV-shielding model with abundances of \( 3 \times 10^{-6} \) (relative to total H). This result is similar to Wei et al.
(2019), which explores releases of carbon from refractory carbon-rich grains. They find the efficient creation of large carbon chain species if carbon grain destruction is included. Though there are differences in the origin of the carbon chains between Wei et al. (2019) and our models, the similar end results suggest that inner disk chemistry drives large carbon chain production whenever there is little atomic oxygen available.

Past models by Woitke et al. (2018) and Anderson et al. (2021) have found low abundances and fluxes of C$_2$H$_2$. In their models, matching observation and theory requires a high C/O ratio, thus creating an inability to reproduce H$_2$O observations. Figure 1 shows that the C$_2$H$_2$ abundance is elevated in an effectively oxygen-poor environment, as created by UV-shielding in gas that is oxygen-rich (i.e. stellar O/H in content). As T$_{\text{gas}}$ > T$_{\text{dust}}$ in this region, this should lead to a strong increase in 13.7 µm C$_2$H$_2$ emission. At 0.3 au, our models produce a C$_2$H$_2$ column density of 8.4 × 10$^{17}$ cm$^{-2}$ in the region of the disk in the IR emitting layer. The models of Anderson et al. (2021) have found the column density of C$_2$H$_2$ to be in the range of 10$^{14}$ − 10$^{16}$ cm$^{-2}$, and Woitke et al. (2018) found it to be equal to 10$^{17}$ cm$^{-2}$ for a C/O ratio of 0.46. It should be noted that most of this column is at a low gas temperature of 230K and thus only weakly contributes to any line emission. Our models thus produce a larger amount of C$_2$H$_2$ in higher regions of the disk without invoking a elevated C/O ratio.

Comparing to the observations of Salyk et al. (2011b), they find best fit columns on the order of 10$^{14}$ – 10$^{15}$ cm$^{-2}$ for C$_2$H$_2$. This is low compared to our value of 10$^{18}$ cm$^{-2}$ at 0.3 au. This discrepancy could be explained by the way the column in derived in Salyk et al. (2011b), in which the emitting area for water was determined and applied it to all species. The region in which C$_2$H$_2$ has a high abundance is smaller than that of water, so it is expected that the C$_2$H$_2$ emitting region is smaller as well. This smaller emitting region would also imply a C$_2$H$_2$ excitation temperature that is higher than that of H$_2$O as is seen in Salyk et al. (2011b). If the actual emitting region of C$_2$H$_2$ is smaller than assumed in the fitting by Salyk et al. (2011b), then the column will have to be decreased significantly to compensate and still produce the same total flux. This could explain the mismatch between the observation derived columns and our predicted columns.

Finally, it is important to note the carbon species that we expect to see in this region. We likely expect to observe CH$_4$ with a column 8 × 10$^{15}$ cm$^{-2}$ at 0.3 au. High abundances of C$_3$ and long carbon chains with low hydrogenation are seen in Fig. 3 which indicates that these species could have detectable band emission. It is unlikely to detect C$_2$H$_6$ and C$_2$H$_4$ in this region as the models produced columns of less than 6 × 10$^{13}$ cm$^{-2}$ and 2 × 10$^{14}$ cm$^{-2}$, respectively.

4.2. Nitrogen

Water UV-shielding has a strong effect on the nitrogen-bearing species, increasing abundances of HCN, NH$_3$ and CH$_3$CN while lowering the abundance of NO. The abundance of HCN is known to be sensitive to the gas phase C/O ratio (e.g. Cleeves et al. 2018). Our model effectively changes the C/O ratio and thus, HCN rises in abundance for the water UV-shielding model. This is in part driven by the chemistry discussed in Sec. 4.1. However, the changes in NH$_3$ and NO imply that the active nitrogen chemistry is also changed.

There seems to be three driving factors for the increased abundance of NH$_3$, HCN and CH$_3$CN. The first driving factor is due to an impediment placed within the formation pathway of N$_2$. N$_2$ is primarily formed from atomic N by
N + OH $\rightarrow$ NO + H
NO + N $\rightarrow$ N$_2$ + O. \hfill (2)

With the inclusion of water self-shielding the OH abundance is lowered and this channel is suppressed. Further, in both the standard and full models, the N$_2$ formation through CN + N $\rightarrow$ N$_2$ + C is suppressed by the competition with the CN + H$_2$ $\rightarrow$ HCN + H reaction. The slow N$_2$ formation leads to more nitrogen being available for species beyond N$_2$, most notably HCN and NH$_3$. This also impacts the abundance of NO which is formed less efficiently in the UV-shielding model and thus has a lower abundance (Fig. 1).

NH$_3$ formation is initiated by the reaction of He$^+$ with N$_2$ or HCN, forming N$^+$. The addition reaction with H$_2$ allows for the eventual formation of NH$_4^+$, the precursor to NH$_3$. The main destruction channel for NH$_3$ in these hot layers is atomic H. Suppressing the photo-dissociation of H$_2$O lowers the production, and thus abundance of atomic H. This increases the NH$_3$ lifetime and thus abundance as more hydrogen is available in the form of H$_2$. We see that NH$_3$ has a maximum abundance occurring at the water iceline with the inclusion of UV-shielding of roughly 10$^{-7}$, a value four orders of magnitude higher than when UV-shielding is excluded.

Lastly, the active carbon chemistry allows for atomic nitrogen to react with the abundant carbon chains (C$_x$H, C$_y$N), which produces CN, which reacts with H$_2$ to form HCN. HCN can then react with the more abundant CH$_3^+$ to form CH$_3$CNH$^+$ the precursor for CH$_3$CN.

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Figure 4. 2D distributions of the inner 5 au of the disk showing the structure of the gas temperature and density, dust density, gas-to-dust ratio, and UV and X-ray radiation fields for the model with water UV-shielding. The UV radiation field is relative to the interstellar radiation field (Draine 1978). The red line at z/r ∼ 0.15 signifies our estimation of the location of the IR emitting layer.

APPENDIX

A. 2D STRUCTURE COMPARISONS

Figure 4 shows the 2D structure of the gas temperature and density, dust density, gas-to-dust ratio, and UV and X-ray radiation fields for the model with water UV-shielding. The UV radiation field is relative to the interstellar radiation field (Draine 1978). The red line at z/r ∼ 0.15 signifies the lower bound of the IR emitting layer. Figure 5 compares the 2D abundance structure of H$_2$O and CO$_2$ for a full chemical network, as employed in this work, and a reduced chemical network, used in (Bosman et al. 2022a). We can see that for both the standard model and model with water UV-shielding, the resulting abundances in our estimation of the IR emitting layer for both species is independent of the chemical network used.
Figure 5. 2D distributions of water and CO$_2$ for a full and reduced chemical network shown in the top and bottom panels, respectively. The reduced chemical network is used in Bosman et al. (2022a). The region above the red line at z/r $\sim$ 0.15 corresponds to the location of our estimation of the IR emitting layer. For water, we can see specifically around 1 au near the IR emitting layer that the model with UV-shielding has a noticeably larger abundance than the standard model, as expected. For a reduced chemical network, the abundances drop at closer in radii due to the fact that the water icelines are at smaller radii (Bosman et al. 2022a). We are focusing on the region in the IR emitting layer, so between the models, the abundance is about the same, validating the use of a smaller chemical network for obtaining the emitting area of water. For CO$_2$, we also see very similar abundances in the IR emitting layer between a full and reduced chemical network.