Destruction of Refractory Carbon Grains Drives the Final Stage of Protoplanetary Disk Chemistry

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Abstract

Here we aim to explore the origin of the strong C2H lines to reimagine the chemistry of protoplanetary disks. There are a few key aspects that drive our analysis. First, C2H is detected in young and old systems, hinting at a long-lived chemistry. Second, as a radical, C2H is rapidly destroyed, within <1000 yr. These two statements hint that the chemistry responsible for C2H emission must be predominantly in the gas phase and must be in equilibrium. Combining new and published chemical models, we find that elevating the total volatile (gas and ice) C/O ratio is the only natural way to create a long-lived, high C2H abundance. Most of the C2H resides in gas with an F_{UV}/n_{gas} \sim 10^{-7} G_0 \text{ cm}^3. To elevate the volatile C/O ratio, additional carbon has to be released into the gas to enable equilibrium chemistry under oxygen-poor conditions. Photoablation of carbon-rich grains seems the most straightforward way to elevate the C/O ratio above 1.5, powering a long-lived equilibrium cycle. The regions at which the conditions are optimal for the presence of high C/O ratio and elevated C2H abundances in the gas disk set by the F_{UV}/n_{gas} condition lie just outside the pebble disk as well as possibly in disk gaps. This process can thus also explain the (hints of) structure seen in C2H observations.

Unified Astronomy Thesaurus concepts: Astrochemistry (75); Chemical abundances (224); Protoplanetary disks (1300)

1. Introduction

The abundance of the volatile elements (carbon, nitrogen, oxygen, and sulfur), and whether these are in the gas, incorporated in ices, or part of the refractory material, is an important parameter in protoplanetary disk physics and chemistry. Volatile elemental abundances influence the molecular composition, which in turn influences the ionization and temperature of the gas. Furthermore, giant planets forming in the disk will accrete the local gas, so the elemental composition of the gas will influence the final (elemental) composition of the planet.

The abundance of volatile elements, both in the gas and in the ice, in protoplanetary disk atmospheres appears to be different from the volatile ISM abundances. Herschel studies have shown that H2O vapor and ice are strongly underabundant, a factor of 10 to 1000 lower, than expected in ISM composition chemical models in the upper layers beyond the snowline (Bergin et al. 2010; Hogerheijde et al. 2011; Kamp et al. 2013; Du et al. 2017). This water is most likely trapped in ice on large grains that have settled to the midplane (e.g., Krijt et al. 2016). Furthermore, submillimeter studies are showing that CO isotopolog emission is weaker than expected (e.g., Favre et al. 2013; Ansdell et al. 2016; Miotello et al. 2017). This indicates that the CO abundance is reduced from its expected value (<10^{-4} relative to H2) in the surface layers of the outer (\geq 20 au) disk. As such, the dominant carriers of volatile oxygen and carbon are missing in both the gas and the ice from the surface layers of the outer disk.

As disk mass estimates are usually based on the dust mass, these low oxygen and carbon abundances could be interpreted as a low gas-to-dust ratio. However, hydrogen-deuteride (HD) observations toward a handful of disks provide an independent measurement of the gas mass, finding gas-to-dust ratios in agreement with earlier assumptions (Bergin et al. 2013; McClure et al. 2016). On top of this, measured accretion rates and the composition of accreting material imply disk gas-to-dust ratios that are 100 (ISM) or higher (Kama et al. 2015; Manara et al. 2016; McClure 2019). Nitrogen-bearing molecules provide an additional constraint, with the analysis of N2H+ and HCN also implying gas-to-dust ratios of 100 (van ‘t Hoff et al. 2017; Cleeves et al. 2018; Anderson et al. 2019).

Finally, observations of atomic carbon and oxygen lines toward TW Hya are consistent with the missing CO and H2O (Kama et al. 2016; Trapman et al. 2017). So, it is unlikely that the missing carbon and oxygen are present in unobservable species such as CH4 and O2 in the upper layers.

At face value, current data and analysis suggest that the carbon and oxygen are sequestered in ices on large grains near the midplane. Observational evidence is suggesting that this process is relatively fast and takes place in the first Myr after disk formation (Bergner et al. 2020; Zhang et al. 2020).

The low total abundance of CO and the even lower abundance of H2O indicate that total volatile C/O ratios are elevated above the ISM ratio of 0.4. This is confirmed by the brightness of the C2H lines detected toward many disks (Guilloteau et al. 2016; Bergner et al. 2019; Miotello et al. 2019), with the C2H line fluxes comparable to 13CO (Kastner et al. 2014). Models that match these observations require C/O ratios of 1.5–2 (Bergin et al. 2016; Miotello et al. 2019). Under these high C/O ratio conditions, CO is the dominant oxygen-bearing molecule, so these conditions also explain the low H2O fluxes observed with Herschel (Kamp et al. 2013). To get to these higher C/O ratios, it is not enough to remove volatiles from the surface layers and leave a small fraction of the CO. It is necessary to create a surplus of carbon relative to oxygen. This can be done by extracting oxygen from CO and putting it into water ice sequestered near the midplane, or by releasing excess carbon from a refractory reservoir, carbonaceous grains, or polycyclic aromatic hydrocarbons (PAHs; Draine 1979; Finocchi et al. 1997; Visser et al. 2007; Alata et al. 2014, 2015;
Carbon chemistry network showing the important reaction pathways in the UV-dominated layers of protoplanetary disks. Thick arrows show major pathways, thin arrows show minor pathways. Reactions involving oxygen, which always end in CO, are shown in yellow arrows. CH4 and C2H2 (light blue background) are species that can only be efficiently destroyed by UV photons. In the absence of UV photons, these species can contain a significant amount of carbon. C2H (red background) can only be formed if the cycle is active, that is, when there are sufficient UV photons to release carbon from CH4 and C2H2. If water ice is present, these same photons would release atomic oxygen from any present H2O ice, quenching the C2H production, in regions with large amounts of water ice.

Figure 1. Carbon chemistry network showing the important reaction pathways in the UV-dominated layers of protoplanetary disks. Thick arrows show major pathways, thin arrows show minor pathways. Reactions involving oxygen, which always end in CO, are shown in yellow arrows. CH4 and C2H2 (light blue background) are species that can only be efficiently destroyed by UV photons. In the absence of UV photons, these species can contain a significant amount of carbon. C2H (red background) can only be formed if the cycle is active, that is, when there are sufficient UV photons to release carbon from CH4 and C2H2. If water ice is present, these same photons would release atomic oxygen from any present H2O ice, quenching the C2H production, in regions with large amounts of water ice.

2. Chemistry of C2H

The ethynyl radical, C2H, is a radical that is often used to trace the C/O ratio of gas (e.g., Bergin et al. 2016; Cleefes et al. 2018; Miotello et al. 2019). A simplified reaction network for the chemistry that leads to C2H is shown in Figure 1. The C2H abundance is strongly dependent on the amount of free carbon, that is, carbon not contained in CO. Furthermore C2H and related hydrocarbons react very quickly, especially with atomic oxygen and the OH radical. Reactions with oxygen-bearing species inevitably lead to CO as one of the products. As such, to produce a high abundance of C2H, a high C/O ratio is necessary (Bergin et al. 2016; Miotello et al. 2019).

As Figure 1 shows, to form C2H, a significant level of UV is also necessary, as further exemplified by its use as a PDR tracer (e.g., Jansen et al. 1995; Nagy et al. 2015). The level of UV necessary to create abundant C2H depends on the density of the gas and the C/O ratio. For a C/O of 0.4 and the low-density \(10^5 \text{ cm}^{-3}\) outer regions of the disk, \(F_{\text{UV}} = 1 \times 10^3 \text{ G}_{0}\) is enough, while in denser disk surface layers \(10^9 \text{ cm}^{-3}\), \(F_{\text{UV}} = 10^4 \text{ G}_{0}\) is necessary, where \(\text{G}_{0}\) is the Habing (1968) flux of \(1.6 \times 10^6 \text{ erg s}^{-1} \text{ cm}^{-2}\). This means that C2H is most abundant in regions with active chemistry that equilibrates quickly. Figure 2 shows the converging behavior of the C2H abundance in a set of chemical point models for conditions relevant to the disk layers with abundant C2H. As UV photons are abundant in the regions where C2H is produced, it is not just enough to change the C/O ratio in the gas phase, for example, by freezing out H2O. Only by also removing the oxygen from the UV-dominated layer, so that neither photodesorption nor photodissociation can replenish oxygen to the gas phase, is it possible to increase the C2H abundance.

The chemical models in Figure 2 are based on the network presented in Bosman et al. (2018b) with photodissociation reactions from Heays et al. (2017). The conditions were chosen to encompass the PDR layer of a protoplanetary disk model around a T Tauri star. The density was varied between \(10^6\) and \(10^{10} \text{ cm}^{-3}\) with a UV field between 10 and \(10^2 \text{ G}_{0}\). Gas and dust temperatures were varied between 30 and 300 K. Finally, the C/O ratio was varied between 0.4 and 2.0. All models that

\[ \text{C}/\text{O} = \frac{N_{\text{C}}}{N_{\text{O}}} \]

\[ \text{UV} = \frac{F_{\text{UV}}}{10^{-16} \text{ erg s}^{-1} \text{ cm}^{-2}} \]

\[ \text{G}_{0} = \frac{F_{\text{G}_{0}}}{10^{-16} \text{ erg s}^{-1} \text{ cm}^{-2}} \]

\[ \text{C}_2\text{H} \]

\[ \text{CO} \]

\[ \text{CH}_4 \]

\[ \text{CH}_2\text{H} \]

\[ \text{CH}_3\text{H} \]

\[ \text{C}_2\text{H}_2 \]

\[ \text{C}_2\text{H}_3 \]

\[ \text{C}_2\text{H}_4 \]

\[ \text{C}_2\text{H}_5 \]

\[ \text{C}_2\text{H}_6 \]
end up with a C2H abundance larger than $10^{-10}$ equilibrium within 1 Myr.

Variations of the initial composition in these chemical models show, as also shown in Bergin et al. (2016), that a high initial abundance of C2H2 or CH4 will initially lead to high, $>10^{-10}$, C2H abundances. However, the high C2H abundance is not long lived unless the conditions are right to have a high C2H abundance in kinetic equilibrium, which is reached in $10^7$–$10^8$ yr (Figure 2 and Bergin et al. 2016). The physical parameter space in which this happens is bigger when the total C/O ratio is larger than 1. Put simply, there must be more carbon available for the chemistry than oxygen.

This can be clearly seen in the C2H abundances in the thermochemical models from Bergin et al. (2016). Figure 3 shows the mass-averaged C2H abundance as a function of $F_{\text{UV}}/n_{\text{gas}}$ for a TW Hya disk model (Bergin et al. 2016). The chemical network used in these thermochemical models is different from the one used in the single point models in Figure 2. It contains a more restricted grain surface chemistry and the gas-phase chemistry in RAC2D is based on UMIST06 (Woodall et al. 2007; Du & Bergin 2014), while the Bosman et al. (2018b) model is based on UMIST12 (McElroy et al. 2013). The reactions important for C2H formation and destruction (see Figure 1) are the same between the two networks.

$F_{\text{UV}}/n_{\text{gas}}$ is a central parameter in describing effects on the chemistry and thermal physics within PDR models (Kaufman et al. 1999) as it balances destruction and heating ($\propto F_{\text{UV}}$) and the formation and cooling ($\propto n_{\text{gas}}$) rates of molecules, respectively. Throughout the paper, $F_{\text{UV}}/n_{\text{gas}}$ will be expressed in units of $G_0 \text{ cm}^{-3}$.

High C2H abundances are found between $F_{\text{UV}}/n_{\text{gas}} = 10^{-8}$–$10^{-5}$ $G_0 \text{ cm}^{-3}$, with conditions between $10^{-8}$–$10^{-5}$ $G_0 \text{ cm}^{-3}$ most sensitive to changes in the C/O ratio. As densities in the disk are greater than $10^6 \text{ cm}^{-3}$, these conditions always correspond to an effective radiation field >0.1 $G_0$. This effectively means that the gas responsible for C2H emission is not fully shielded from UV emission. This supports the conclusion of Bergin et al. (2016) that dust evolution is important for C2H formation: dust evolution, especially grain growth and settling, increases the penetration of UV in the disk, increasing the mass fraction of the disk where C2H can be abundant. Figure 3 also demonstrates that high C/O ratios are needed to elevate the C2H abundance within regions that carry significant mass. As in all our models, the maximum C2H abundance seems to be around $10^{-8}$, or ~0.01% of the total carbon. In the CO/C $^+$ transition layer, which is the layer that produces C2H at low C/O ratios, this only allows a C2H column of order $10^{12} \text{ cm}^{-2}$. Thus, an increase in abundance in the deeper, denser layers of the disk is necessary to reproduce the high C2H columns, $10^{14}$–$10^{15} \text{ cm}^{-2}$, observed, which only happens when the C/O ratio is above 1.0 (e.g., Bergin et al. 2016; Bergner et al. 2019).

3. Toward a High C/O Ratio

3.1. High C/O Due to Volatile Depletion?

It is currently unclear what exactly is causing the loss of oxygen- and carbon-bearing species from the surface and outer regions of protoplanetary disks, with leading theories exploring dust evolution or chemical processing (Krijt et al. 2016; Schwarz et al. 2018; Krijt et al. 2018; Bosman et al. 2018a). The high sublimation temperature of water (150–300 K, depending on density; Bergin & Cleeves 2018) lends it to be found as water ice for the majority of the disk mass, and hence dust grain growth would appear to be most relevant (Krijt & Ciesla 2016). For CO, the much lower sublimation temperature (20–25 K; Schwarz et al. 2016; Pinte et al. 2018; Qi et al. 2019) makes it more difficult for dust evolution to be the sole process, and models have therefore also explored chemical processing of CO into less volatile forms such as CO2 or CH3OH (Furuya & Aikawa 2014; Schwarz et al. 2018; Bosman et al. 2018a; Dodson-Robinson et al. 2018; Schwarz et al. 2019).

It seems, however, that the CO removal process is relatively fast and happens within the first Myr after disk formation (Zhang et al. 2020). This is shorter than the timescales necessary to reduce the CO abundance in chemical models using cosmic-ray-driven gas-grain chemistry, which are generally >1 Myr, unless elevated cosmic-ray ionization rates are assumed (e.g., Schwarz et al. 2018; Bosman et al. 2018b).
Furthermore, as C$_2$H is created in a photon-dominated layer, oxygen-carrying species in the ice which are formed from CO destruction, such as H$_2$O and CO$_2$, would be photodesorbed and dissociated by the same UV that is necessary to form C$_2$H. The released oxygen would destroy the C$_2$H in the gas phase. Chemical conversion into CO thus does not directly create the high C/O ratio conditions necessary for the high observed C$_2$H abundances.

A combined chemical-dynamical process would thus be necessary, and the interaction of chemical and dynamical effects seems to strengthen each other, shortening the CO depletion timescale (Krijt et al. 2020). In these models, the total C/O ratio is tracked and a rise in C/O ratio is seen. The total, gas+ice C/O does rise to 1.0 between the CO and CH$_4$ snow surfaces, with a low column layer. In these models, the gas-phase C/O ratio is greater than one, but this excess carbon is balanced by CO$_2$ and H$_2$O in the ice. Under the UV conditions necessary for C$_2$H production, this oxygen would be released from this ice and smother C$_2$H formation. These chemical-dynamical models thus do not create the conditions for strong C$_2$H emission naturally.

Furthermore, if the process of CO depletion is linked with the increase of the C/O ratio above 1.0, there should be a clear trend between CO abundance and C$_2$H flux. This, however, is not seen observationally (Miotello et al. 2019). Finally, the C$_2$H emission is structured in both TW Hya and DM Tau. Thus, it is likely that the C/O ratio is similarly structured. This is not easily explained by volatile depletion, which seems to be relatively smooth (Zhang et al. 2019; Krijt et al. 2020). The depletion of CO is not directly responsible for the high C/O ratios necessary to explain the C$_2$H abundances. However, the lower elemental abundance of oxygen in the surface layers due to CO depletion does make it easier for a source of additional carbon to elevate the C/O ratio. We therefore propose that the depletion of CO is a necessary precondition for the high C/O ratios observed.

### 3.2. Photoablation of Refractory Carbon

The initial evolution of the disk leaves the surface layer and outer disk depleted of volatiles and dust. The volatile carbon and oxygen budget are dominated by CO at an abundance between $10^{-6}$ and $10^{-5}$ with respect to H. The gas thus has a C/H that is one to two orders lower than the volatile ISM and a C/O close to unity as a result of the CO and H$_2$O depletion episode. Finally, the grain growth and settling also allow the UV to penetrate more deeply into the disk.

If the excess carbon is not drawn from a volatile source, it thus has to originate from a refractory source. In interstellar space, about 50% of the carbon is contained in refractory form, from PAHs and nanoparticles, to amorphous carbon grains and carbon “goo” coatings on silicate grains (Greenberg et al. 1995; Jones et al. 2013; Chiar et al. 2013; Mishra & Li 2015). Carbon can be extracted from these refractory forms by interactions with energetic particles or by oxidation (Draine 1979; Finocchi et al. 1997; Alata et al. 2014, 2015; Anderson et al. 2017). As the region of interest here are mostly cold (<100 K), and oxygen poor, oxidation should not play a role. As such, we will only consider the release of carbon by energetic photons, which can penetrate more deeply into the disk due to the dust evolution. Specifically, we consider the release of carbon from carbonaceous grains due to UV photons; other carbon release mechanisms and carbon reservoirs will be considered in the discussion (Section 4.2).

Hydrogenated amorphous carbon on the surface of grains can be photoablated, releasing the carbon, mostly in the form of CH$_4$ to the gas phase (Alata et al. 2014). The grain lifetime, following Anderson et al. (2017), is given by

$$\tau_{\text{col}} = \frac{N_{\text{grain}}}{\sigma Y_{\text{c}} F_{\text{UV}}}$$

where

$$N_{\text{grain}} = \frac{4}{3} \pi a^3 / m_c$$

is the number of carbon atoms per grain, $\sigma$ is the geometric cross section of the grain, $Y_c = 8 \times 10^{-4}$ photon$^{-1}$ is the carbon sputtering yield (Alata et al. 2014, 2015), $F_{\text{UV}}$ is the UV field, $10^8 \times G_0$ photons cm$^{-2}$ s$^{-1}$, $\rho_{\text{col}} = 2.24$ g cm$^{-3}$ is the density of carbonaceous grains, $a = 0.1$ µm is the grain radius, and $m_c$ is the mass of a carbon atom. This carbonaceous grain lifetime is calculated for TW Hya and DM Tau disks using the model structures from Bergin et al. (2016) and shown in Figure 4.

The carbon grain lifetime is significantly less than a few million years for most of the C$_2$H-emitting region. This is less than the expected disk lifetime or even the age of the 5–10 Myr TW Hya disk (Weinberger et al. 2013). Carbonaceous grains can thus be processed enough to remove a significant fraction of the carbon from the grains, enriching the gas. As the carbon grain lifetimes are short, a single enrichment event is expected, in contrast to a slow continuous release of carbon over the disk’s lifetime.

It is thus qualitatively possible to enrich the gas with carbon from a refractory origin, but what is necessary to quantitatively...
match the extreme C/O ratios (C/O ≈ 2)? In the ISM grains contain ~50% of the total carbon, $10^{-4}$ w.r.t. H (Draine 2003; Mishra & Li 2015). However, the grains have grown and settled, lowering the abundance of small grains, those grains that are well coupled to the gas, increasing the gas-to-dust ratio above 100 in the C$_2$H-emitting layers. The available carbon abundance in refractory form is thus $10^{-4} \times 100$ gas-to-dust ratio. To elevate the C/O ratio from the depleted state with a C/O of 1.0–2.0, it is thus necessary to add as much carbon as there already is in the gas phase, which is between $10^{-6}$–$10^{-5}$ w.r.t. H. This requires ablation of 1%–10% of all the refractory carbon originally in the disk surface layers. To have enough grains to provide the carbon, it is thus necessary that the gas-to-dust ratio is $\lesssim 1/(100 \times (C/H)_{\text{gas}})$ in the layers where carbon is efficiently photoablated. For strongly volatile-depleted disks, the surface layer gas-to-dust ratio should thus be less than $10^4$ while for less depleted disks a lower gas-to-dust ratio (around 1000) is necessary to be able to provide the required carbon to the gas.

The actual grain abundance in the surface layers and outer regions of the disk is hard to constrain.SED fitting models generally use a gas-to-dust ratio of 1000–10,000 in the surface layers (e.g., Andrews et al. 2013). The TW Hya scattered-light model of van Boekel et al. (2017) also has a gas-to-dust ratio of 10,000 in the surface layers, consistent with the SED models; this is a factor of 5 higher than the gas-to-dust ratio in the thermochemical model of Bergin et al. (2016), which also matches a host of other gas tracers (Du et al. 2015). The DM Tau model of Bergin et al. (2016) even has a gas-to-dust ratio of 125 in the surface layers, enough to elevate the C/O ratio to approximately 2.0, even if there is very little carbon and oxygen depletion. These models, while highly degenerate, are at least in the right ballpark to provide enough grain material in these regions to elevate the C/O ratio to the required values. Setting and drift models show a larger range of dust depletions in the outer disk. Models with a low $\alpha$ ($<10^{-5}$), as inferred from observations (Pinte et al. 2016; Flaherty et al. 2017; Teague et al. 2018), predict more than a factor of 10 depletion of the small dust grains in the surface layers, in general predicting less dust than necessary in SED models (e.g., Facchini et al. 2017; Krijt et al. 2018; Woitke et al. 2019). All these things considered, it is very hard to say what is, and what is not, enough turbulence to provide the small grains, and thus excess carbon necessary for the elevated C/O ratios. Disks that have a close to ISM O/H ratio in the surface layers, need a lot of small dust, consistent with no settling, and thus high very high turbulence ($\alpha > 10^{-5}$). Very oxygen-depleted disks, such as TW Hya, however, have 1% of the original dust, which for that disk is consistent with an $\alpha$ of $10^{-3}$ (van Boekel et al. 2017).

We note, however, that it only needs a single injection of excess carbon from the small grains. So, even if the current levels of small grains, or by extension, current turbulent $\alpha$ is not enough, it is possible that the high C/O ratios are a result of a previous stage of the disk evolution in which there were enough carbonaceous grains in the disk atmosphere.

4. Discussion

4.1. Structure in C$_2$H

Observations of C$_2$H show that the C$_2$H is structured. The high resolution of DM Tau and TW Hya shows an emission ring outside of the pebble disk while lower-resolution data from Bergner et al. (2019) and Miotello et al. (2019) hints at structure below the observed resolution in many of the disks observed to date.

A typical disk model with a tapered power-law surface density structure and a constant gas-to-dust ratio will lead to very smooth C$_2$H surface density profiles outside of ~20 au (e.g., Bergin et al. 2016, Figure 7). The structures that are visible are thus due to a combination of radial changes in the C/O ratio and changes in the UV penetration. As the UV penetration can only significantly change the C$_2$H abundance for elevated C/O ratios, changes in the C/O ratio are the expected dominant driver in the C$_2$H structure. If the C/O ratio is elevated due to the photoablation of carbonaceous grains, then the C/O ratio is linked to the (historical) UV penetration and small grain abundances.

4.1.1. Rings outside of the Pebble Disk

Outside of the pebble disk, the radiation field is a combination of the interstellar radiation field, which can reach a large volume of the outer disk, and stellar UV photons that
of small grains ($\alpha < 0.1 \mu m$) exposed to UV photons. On top of that, vertical mixing is expected to concentrate volatiles in ices on pebbles near the disk midplane; as there is a lack of pebbles near the midplane, this volatile sink is not present, and the excess carbon can potentially stay in the gas phase for the entire disk lifetime. Of course, this does depend on timescales for radial motions and gas loss via winds. However, beyond the pebble disk, it is clear that the depletion cycle will not be activated.

4.1.2. Structures in the Pebble Disk

Axisymmetric structures in and above the pebble disks have been observed in many disks in the (sub)millimeter (e.g., Andrews et al. 2018) and scattered light (e.g., Garufi et al. 2017). These features are attributed to changes in the physical conditions that impact the distribution of dust and thus the penetration of UV photon, which directly affects the C$_2$H abundance.

Locations of prime interest in this regard would be planet-created gaps. Alarcon et al. (2020) looked at the chemistry in the gaps of AS 209 and found little to no effect of the inclusion of a gap on the C$_2$H columns and fluxes for a solar C/O ratio. These models only considered a constant gas-to-small-dust ratio in the gap, while increasing this ratio would enhance the UV penetration and increase the amount of mass available at a given $F_{UV}/n_{gas}$.

To check the effects of a possible gap on the distribution of $F_{UV}/n_{gas}$ in the gap region three models were run, based on the AS 209 model of Alarcon et al. (2020) (see their Table 1 for general model parameters). The model includes a gap, centered around 100 au. The gap is modeled as a Gaussian with an FWHM of 16 au and has a factor 12 depletion in the gas and large dust. For the small dust, we consider here three different distributions: a model in which the small dust is depressed by the same value as the gas, keeping a constant gas-to-dust ratio in the gap; a model in which the dust is only depleted by 20% w.r.t. a smooth model, having a factor of $\sim$10 lower gas-to-dust ratio in the gap center; and a model with a small dust depression that is 10 times stronger than the depression in the gas surface density, leading to a higher gas-to-dust ratio in the gap.

The gas and small dust surface densities, as well as the mass that is in the strongly irradiated and mildly irradiated layers in the vicinity of the gap, are shown in Figure 5. Interestingly, changing the gas-to-small-dust does not change the amount of mass in the strongly irradiated layer, $F_{UV}/n_{gas} = 10^{-5} - 10^{-3} G_0$ cm$^3$.

The mass in the mildly irradiated layer, $F_{UV}/n_{gas} = 10^{-8} - 10^{-5} G_0$ cm$^3$, does show dependence on the small-dust surface density. Thus, gaps with C/O > 1.0 will have an increased column density as long as there is a depletion of the small dust in the gap. We note however that a factor of 5 depletion in the small dust only leads to an increase of a factor of 2 in the available mass in these models. This indicates that large variations in the C$_2$H column are more likely due to changes in C/O ratios, but that factor of few changes in the C$_2$H column can still be directly due to changes in UV penetration.

Gaps have an increased UV field in deeper layers of the disk. Aside from the effect that this has on the chemistry directly through changing the distribution $F_{UV}/n_{gas}$, it also exposes more and unprocessed dust grains. Photodesorption and ablation can then release species from the dust surfaces into the gas.

Figure 5. Gas (scaled down by a factor 100) and small dust surface densities (top), and gas density that has an $F_{UV}/n_{gas}$ between $10^{-5}$ and $10^{-3}$ (middle), and $10^{-8}$ and $10^{-5}$ $G_0$ cm$^3$ (bottom) for the 100 au gap of the AS 209 model of Alarcon et al. (2020). The small dust surface density is varied in the gap, with a gap that is shallower in the small dust than in the gas (blue), has equal depth in the gas and the small dust (purple), and is deeper in the small dust than in the gap (red). The surface density in the high $F_{UV}/n_{gas}$ layer follows a radial profile of the gas density and does not depend on the amount of small dust. The lower $F_{UV}/n_{gas}$ layer, however, is dependent on the levels of small dust depletion, and this layer contains more mass and thus is brighter in C$_2$H at lower dust surface densities.

scatter from the disk surface downward. The radiation field is typically between 0.1 and $10 \times G_0$. As the external UV is only barely attenuated in these disk regions, changing the amount of small dust does little to change the UV field in the outer disk. As such, the increase in C$_2$H column must be due to a change in the C/O ratio outside of the pebble disk.

The region outside the pebble disk is a natural place for elevated C/O ratios to occur due to photoablation. Grain coagulation is less effective at larger disk radii as densities are lower (e.g., Brauer et al. 2008). With less growth, a smaller fractions of grains will have settled, leaving a larger reservoir
the gas. If the grains are water-ice poor, this can increase the C/O ratio, and thus increase the C$_2$H abundance. Meridional flows can also be efficient in bringing unprocessed material into regions of high UV flux (Morbidelli et al. 2014; Teague et al. 2019). This could lead to C$_2$H rings around the millimeter dust gaps that have been imaged. Hints of this can be seen in the DM Tau disk (Bergin et al. 2016), although conversely, the rings in TW Hya do not show corresponding C$_2$H rings. The C$_2$H emission in Bergner et al. (2019) does show some hints of structure; however, the resolution of the data is not enough to correlate it with the location of the millimeter structure. Further, high-resolution data of C$_2$H are thus needed to check for a millimeter gap versus C$_2$H ring location correlation in a large sample of disks.

4.2. Source of Refractory Carbon

So far, it has been assumed that the source of the excess carbon is on grains in the form of a hydrogenated amorphous carbon. This is, however, not the only source of refractory carbon in the disk. Up to 20% of the refractory carbon in the ISM is in the form of PAHs (Tielens 2008). These PAHs could thus provide a significant amount of carbon to the gas, if they are present and can be efficiently destroyed. It is clear from observations that PAHs are not present above the 10 $\mu$m continuum disk photosphere (Geers et al. 2007), which means that PAHs are not present in the C$_2$H-emitting layers. If PAHs act like a large molecule, with corresponding freeze-out behavior, then they should be depleted together with the volatiles and sequestered into the midplane. If this is not the case, then the PAH absence needs to be explained by the destruction of PAHs.

UV photons, especially in T Tauri disks, have difficulty destroying PAHs (Visser et al. 2007), so they can be ruled out as a reason for the lack of PAHs in the disk surface. X-rays are, however, able to destroy PAHs around T Tauri stars (e.g., Siebenmorgen & Krügel 2010; Siebenmorgen & Heymann 2012). In this case, the disk surface layers can easily be enriched in carbon for T Tauri disks, but for the disks around the X-ray, weaker Herbig Ae/Be stars this might not be the case. At the same time, a large reservoir of gas outside the pebble disk near the midplane is shielded from X-rays (Rab et al. 2018). This is the region, however, that can contribute significantly to the C$_2$H emission rings outside of the submillimeter continuum. It is thus unlikely that PAH destruction by X-rays can explain all the necessary excess carbon.

As such, to elevate the C/O ratio, it is critical that there is enough carbonaceous material in small grains in the outer disk. Collision experiments with carbonaceous grains are scarce; however, there is evidence that carbonaceous grains stick less efficiently than silicate grains at temperatures below 220 K (Kouchi et al. 2002). However, no experiments at cryogenic temperatures have been performed. If the sticking of carbonaceous material is lower than that for silicate materials, it would naturally lead to a high fraction of small carbonaceous grains in the surface layers of the disk. This could lead to an observable increase of carbonaceous material in the lower-density regions of protoplanetary disks and could even help explain the low carbon content of carbonaceous chondrites.

5. Conclusions

We have studied the chemistry of C$_2$H in the photon-dominated layers of protoplanetary disks. To be able to explain the observed C$_2$H, we find a specific set of conditions that need to be satisfied. These are also shown schematically in Figure 6.

1. The short chemical timescales of C$_2$H necessitate a gas-phase equilibrium cycle.
2. As previously concluded by, for example, Bergin et al. (2015) and Miotello et al. (2019), this cycle is active in disk regions with a C/O ratio $>$1.5. These high C/O ratios allow the C$_2$H-emitting layer to extend deeper, from just the top $F_{UV}/n_{gas} = 10^{-5}–10^{-3}$ layer at C/O $< 1.0$, down to the $F_{UV}/n_{gas} = 10^{-8}–10^{-3}$ layer.
3. To replicate the elevated C/O ratio, we propose the photoablation refractory carbon carried by carbonaceous grains as the source of the excess carbon in the gas. As significant amounts of oxygen carried by CO and H$_2$O are no longer present in the disk surface layers, only 1%–10% of the refractory carbon is necessary to increase the C/O ratio >1.5. Based on the existing laboratory data, the timescale for photoablation is <1 Myr for the C$_2$H-emitting area.

4. These processes reach a maximum in areas where the small grain population dominates in the midplane, which naturally occurs at the edges of pebble disks, as well as possibly at the locations of the millimeter gaps, leading to the formation of long-lived rings rich in hydrocarbons.

Chemical models coupled with gas-grain dynamics can be used to test the efficiency of carbon photoablation in increasing the C/O ratios. This vertical motion of the grains and gas needs to be accounted for to assess the fraction of grain that can lose their carbon during the disk lifetime and the longevity of the high C/O ratios. These models are out of the scope of this paper, but will be considered in follow-up studies.

Furthermore, future infrared scattered light and absorption studies will be critical in constraining the abundance as well as the composition of the small grains. Absorption studies of edge-on protoplanetary disks should show especially the absence or presence of the C–H stretch of hydrogenated amorphous carbon and PAHs around 3 µm.

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Software: RAC2D (Du & Bergin 2014), SciPy (Virtanen et al. 2020), NumPy (Van Der Walt et al. 2011), Matplotlib (Hunter 2007).

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