IMPACT OF GRAIN EVOLUTION ON THE CHEMICAL STRUCTURE OF PROTOPLANETARY DISKS

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ABSTRACT

We study the impact of dust evolution in a protoplanetary disk (PPD) around a T Tauri star on the disk’s chemical composition. For the first time, we utilize a comprehensive model of dust evolution, which includes growth, fragmentation, and sedimentation. Specific attention is paid to the influence of grain evolution on the penetration of the UV field in the disk. A chemical model that includes a comprehensive set of gas-phase and grain-surface chemical reactions is used to simulate the chemical structure of the disk. The main effect of grain evolution on the disk’s chemical composition comes from sedimentation and, to a lesser degree, from reduction of the total grain-surface area. The net effect of grain growth is suppressed by the fragmentation process which maintains a population of small grains, dominating the total grain surface area. We consider three models of dust properties. In model GS, both growth and sedimentation are taken into account. In models A5 and A4, all grains are assumed to be the same size ($10^{-5}$ cm and $10^{-4}$ cm, respectively) with a constant gas-to-dust mass ratio of 100. As in previous studies, the “three-layer” pattern (cold midplane, warm molecular layer, and hot atmosphere) in the disk-chemical structure is preserved in all models, but shifted closer to the midplane in models with increased grain size (GS and A4). Unlike other similar studies, we find that in models GS and A4, the column densities of most gas-phase species are enhanced by 1–3 orders of magnitude relative to those in a model with pristine dust (A5), while column densities of their surface counterparts are decreased. We show that column densities of certain species, such as C$_2$H, HC$_{2n+1}$N ($n = 0–3$), H$_2$O, and some other molecules, as well as the C$_2$H/$/$HCN abundance ratio, all of which are accessible with Herschel and ALMA, can be used as observational tracers of early stages of the grain evolution process in PPDs.

Key words: accretion, accretion disks – astrochemistry – opacity – ultraviolet: planetary systems

Online-only material: color figures

1. INTRODUCTION

The presence of numerous exoplanets and protoplanetary disks (PPDs), as well as our own existence, strongly suggests that planet formation is ubiquitous in the Milky Way (e.g., Mayor & Queloz 1995; Mayor & Frei 2003; Udry & Santos 2007). Still, one of the most challenging problems for modern astronomy is to understand how planets form. This topic covers a tremendous range of microphysics and macrophysics and involves a wide variety of physical, dynamical, and chemical processes.

According to the current paradigm, planets are assembled in PPDs surrounding young stars, starting from the coagulation of sub-micron dust grains into larger bodies (e.g., Natta et al. 2007; Henning 2008). Circumstantial evidence indicates that this process is quite effective and rapid. For example, large-scale IR spectroscopic surveys of young stars in stellar clusters of various ages tightly constrain typical dispersal timescales of circumstellar dust disks of $\sim 5–10$ Myr, and mass accretion rates of $\dot{M}_{\text{Disk}} \sim 10^{-8} M_\odot$ yr$^{-1}$ (Haisch et al. 2001; Sicilia-Aguilar et al. 2006, 2009; Hernández et al. 2008; Oliveira et al. 2009; Fedele et al. 2010). Inner planet-forming zones of some older disks are cleared of sub-micron-sized dust grains within $\sim 1$ Myr (e.g., Graham et al. 2007; Dutrey et al. 2008; Salyk et al. 2009; Thalmann et al. 2010). Furthermore, the analysis of the mineralogical and chemical compositions of unaltered chondritic meteorites shows that in the Solar Nebula, different types of meteorites have condensed and formed via grain agglomeration within a period of $\sim 2–5$ Myr (e.g., Wasson & Kallemeyn 1988; Podosek & Cassen 1994; Thrane et al. 2006).

However, observational data on grain growth are still scarce and limited to the overall spectral energy distribution (SED) parameters. The presence of micron-sized grains in disks has been inferred from mid-infrared spectroscopy (e.g., Bouwman et al. 2001, 2008; Apai et al. 2004; van Boekel et al. 2004; Kessler-Silacci et al. 2006). A number of nearby PPDs have been imaged with the Very Large Array and Australia Telescope Compact Array at millimeter and centimeter wavelengths, showing evidence of significant grain growth up to at least pebble (cm) sizes (Testi et al. 2003; Wilner et al. 2005; Rodmann et al. 2006; Natta et al. 2007; Cortes et al. 2009; Lommen et al. 2009). On the other hand, there can be other observables indicative of grain ensemble evolution.

In essence, grain evolution is controlled by collisions, leading to coagulation and fragmentation of dust particles. For millimeter-sized particles, the bouncing effect comes into play, making the process more complicated and further growth less efficient (Zsom et al. 2010). Radial drift and sedimentation in the disk midplane become important if the growth of grain particles proceeds farther than about 1 cm. Grains evolve faster in the dense disk interior ($\lesssim 20$ AU), while in the outer regions ($R \gtrsim 100$ AU) the grain ensemble may remain unchanged (interstellar medium-like) for the entire life of the system (Schmitt et al. 1997; Weidenschilling 1997; Ciesla 2007; Ormel et al.
formally over the entire disk or that it can be described by artificially varying the grain number density and upper grain size limit. The goal is to isolate possible molecular tracers of grain evolution when grain-size distribution, and dust-to-gas mass ratio vary smoothly in the disk, as predicted by a dust evolution model. The model used includes coagulation, fragmentation, and sedimentation, assuming equilibrium between turbulent stirring and gravitational settling, as proposed in Dullemen & Dominik (2004). No bouncing effects are included. We focus on the combined effect of dust growth and settling on the chemistry of a PPD around a low-mass T Tauri star. A large gas–dust chemical network with surface reactions is utilized. This is the first paper in a series, in which we intend to study various aspects of interrelations between grain evolution and chemistry.

The paper is structured as follows. In Section 2, the setup we constructed to model the physical structure of disk with evolving dust is described. Section 3 contains a description of the detailed chemical model used to simulate the chemical structure of the PPD. In Section 4, we present modeling results. In Section 4.1, dust evolution due to growth, fragmentation, and sedimentation is discussed briefly. In Section 4.2, changes to the UV field in the disk caused by evolution of dust properties are discussed. Section 4.3 is devoted to the analysis of the impact of grain evolution on the chemistry of a PPD. In Section 5, we discuss whether or not the chemical composition of a PPD can be used as a tracer of grain evolution, and in which ways our model can be improved. Section 6 contains the conclusions of this study.

2. DESCRIPTION OF THE MODEL

A PPD, even in a simplified description, is a complicated evolving system controlled by a large number of interrelated physical and chemical processes. However, given the uncertainties and deficiencies in the physical description of such a system, it would be impossible and impractical to try to build a self-consistent dynamical model coupled to grain evolution and disk chemistry. For this reason, we have selected an approach that is by no means self-consistent but is relatively straightforward to implement and allows us to isolate the purely chemical effect of dust growth.

The disk chemical modeling in this study comprises five independent steps. First, we need a template of a disk’s physical structure, i.e., gas density and temperature distributions. These distributions are obtained from a (1+1)-dimensional steady-state accretion disk model. In the second step, the resulting thermal and density structures are used as inputs for the grain growth model. The third step is to simulate the evolution of the dust grain ensemble in the disk midplane due to grain coagulation, fragmentation, and sedimentation according to Birnstiel et al. (2009, 2010). Fourth, the vertical distribution of dust is reconstructed in stirring–mixing equilibrium based on the work by Dullemen & Dominik (2004).

Finally, the grain parameters (size distribution at each disk location as well as dust-to-gas ratios) after 2 Myr of evolution are used in the simulation of the disk chemical structure. These steps are described in more detail in the following subsections.

2.1. Physical Structure of the Disk

A popular formalism, which is used in many studies of disks surrounding young stars, is based on the so-called α-model of Shakura & Sunyaev (1973). In this model, it is assumed that the transport of angular momentum in the disk is caused by turbulent viscosity, with the viscosity coefficient ν expressed as \( \alpha H c_s \), where \( H \) is the disk semi-thickness at a given radius, \( c_s \)...
is the isothermal sound speed, and $\alpha$ is the viscosity parameter, which is usually assumed to be of the order of $10^{-2}$ in PPDs.

As a first approximation for calculating the thermal structure of the disk, we assume thermal coupling between dust and gas. This assumption is well justified for optical depths $\tau \gtrsim 1$, as was shown by the disk models with detail, thermal balance (Aikawa & Nomura 2006; Jonkheid et al. 2006). Sedimentation and coagulation of grains influence the disk temperature via a decrease in dust opacities (Birnstiel et al. 2009), which makes the atmosphere more transparent and hotter and shifts the $\tau = 1$ surface deeper into disk. The investigation of the response of disk thermal structure to dust evolution is a separate problem, and will be addressed by future papers in this series.

Disk structure is calculated with a simplified version of the disk model described by D'Alessio et al. (1998, 1999). Unlike D'Alessio et al., in the calculation of gas temperature we take into account only two heating sources, namely, viscous dissipation and disk irradiation by the central star. Comparison of our disk models with the D'Alessio et al. results shows that this simplification does not significantly alter the derived physical structure of the disk, and thus modeling of disk's chemistry is not affected.

The following equations are used to describe the disk's vertical structure:

$$\frac{dP}{dz} = -\rho g,$$

(1)

$$\frac{dT}{dz} = \frac{3\kappa \rho F}{4acT^3},$$

(2)

$$\frac{dF}{dz} = \frac{9}{4} \alpha P \Omega(R) + \Gamma_{\text{irr}}.$$

(3)

Here, $P$ is the gas pressure, $g$ is the acceleration due to gravity, $\rho$ is the gas density, $T$ is the gas temperature, $F$ is the flux of the disk's thermal emission, and $\Omega(R)$ is the disk's (Keplerian) angular velocity at a distance $R$ from the central object. The first term on the right-hand side of Equation (3) gives the viscous heating of the disk, while $\Gamma_{\text{irr}}$ is the heating rate due to disk irradiation by the central object.

The 2D structure of the disk is modeled in the so-called (1+1)-dimensional approximation. It is assumed that at each radius the disk is in hydrostatic equilibrium (Equation (1)). Thus, the vertical structure of the disk can be found from the solution of Equations (1)–(3) independently at each $R$. To calculate the disk temperature at each vertical slice, we integrate the transfer Equation (2). The disk itself is described by the following parameters:

1. accretion rate $\dot{M}$;
2. viscous parameter $\alpha$;
3. temperature, radius, and mass of the central object, $T_*, R_*$, and $M_*$ (radiation is assumed to be that of a black-body);
4. inner and outer disk radii, $R_{in}$ and $R_{out}$.

The outputs of the model are gas surface density distribution $\Sigma_{\text{gas}}(R)$, and the 2D density and temperature structure of the gas. The strengths of the UV and X-ray fields over the disk can then be calculated using the information about the gas and dust properties in the disk.

Using this model, we simulate a DM Tau-like system. The system has a disk with an outer radius of 550 AU, an inner radius of 0.03 AU, an accretion rate $\dot{M} = 2 \times 10^{-9} M_\odot$ yr$^{-1}$, and a viscosity parameter $\alpha = 0.01$. The disk is illuminated by UV radiation from the central star, with an intensity $\chi = 500$ at $R = 100$ AU in units of the mean UV field of Draine (1978), and by interstellar UV radiation. Two representations of the stellar UV field are used. One is the scaled Draine field and another one is the representative observed spectrum as discussed by Bergin et al. (2003). The effect of these different radiation fields will be discussed in Section 3.1.

The star is assumed to have an X-ray luminosity of $10^{30}$ erg s$^{-1}$ (Glassgold et al. 1997). X-rays induce the same reactions as cosmic-ray (CR) particles, so that the X-ray ionization rate is in fact simply added to the CR ionization rate. The disk mass is $M = 0.055 M_\odot$. The disk surface density profile and its power-law approximation are depicted in Figure 1. The best-fit line has a slope of 0.84, which is somewhere in between the Minimum Mass Solar Nebula index (1.5; Weidenschilling 1977; Hayashi 1981) and the value derived for PPDs from SED at millimeter wavelengths ($\geq 0.5$; Andrews & Williams 2007). The density and thermal structure of the disk are shown in Figure 2. The main model parameters are listed in Table 1. We do not consider a disk region beyond $R_{out}$.

### 2.2. Dust Evolution in the Disk

Several authors have constructed theoretical models for grain growth in PPDs (e.g., Nakagawa et al. 1981; Schmitt et al. 1997; Weidenschilling 1997; Dullemond & Dominik 2005; Ormel et al. 2007; Zsom & Dullemond 2008; Brauer et al. 2008). The

![Figure 1. Solid line shows the radial dependence of the gas surface density in the adopted disk model. The dashed line represents a power-law fit with a slope of $-0.85$.](image-url)
main challenges of grain growth modeling are the following: first, growth from \(~0.01\ \mu m\) grains to centimeter-sized grains encompasses many orders of magnitude. A growth simulation must be able to conserve mass, because large particles can grow by accreting large numbers of very small grains. Second, particle size is not the only parameter determining the properties of grains; porosity, composition, and the various possible outcomes of collisions further extend the parameter space (see Schmitt et al. 1997; Gütler et al. 2010).

Here we use a slightly modified version of the code presented in Birnstiel et al. (2010; see also Brauer et al. 2008). This is a statistical, mass-conserving code which implicitly solves the Smoluchowski equation, taking coagulation, fragmentation, and cratering into account. It is important to note that we ignore radial drift of dust particles in the present study.

The mathematical formalism of the model is the following. The number density distribution \(\eta(m, r, z)\) is a function of mass \(m\), radius \(r\), height \(z\) above the midplane, and time. We do not consider grain porosity as an additional parameter. We define the vertically integrated number density per mass \(m\) as

\[
N(m, r) \equiv \int_{-\infty}^{\infty} \eta(m, r, z) \, dz. \tag{4}
\]

We assume that coagulation and fragmentation kernels \(K\) and \(L\) (defined below) are independent of \(z\). We can now describe the time evolution of this distribution by a vertically integrated version of the Smoluchowski equation:

\[
\frac{\partial N(m)}{\partial t} = \int_0^{m/2} N(m') \, K(m', m - m') \, dm' - \int_{m/2}^{\infty} N(m') \, K(m, m') \, dm' + \frac{1}{2} \int_0^{m/2} N(m') \, L(m', m') \, dm'

+ \int_{m/2}^{\infty} N(m') \, L(m, m') \, dm' \times S(m, m', m'') \, dm' \, dm'' - \int_{m/2}^{\infty} N(m') \, L(m', m') \, dm'. \tag{5}
\]

where the radial dependence has been omitted, because we treat each radius independently, neglecting radial movement of dust. The right-hand side terms of Equation (5) (from top to bottom) correspond to gain and loss by coagulation and gain and loss through fragmentation.

The coagulation kernel \(K(m, m')\) and the fragmentation kernel \(L(m, m')\) are then given by

\[
K(m, m') = \frac{1}{\sqrt{2\pi (h(m)^2 + h(m')^2)}} \cdot p_c \cdot \sigma(m, m') \cdot \Delta u(m, m'), \tag{6}
\]

\[
L(m, m') = \frac{1}{\sqrt{2\pi (h(m)^2 + h(m')^2)}} \cdot p_l \cdot \sigma(m, m') \cdot \Delta u(m, m'),
\]

where \(p_c\) and \(p_l\) are the coagulation and fragmentation probabilities, respectively, that have a sum of unity; \(\Delta u(m, m')\) is the relative particle velocity; and \(\sigma(m, m')\) is the sum of their geometrical cross-sections. In this work, we consider Brownian motion, vertical settling (see Brauer et al. 2008), and turbulent motion (see Ormel & Cuzzi 2007) as physical effects that produce the relative particle velocities.

Particles colliding with a relative velocity higher than the critical velocity \(u_c\) are assumed to fragment into a power-law size distribution of fragments (i.e., \(S(m, m', m'') \propto m^{-1.83}\); see Brauer et al. 2008) if the particle masses differ by less than one order of magnitude. Otherwise, the smaller body is assumed to excavate mass from the larger one by cratering, in which the amount of excavated mass equals the mass of the smaller body. The fragmentation velocity \(u_c\) is taken to be 10 m s\(^{-1}\) (Birnstiel et al. 2009).

This model is related to a model of gas disk structure through two input parameters: radial midplane temperature distribution \(T_{\text{mid}}(R)\) and radial gas surface-density distribution \(\Sigma_{\text{gas}}(R)\). A more comprehensive description of the physics of coagulation/fragmentation and of its numerical implementation can be found in Brauer et al. (2008) and Birnstiel et al. (2010).

The numerical model described above provides us with surface densities of grains of different masses. To calculate the vertical distribution \(\rho_\ell(R, z)\) of grains, we assume that it is controlled by the equilibrium between gravitational settling and turbulent stirring, as proposed by Dullemond & Dominik (2004). Vertical scale heights are computed separately for each size bin.

### 2.3. Average Grain Size for the Chemical Model

An output of the dust evolution model is the grain size distribution at each disk location. In principle, this distribution can be incorporated into the chemical model by considering surface reactions and gas–dust interactions for each size bin separately.
However, this would make the model too complicated, and we elect to use a single grain size $\bar{a}(r,z)$ in the chemical model, which is computed from the equilibrium local grain size distribution in each disk location. The averaging is performed in a way that preserves the total surface area and total dust mass. For a grain size distribution $f(a,r,z)$, where $f(a,r,z)da$ is the number of grains with radii between $a$ and $a+da$ in the disk point with circumstellar radius $r$ and height above midplane $z$, this means that

$$4\pi \bar{a}^3(r,z)\bar{\eta} = 4\pi \int_{a_{\text{min}}}^{a_{\text{max}}} f(a,r,z)a^3 da,$$

$$4\pi \bar{a}^2(r,z)\bar{\eta} = 4\pi \int_{a_{\text{min}}}^{a_{\text{max}}} f(a,r,z)a^2 da,$$

where $\bar{\eta}$ is the total number density of “representative” equal-sized particles. By dividing Equation (7) by Equation (8), one obtains

$$\bar{\eta}(r,z) = \frac{\int_{a_{\text{min}}}^{a_{\text{max}}} f(a,r,z)a^3 da}{\int_{a_{\text{min}}}^{a_{\text{max}}} f(a,r,z)a^2 da}.$$  

An ensemble of grains with the mean radius $\bar{a}(r,z)$ has the same mass and total surface area as the original ensemble. We use $\bar{\eta}(r,z)$ exclusively in our astrochemical model, described below, when dealing with gas–grain interactions and surface chemical processes.

It is important to note that the way we calculate the average grain size is different from methods usually used in works on grain growth (e.g., Brauer et al. 2008; Birnstiel et al. 2010). In such works, the averaging is mass weighted, i.e., emphasis is put on the size of a small fraction of the most massive grains. In this paper, on the other hand, averaging is surface weighted, i.e., emphasis is put on a population of small grains that dominate the grain surface area, as well as the total number of grains. In other words, if simulations of grain growth would give us a distribution of grains in which a small number of big boulders co-exist with a large number of tiny grains, the average grain size of such a distribution calculated with Equation (9) will be close to the size of small grains, contrary to the “usual” definition of average grain size.

3. CHEMICAL MODEL OF THE DISK

In principle, simultaneous modeling of disk chemical evolution, and grain evolution requires a non-local approach. Grains not only grow, but also move within the disk due to sedimentation and radial drift (e.g., Brauer et al. 2008), bringing with them molecules in icy mantles. However, a coupled chemo–dynamical disk model with grain growth would be computationally expensive, and difficult to analyze from the chemical point of view, so in the present study we choose to neglect transport effects. Thus, we model a chemical structure in the disk, taking dust properties and physical conditions from the previously described disk model, assuming that these conditions do not change over the timespan of chemical evolution considered. This timespan is taken to be 2 Myr, but the particular choice does not significantly affect our conclusions, as the abundances of most species are equilibrated very quickly.

In this study, we utilize the chemical model described in Vasyunin et al. (2008). Initial elemental abundances are taken from Table 1 in Vasyunin et al. (2008). Compared with the original chemical model, we made several modifications. First, dissociative recombination of ions on grain particles is included, according to Umebayashi & Nakano (1980) and Semenov et al. (2004). Second, for gas–grain chemical interactions and grain surface reactions, we used variable dust-to-gas mass ratios and the average grain size calculated at each disk point using data from the grain growth model. For grain surface reactions, we utilized model H from Vasyunin et al. (2009). In this model, only thermal hopping is a source of mobility of surface species, and a high diffusion-to-desorption energy ratio of 0.77 is adopted for all species. Under these conditions, stochastic effects in grain surface chemistry are negligible, and classical rate equations may be safely used (Vasyunin et al. 2009; Garrod et al. 2009).

In our model, molecular hydrogen is formed via the surface reaction $H + H \rightarrow H_2$. The rate of this reaction, as well as of other surface reactions, is calculated according to the formalism described by Hasegawa et al. (1992). The rates are inversely proportional to the surface area of an individual dust grain.

The CR ionization rate has been adopted according to Equation (19) from Sano et al. (2000). The unattenuated CR ionization rate was taken to be $1.3 \times 10^{-17}$ s$^{-1}$. The final and most important change is the detailed treatment of photoprocesses that take into account the shape of the UV spectrum of the central star and its attenuation in the disk due to absorption of UV photons by dust grains (see Section 3.1). Below, we discuss in detail the treatment of these photoprocesses.

3.1. Photoreactions

Photoreactions represent the crucial element of chemical networks designed for the upper disk atmosphere, and it is this element that is most affected by dust evolution. In the conventional approach, photoreaction rates are estimated as

$$k^\text{ph} = \chi k_0 \exp(-\gamma A_V),$$

where $k_0$ is the reaction rate for the unshielded interstellar UV radiation field, $\chi$ is the UV intensity scaling factor, and $A_V$ is a parameter used to account for the different dust extinction in the UV and visual wavelengths. Generally speaking, $A_V$ estimated from gas column density cannot be used in this case, because it is based on a particular choice of dust properties (opacities and the dust-to-gas mass ratio), and on the assumption that these properties do not vary in the medium. In our study, dust parameters are position-dependent, so we have to be more careful. To compute rates of photodissociation and photoionization, one uses the general expression

$$k^\text{ph}(r,z) = 4\pi \int \frac{I_\nu(r,z)}{h\nu} \sigma_\nu d\nu,$$

where the mean UV field intensity $I_\nu(r,z)$ is obtained as a solution of the radiation transfer problem. In this study, we adopt a simplified approach in which $I_\nu(r,z)$ is given by the equation

$$I_\nu(r,z) = I_\nu^\text{in}(r,z) \exp(-\tau_\nu^\text{in}(r,z)) + I_\nu^\text{D} \exp(-\tau_\nu^\text{IS}(r,z)),$$

where $I_\nu^\text{in}(r,z)$ is the unattenuated, diluted stellar radiation field and $I_\nu^\text{D}$ is the so-called Draine radiation field (Draine 1978). We investigate two representations for the stellar radiation field. In the first representation, the observed spectrum for TW Hya is used, scaled in such a way that the integrated UV intensity is about 500 in units of the Draine field at 100 AU from the star (Bergin et al. 2003). A combination of Far Ultraviolet Spectroscopic Explorer (Herczeg et al. 2002) and Hubble Space
Telescope (Ayres 2010) data is utilized, and the resulting spectrum is shown in Figure 8. Essentially, this spectrum is very close to the one used in Bergin et al. (2003). In another representation, stellar radiation is assumed to be given by the scaled Draine interstellar field, with the same normalization. Comparison of results for the two representations shows that both spectra lead to the same general conclusions about the chemical structure of disk's with both evolved and unevolved dust. This is consistent with the findings of van Zadelhoff et al. (2003). These authors compared molecular distributions and column densities for the cases when the UV spectrum is given either by the scaled interstellar radiation field (ISRF) spectrum or the smoothed TW Hya spectrum and found no significant differences (their models A and B). In our case, the relative similarity of results for the two representations is caused by effective attenuation of the stellar radiation in the disk, so that the radiation field is in both cases dominated by the interstellar field everywhere in the disk, except for the uppermost layers. The situation would have been different if scattering were present in our model. When the scaled ISRF is used to represent stellar radiation, scattering is in some sense equivalent to just a somewhat different scaling factor for vertically penetrating radiation. However, when a more realistic stellar spectrum is used, like the Lα-dominated TW Hya spectrum, scattered stellar radiation would noticeably change photoreaction rates for species with large cross sections in the Lα range (Bergin et al. 2003). Note that van Zadelhoff et al. (2003) did find a significant dependence on the spectrum of the radiation field in a more general sense, that is, for the case when no UV excess is taken into account at all (their model C).

Also, van Zadelhoff et al. (2003) investigated how different approaches to radiation transfer, namely, full 2D and simplified calculations, such as those described below, impact the chemical composition of a PPD. They found that column densities of most species are not sensitive to the chosen approach. Important exceptions are the molecules CN, C2H, CS, and HCN, but only in the inner disk. Their column densities do significantly depend on the adopted UV radiation transfer model. However, in our model, the strength of the stellar UV field is more than an order of magnitude weaker than that considered by van Zadelhoff et al. (2003).

The optical depth \( \tau_{\nu}^{st} (r, z) \) is computed along the ray between the star and the current location, so that

\[
\tau_{\nu}^{st} = \int \kappa_{\nu} (r, z) \rho(r, z) ds. \tag{13}
\]

Dust sedimentation is taken into account in the dust density \( \rho(r, z) \). The absorption coefficient \( \kappa_{\nu} (r, z) \) per unit dust mass is calculated at each location along the ray as

\[
\kappa_{\nu} (r, z) = C \int da f(a, r, z) Q(a, \nu) \pi a^2, \tag{14}
\]

where the normalization coefficient \( C \) is defined by the condition

\[
1 = C \int da f(a, r, z) \frac{4}{3} \pi a^3 \rho_d. \tag{15}
\]

Absorption efficiency factors \( Q(a, \nu) \) are taken from Draine & Lee (1984) and Weingartner & Draine (2001). For the purpose of opacity computation, we assume that dust consists of silicate and carbon (graphite) components contributing, correspondingly, 70% and 30% to the total dust mass density (Weingartner & Draine 2001). In Equation (15) \( \rho_d \) is the density of dust material, taken to be 3 g cm\(^{-3}\) for silicate grains and 2.24 g cm\(^{-3}\) for graphite grains. In the expressions above, \( f(a, r, z) \) is the local evolved grain size distribution that comes from the dust growth and sedimentation model. Considering coagulation and fragmentation, we do not distinguish between the two materials as experimental data show similar dust evolution behavior for both types of grains (J. Blum 2009, private communication).

The optical depth \( \tau_{\nu}^{st} (r, z) \) is computed in the same way, but in a vertical direction from the disk surface to the height \( z \).

The reaction cross-sections are taken from van Dishoeck et al. (2006) and supplemented with the additional data for the Ly\(\alpha\) wavelength, with the exception of the photodissociation cross-sections for NO, HCN, NO\(_2\), SO\(_2\), OCS, NH\(_3\), CH\(_4\), H\(_2\)O\(_2\), and C\(_2\)H\(_2\). For these molecules, monochromatic photodissociation cross-sections from the AMOP\(^5\) database have been used in our study.

To compute the rates of photoreactions for which wavelength-dependent cross-sections are not available, we use the standard Equation (10), but with the modified procedure for computing \( A_\nu \). The conventional expression for optical extinction

\[ A_\nu = N_H/1.59 \times 10^{21} \text{cm}^{-2} \tag{16} \]

is valid for dust that is well mixed with gas, consists of single-sized grains (10\(^{-3}\) cm) and has a dust-to-gas mass ratio of 0.01, but it can easily be re-normalized for other values of these parameters. We integrate \( A_\nu \) along the ray between the star and the considered location (or in a vertical direction for interstellar radiation), taking into account the variable dust-to-gas ratio along the ray and a variable average grain size \( \bar{a}(r, z) \).

Self-shielding for H\(_2\) photodissociation is computed using the Draine & Bertoldi (1996) formalism, with the modified \( A_\nu \) value used to account for dust attenuation. The self- and mutual shielding for CO photodissociation are computed with data from Lee et al. (1996). Their dust attenuation is not included in the resultant shielding value, as it is replaced by our optical depths. To compute self-shielding factors, one would need to know the CO column density along the ray, which in the chemical study would entail iterations. We adopted a much simpler approach, assuming that CO self-shielding is proportional to the overall column density, with an average abundance of 10\(^{-6}\).

To check whether this simplification affects our conclusion, we run two models, bracketing possible self-shielding values. In one of the models, maximum self-shielding is assumed, which would correspond to all CO atoms being in CO molecules. In the other model, CO self-shielding is assumed to be zero. Comparison of these two models showed that various treatments of self-shielding do not change our main conclusions, but they do change some numbers, so we believe that the use of this simplification is acceptable. Anyway, species that turned out to be sensitive to the CO self-shielding treatment (CS and H\(_2\)CO) are not included in Tables 2 and 3.

In the model, several important simplifications are made. First, we assume that dust and gas temperatures are equal everywhere in the disk. Next, we neglect transport processes, such as radial and vertical mixing, and their influence on molecular abundances. Finally, when simulating grain-surface chemistry, we utilize the single average grain size instead of the real grain size distribution. The impact of these simplifying assumptions on the results of this study is discussed in Section 5.

\(^5\) http://amop.space.swri.edu/
Because the disk density is higher closer to the star, grain growth proceeds faster there (in our model we do not consider the radial drift of grains). One can see that at \( R \lesssim 10^4 \) AU a steady state in the grain surface density distribution is reached within less than 10^4 yr. However, in the outer disk (\( R \gtrsim 100 \) AU) grain surface density evolves much slower. A steady-state distribution is achieved in the inner disk midplane (10 AU \( \gtrsim \) 100 AU)

4. RESULTS

4.1. Dust Evolution in the Disk

Using the model of grain growth and fragmentation described in Section 2.2, we calculated the evolution of surface densities for grains of different sizes, starting from the standard Mathis–Rumpl–Nordsieck (MRN) grain size distribution at \( t = 0 \) (Mathis et al. 1977). Snapshots of surface density as a function of grain size for four time moments are shown in Figure 3. The corresponding vertically integrated average grain size calculated according to Equation (9) using vertically integrated number densities from Equation (4) is shown in Figure 4.

The two peaks in Figure 4 appear because small grains typically grow together in a more or less uniform bump moving to larger sizes. So, the whole distribution shifts up in size until grains reach the fragmentation barrier. Once that happens, most of them fragment, and the small size grains get re-populated. The average grain size drops again, and an equilibrium between growth and fragmentation is established.

\[
\text{Note. Observed column densities are compiled from Dutrey et al. (1997), Qi (2000), Aikawa et al. (2002), Dutrey et al. (2007), Bergin et al. (2010), and Henning et al. (2010).}
\]

\[
\text{Table 2: Species Sensitive to Grain Evolution}
\]

| Species       | 10 AU Column Densities (cm\(^{-2}\)) | 100 AU Column Densities (cm\(^{-2}\)) | 550 AU Column Densities (cm\(^{-2}\)) | Peak Abundance | Observed Column Densities (cm\(^{-2}\)) |
|---------------|---------------------------------|---------------------------------|---------------------------------|----------------|---------------------------------|
| A5 GS         |                                 |                                 |                                 | n(X)/n(H)      |                                 |

\[
\text{Table 3: Species Insensitive to Grain Evolution}
\]

| Species       | 10 AU Column Densities (cm\(^{-2}\)) | 100 AU Column Densities (cm\(^{-2}\)) | 550 AU Column Densities (cm\(^{-2}\)) | Peak Abundance | Observed Column Densities (cm\(^{-2}\)) |
|---------------|---------------------------------|---------------------------------|---------------------------------|----------------|---------------------------------|
| A5 GS         |                                 |                                 |                                 | n(X)/n(H)      |                                 |

\[
\text{Note. Observed column densities are compiled from Dutrey et al. (1997), Qi (2000), and Dutrey et al. (2007).}
\]
with a mean grain size of $10^{-4}$ cm (1 μm). In the outer disk region ($R \geq 100$ AU), the average grain radius increases relative to the initial value by a factor of only 3–5.

In contrast, differential dust settling seems to be much more significant. 2D distributions of the total dust-to-gas mass ratio and average grain size are shown in Figure 5. Dust settling reduces the dust-to-gas mass ratio in disk regions above the midplane. Everywhere above $Z/R \sim 0.1$, this ratio is significantly below the canonical value of 0.01. In the chemically rich intermediate layer, it varies between 0.001 and 0.01, while in the disk atmosphere it drops to $10^{-4}$ to $10^{-5}$. At the same time, in the midplane, the dust-to-gas mass ratio can reach a value of 0.02. Similarly, the average grain radius decreases above the midplane, though its change is not that dramatic. In the disk atmosphere, the average grain radius is only $10^{-6}$ cm (0.01 μm), because large grains efficiently settle down to the midplane.

Summarizing both the vertically averaged and 2D parameters of the evolved dust, we note that the overall effect of grain growth and sedimentation in our disk model is the global decrease of the total surface area of dust grains (see Figure 6). This is less pronounced in the outer part of the disk ($R \geq 100$ AU), corresponding to a factor of only 2–3. In the inner disk region ($R \leq 100$ AU), the decrease of the dust surface area is more prominent, i.e., up to one order of magnitude. The ratio of evolved to original grain surface area has a steeper radial dependence than variations in the vertical direction. This is because the decrease in total dust surface area above the midplane, caused by dust settling, is partly compensated by the presence of small particles dominating the surface area.

4.2. UV Field in the Disk

For the radiation field in the disk, we consider three basic models. In model A5, all grains are assumed to have a single size of $10^{-5}$ cm. This is the model of choice in most astrochemical computations. Model A4, in which all grains have the same radius of $10^{-4}$ cm, can be considered a rough representation of grain growth (without sedimentation). Finally, in model GS, both grain growth and sedimentation are fully taken into account.
account. For brevity, we will call the GS and A4 models “evolved,” while the A5 model will be referred to as the “standard” model.

In all models, the disk is illuminated by both stellar and interstellar UV radiation. For disk chemistry, the strength and shape of the UV field are of primary importance, as the field controls the rates of photoionization and photodissociation, as well as the efficiency of the photodesorption of grain mantles (e.g., Bourdon et al. 1982; Westley et al. 1995; van Zadelhoff et al. 2003; ¨Oberg et al. 2007). Due to the presence of dust, the UV field is attenuated as it penetrates deep into the disk. As mentioned in the introduction, the attenuation of starlight in the disk’s atmosphere can also be caused by PAH particles. IR observations of PPDs show that PAHs are an abundant component of some disks around Herbig Ae stars (e.g., Acke et al. 2010), but they are usually not seen in the spectra of T Tauri stars (Geers et al. 2006). Therefore, for simplicity, we neglect their possible contribution to the opacity and heating of the disk.

In Figure 7, the distribution of the integrated UV field strength over the disk is shown in logarithmic scale. Contours are labeled in units of the interstellar UV radiation field (Draine 1978). In the evolved models, the disk becomes more transparent to the incident UV radiation. Although, in model A5 (Figure 7, middle panel), one can clearly see the dark zone at the disk midplane (up to Z/R = 0.15), this region is significantly smaller in models GS and A4. On the other hand, in evolved models, the midplane can be divided into two parts. The inner part at R ≤ 100 AU remains as opaque to UV radiation as in the standard model, while the outer midplane can hardly be called “dark,” because of the smaller opacities in models GS and A4. In model A4, the UV strength in this region is ~10^5 times higher than in model A5. Thus, the outer disk in model A4 consists of only two layers: the atmosphere and the moderately UV-illuminated midplane (Figure 7, left panel). In the GS model, the outer disk is not that transparent, even though the inner, dark region of the midplane is still narrower than in model A5. The UV strength in the outer, disk region is higher than in model A5 by a factor of 10–10^3 and is only a small fraction that in the intermediate layer. Therefore, the three-layered chemical structure of the disk is preserved in the GS model, but the midplane is only “dim” rather than “dark” (Figure 7, right panel).

The UV spectrum at various heights above the midplane for a disk radius of R = 100 AU is shown in Figure 8. For illustrative purposes, we also schematically include the Lyα feature. As expected, the dust absorption is stronger at shorter wavelengths. It is important to note that the Lyα feature “disappears” in the densest part of the disk, due to strong absorption and the absence of any efficient scattering mechanisms for UV photons in our model. Hence, we expect only minor differences in column densities of molecules in the current version of our model, with and without Lyα, because the major contribution to column densities comes from the densest parts of the disk. In future works, we plan to treat the scattering of Lyα photons (see Bergin et al. 2003).

Another factor that can affect the UV field in the upper disk atmosphere is gas-phase opacity. Recently, Bethell & Bergin (2009) noted that water and OH molecules can be sources of significant absorption in the UV band. However, to take this effect into account properly, one would need to model chemical and physical disk structures self-consistently.

4.3. Chemical Structure of the Disk

We now want to discuss which effect—grain growth or sedimentation—is dominating changes in column densities of the various gas-phase species. Note that in all three basic models, detailed cross-sections are used, to calculate photoreaction rates whenever possible (see Section 3.1).
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Figure 8. Spectrum of the UV radiation in the disk at different heights above the midplane at \( R = 100 \) \( \text{AU} \) in model GS. Closer to the midplane, the spectrum shape is similar to that of the ISRF because the stellar component is attenuated faster than the interstellar one. For comparison, the spectrum of the scaled-up Draine field is also shown.

(A color version of this figure is available in the online journal.)

4.3.1. Inner Disk: Models GS and A5

First, we compare models GS and A5. The overall trend for these two models is that the column densities in the inner disk are greater for most species (such as CO, CO\(_2\), and NH\(_3\)) in the GS model than in the A5 model, sometimes by orders of magnitude. Of all the gas-phase species, only 10% have greater column densities in the A5 model at \( R = 10 \) \( \text{AU} \) (such as \( \text{S}^+\), HNO, and CP). This result may seem counterintuitive, as the disk that is transparent to UV radiation should represent a more hostile environment for molecules. However, at the same time, the growth of dust particles decreases their total surface area, thus lessening the effectiveness of mantle formation and surface chemical processing. Also, the more intense UV field in the upper disk causes faster photodesorption, shifting the balance between sticking and desorption toward higher gas-phase abundances.

The most dramatic example of this difference is H\(_2\)CS. The column densities of this molecule at 10 \( \text{AU} \) in models GS and A5 differ by almost six orders of magnitude. However, there are also less exotic examples represented by basic carbon compounds, also at 10 \( \text{AU} \), in which the effects of dust evolution are stronger. Both CO (see Figure 9) and CO\(_2\) are concentrated primarily in the warm molecular layer. The peak gas-phase abundances of CO are nearly the same in models GS and A5, as they are essentially equal to the total carbon abundance. However, the location of the peak of the relative abundance of CO in the GS model is shifted downward to the denser disk, region causing the CO column density to increase. The peak of the CO\(_2\) abundance is also located deeper in the GS model, and the maximum abundance of this molecule is two orders of magnitude higher than in the A5 model. Similar behavior is characteristic to the abundances and column densities of N\(_2\)H\(^+\), NH\(_3\), and H\(_2\)O (see Figure 10, fourth row). Although in model A5 the column densities of these species decrease toward the inner disk, in the models with grain growth (A4 and GS) they are nearly constant. Again, this is a manifestation of faster grain evolution in the disk’s interior with respect to the outer region (\( R \geq 50–100 \) \( \text{AU} \)).

In the inner disk midplane, where temperatures are low enough to allow icy mantle formation, all carbon atoms are locked in surface CO\(_2\). Midplane surface and gas-phase abundances of CO and CO\(_2\) do not differ in models GS and A5. At the same time, in model A5, surface hydrogenation products of these species are significantly more abundant. For example, \( \text{s-H}_2\text{CO} \) and \( \text{s-HCOOH} \) (the prefix “s-” denotes surface species) are enhanced by one to two orders of magnitude in the model with “standard” dust properties.

Another noticeable difference between models GS and A5 is the layer of enhanced depletion located right beneath the molecular layer, which is clearly observed in the A5 model but is absent (or at least less pronounced) in model GS. The origin of this depletion layer is related to hydrogen and helium ionization. This effect is most directly seen for CO. In the depletion layer, this molecule is rapidly destroyed in reactions with He\(^+\). Below this layer, helium is not ionized, as X-rays do not penetrate there, and this channel is not important. Above it, the reaction of CO with ionized helium cannot compete with rich ion-molecular chemistry. In the GS model, molecular freezing is less effective because of decreased available dust surface, and photodesorption is enhanced; thus, formation of this depletion layer is suppressed. It is also important to note that CR and

Figure 9. 2D distributions of CO abundance of the species relative to H\(_2\) in models A4, A5, and GS, respectively.

(A color version of this figure is available in the online journal.)
X-ray ionization are not affected by dust sedimentation in our model.

Abundant gas-phase water in the GS model consumes hydrogen ions effectively (produced by CR ionization and in reactions of H$_2$ with He$^+$), and their abundance drops significantly at intermediate heights (about 1.5 AU at $R = 10$ AU). Correspondingly, abundances grow for other species that would otherwise have been destroyed by H$^+$. Among these species are some long carbon chains, such as C$_6$H$_2$, and cyanopolyynes, such as HCN, HC$_5$N, and HC$_5$N (Figure 11, first and second rows). Conditions for the gas-phase synthesis of these compounds are only met in the narrow disk layer, and so the presence or absence of H$^+$ in this layer determines whether or not molecules with long carbon chains can be abundant in the inner disk. This is why their column densities are 4–5 orders of magnitude higher in the GS model, where they bind a significant fraction of C atoms, than in the A5 model.

Thus, the typical net effect of dust evolution is to increase the gas-phase abundances (despite enhanced photodissociation) of most molecules, and to decrease abundances of their surface counterparts. Of course, given the intricate structure of chemical networks, the response is not always straightforward, and there are species for which both gas-phase and surface abundances are increased in the GS model (e.g. H$_2$S), and also species for which
both gas-phase and surface abundances are decreased in the GS model (e.g. HNO). Also, dust evolution suppresses surface hydrogenation and, in particular, formation of the simplest organic molecules in icy mantles.

4.3.2. Outer Disk: Models GS and A4

Yet another comparison that is useful is to compare the results of models GS and A4. An increased average grain size (as well as an increased upper limit of the grain size distribution) can be thought of as a simplified way of modeling grain growth. The main assumption in this representation is that dust evolves uniformly over the entire disk. As we have seen, this is not the case, so the largest deviations should be in those disk regions that are less affected by grain growth and sedimentation (in regions farther from the star). Indeed, at a radius of 10 AU, the vertical abundance profiles in the GS and A4 models for most species are nearly identical, with most differences observed at $R > 100$ AU.

To illustrate features specific to model A4, we turn to the molecular disk content at 550 AU. The biggest differences in column densities are found for surface species, which is expected, as the grain surface area is much smaller in this model than in the other two models. Some complex species, such as $s$-C$_2$O and $s$-C$_3$O, are underabundant in terms of column densities by more than five orders of magnitude in model A4. The column densities of other carbon-bearing surface species,
such as s-CO$_2$, formaldehyde, and methanol, are 2–4 orders of magnitude smaller than in other models. On the other hand, the column densities of ices, which are not affected that much by surface chemistry (s-CO, s-H$_2$O, and s-NH$_3$), differ only slightly in models GS and A4. This is largely because these molecules simply bind nearly all N atoms in both of these models.

For the gas-phase species, the largest difference in column densities is observed for N$_2$O. This molecule is overabundant (in terms of column densities) in model A4 relative to model GS by four orders of magnitude. Similar overabundance is also seen for other N-bearing species as well, such as NO$_2$, OCN, and ammonia. Although the network of chemical pathways connecting all these species is quite complicated, the underlying reason for their higher abundance seems to be simple. Surface transformations, which are less effective at this radius in model A4 than in model GS, lock somewhat fewer nitrogen atoms in surface ammonia making them available for various gas-phase species. It must be kept in mind that the column density of s-NH$_3$ is so high that even minor relative differences in N(s-NH$_3$) between models A4 and GS significantly affect column densities of other, less abundant N-bearing species. Similar trends are observed in other families as well. In general, we can say that dust acts as an irreversible (or nearly irreversible) sink for atoms, locking them in surface species with high desorption energy. As grains get bigger, their total surface area diminishes, and more atoms are available for richer gas-phase chemistry.

Column densities alone are not the unique indicator of a specific chemical structure. Even if the column densities of some molecules are almost the same in models GS and A4, their vertical distributions can be different in terms of both width and location of the molecular layer. In general, as we move from model A5 to GS to A4, at large radii, the molecular layer becomes thinner and is located deeper in the disk.

4.3.3. Comparison to Other Works

The chemistry in a disk with evolved dust was studied by Aikawa & Nomura (2006). In their investigation, H$^+$ was indicated as one of a few species sensitive to grain growth in terms of column density. In our study, model A4 is most suitable for comparison to the model of Aikawa & Nomura (2006), and comparison of models A5 and A4 indeed confirms the statement made in their paper. However, H$^+$ behaves differently in our two evolved models (GS and A4; see Figure 10, sixth row). In model GS, the column density of H$^+$ does not significantly differ from that in model A5. As the formation of H$^+$ is driven by CR ionization of H$_2$, with the same rate in all three models, the difference is related to the destruction of this ion. It is consumed mainly in dissociative recombination reactions with electrons and negatively charged grains, as well as in ion-molecular reactions with CO, H$_2$O, CN, and other radicals. Therefore, the distribution of H$^+$ in the disk is controlled by fractional ionization and by the width and location of the molecular layer. In models GS and A5, peaks of molecular abundances are located at different heights but are still above the midplane. Because of this, the vertical profiles of the H$^+$ abundance in these two models are similar, except for a shift relative to the midplane. Consequently, the column density of H$^+$ is not sensitive to grain evolution, as described by model GS.

On the other hand, in model A4, the molecular layer extends down to the midplane, and, thus, protonation reactions involving H$^+$ are active in a broader disk zone. The main channels of H$^+$ destruction in the outer disk are its reactions with CO and water, which are abundant even in the cold gas in model A4. This emphasizes the need of careful grain growth modeling in chemical studies, because an adopted approach to grain evolution may affect conclusions about even some primary species.

The increase in many molecular column densities seen in model GS seems to contradict the conclusion of Aikawa & Nomura (2006) that grain growth does not affect most column densities. However, they do not consider dust settling and also model dust growth by increasing the upper size limit, thus keeping a significant amount of small grains. This means that the upper disk in their model is, probably, more opaque than our disk in model GS. Thus, the increase in column densities is only observed when dust growth and settling are considered simultaneously.

Our basic results compare favorably with those obtained by Jonkheid et al. (2004, 2007). However, the two models are also quite different. In particular, freeze-out and surface processes are not taken into account by Jonkheid et al., and assumptions about the central star are very different from our work.

Nevertheless, the CO depletion layer is seen in the T Tauri disk model and especially in the Herbig Ae/Be disk model when dust is assumed to be well mixed with the gas. As in our model, this layer disappears when dust settling is included in the modeling by Jonkheid et al. (2007). In both models, the peaks in the vertical distributions of molecular abundances occur closer to the midplane in the models with dust evolution.

In terms of column densities, however, the two models differ. In our model, as grains become larger, the molecular column densities become larger. The opposite trend is observed in the model by Jonkheid et al. (2007, cf. their Figure 8). But this difference is understandable: the disk in their model is warmer because the central star is hotter and more luminous. As the disk becomes more transparent to UV radiation, molecular column densities drop. In our model, chemical interactions between gas and dust are very important, and the difference between column densities in different dust models is not controlled solely by photodissociation.

Another study to be compared with our results is that of Pascucci et al. (2009). These authors found that there is a significant underabundance of HCN relative to C$_2$H$_2$ in disks around cool stars and substellar objects. They attribute this underabundance to the differences in UV radiation fields. The photodissociation of molecular nitrogen is less efficient in the vicinity of cool stars, so there are not enough free nitrogen atoms to be incorporated into HCN molecules, while N atoms are abundant around hotter stars with noticeable UV excess. The UV spectrum of the central object is the same in both the GS and A5 models. However, one of the main results of grain evolution is that the integrated UV field in the upper disk is stronger in model GS than in model A5, and we may expect a similar trend in the HCN abundance.

And we do see this trend in the outer disk (Figure 10, fifth row and Figure 11, first row). Although in model A5 at $R > 100$ AU, column densities of HCN and C$_2$H$_2$ are almost equal, in model GS (with a stronger UV field), HCN is 15 times more abundant than acetylene. Analysis of chemical reactions shows that enhanced HCN is indeed caused by greater abundance of N atoms. The trend is not preserved at smaller radii, though. At $R = 10$ AU in model A5, the column density of HCN exceeds that of acetylene by a factor of 42 (compared to near equality at greater distances). This is because in model A5, with abundant dust in the upper disk, surface HCN synthesis with subsequent
desorption becomes an important factor increasing the gas-phase abundance of this molecule.

One should keep in mind that both underabundance and overabundance of HCN relative to C2H2 in model GS are observed in addition to the overall trend for column densities of most molecules to be greater in this model.

4.3.4. Fractional Ionization in the Disk

Dust evolution is reflected not only in the abundances of some molecules, but also shows up in a more integral way, affecting the fractional ionization \( x_e \) of the disk (see Figure 10, bottom row). Because in our model one grain can adsorb not more than one electron, a change in dust properties impacts disk ionization mainly through change of absorption of the UV field which is important for gas-phase chemistry. Although the ionization degree exceeds \( 10^{-10} \) everywhere in the disk, grain number density is not more than \( 10^{-15} \) in respect to hydrogen nuclei. Therefore, the ionization degree is controlled by cation chemistry, while the contribution of electron sticking to dust grains is less than 1%. In the disk atmosphere, differences are small as the entire ion content is provided by ionized carbon and ionized hydrogen (in the uppermost X-ray ionized layer). Deeper in the disk, different properties of dust cause \( x_e \) in models A5 and GS, to differ by almost two orders of magnitude. This difference is primarily caused by different dominant ions at different heights. Let us consider a slice at \( R = 100 \) AU as an example. When absorption becomes high enough so that C* is no longer a dominant ion (\( z \lesssim 40 \) AU), in model GS, most electrons are provided by metals. Sodium, magnesium, and iron ions stay dominant down to \( z \sim 15 \) AU. Below this level, where most dust is concentrated in model GS, metals are depleted, and the most abundant ions are H+ and H+2 (in almost equal shares).

In model A5, dust is equally abundant everywhere in the disk, and metals are depleted at all heights below 40 AU. Correspondingly, almost all ions at these heights are provided by H+ and H+2. These species are heavily involved in ion-molecular chemistry, so their abundances are very sensitive to overall molecular content. In particular, ionized hydrogen is effectively consumed in reactions with ammonia, water, hydroxyl, etc. These species are abundant in the warm molecular layer (\( z \sim 30 \) AU) and depleted right below it (\( z \sim 20 \) AU). Correspondingly, in the warm molecular layer H+2 is the most abundant ion, while at lower heights the balance shifts toward H+. The equilibrium fractional ionization (for a single ion) is inversely proportional to the square root of the recombination coefficient. This coefficient is significantly lower for H+ than for H+2, so fractional ionization is higher at \( z \sim 20 \) AU, where H+ dominates.

5. DISCUSSION

5.1. Disk Chemistry as a Tracer of Grain Evolution

Can molecular abundances in a PPD be tracers of grain evolution? Because the distance to the Taurus–Auiga complex, where most known disks around low-mass pre-main-sequence stars are located, is \( \sim 140 \) pc (Elias 1978) and the expected angular resolution of ALMA is up to 0.01, the spatial resolution of disk observations should be \( \sim 1-2 \) AU. This is sufficient to study the spatial distribution of molecular abundances in the outer disk (10–600 AU). So, it is worthwhile to ask if there are species sensitive to grain growth at a level that would make them detectable tracers of this process. Immediate products of observations are molecular lines. Therefore, we need to predict not abundances or column densities but the shapes and intensities of molecular lines, as well as the variations caused by grain evolution (e.g., Semenov et al. 2008). The physical model of the disk employed in this study is quite simple, however, so it does not make sense to perform realistic radiative transfer modeling. In this situation, we have chosen to consider only a given species as a possible grain evolution tracer if its column density differs in models A5 and GS by an order of magnitude or more in at least one of the representative radial regions around 10 AU, 100 AU, and 550 AU. An exception is made for CO, which has a very high column density. In the inner disk and at \( R = 100 \) AU from the star CO column density becomes higher by a factor of 5–7 in model GS in comparison to model A5.

Major species, both sensitive and insensitive to grain evolution in our model, are grouped in Tables 2 and 3, respectively. Additionally, Table 2 shows the observed column densities of several species, taken from Semenov et al. (2004; except for HCO+ and N2H+ which are taken from Table 3 in Dutrey et al. 2007, and C2H, which is taken from Henning et al. 2010). It is clear that the column densities of species that have already been observed in disks do not seem to be strongly influenced by the changing dust properties at large distances from the star, i.e., in the domain of single-dish observations. Closer to the star, however, the differences are more significant. Specifically, at \( R = 10 \) AU, the column density of water in model GS exceeds that in model A5 by a factor of 560. A word of caution must be said about water abundance. Although column densities for all other molecules have reasonable values in our models (as compared to available observations), water seems to be an exception. Recent Herschel results (Bergin et al. 2010) show no observable water lines in the DM Tau spectrum. Bergin et al. (2010) estimated the upper limit for the water column density in the outer disk to be about \( 3 \times 10^{13} \) cm⁻², which is much lower than the water column density in our models. They suggested that low water abundance may serve as an indication of grain growth and sedimentation. However, as we said previously, our model does not predict significant grain evolution in the outer disk, so the DM Tau disk may represent a later stage of the grain growth than our model.

Of course, not only abundances (i.e., column densities) but also their ratios, can be indicators of grain growth. However, as in the example of HCN and C2H2 considered above and motivated by observations by Pascucci et al. (2009), the influence of grain evolution on the abundance ratio can be at least twofold and calls for a more detailed consideration.

Another pair of observed species that may potentially be useful as a tracer of grain evolution is HCO+ and N2H+ (Dutrey et al. 2007). Although the average column densities of these species in model GS agree quite well with observations of Dutrey et al. (2007), the ratios of their column densities in models GS and A4 are quite different: at \( R = 550 \) AU the ratio \( \lambda(N(\text{HCO}^+)/N(N_2\text{H}^+)) \) is 150 in model GS, and 1500 in model A4. Although the main focus of our work was on comparison between models GS and A5, not between models GS and A4, the difference mentioned here shows that this ratio is worth checking in a more detailed model.

At the disk periphery, where dust evolution is least prominent, the only species that is sensitive to dust growth and sedimentation on the level of an order of magnitude is methanol. However, the methanol column density is quite modest (\( 2 \times 10^{13} \) cm⁻²) and even smaller closer to the star.

In general, we may conclude that the chemical signatures of early grain evolution are hardly observable with single-dish
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5.2. Model Limitations and Future Work

We have already mentioned that column densities are only a partial indicator of grain growth. Line emission modeling is needed to assess observable tracers of dust evolution with more confidence. But there are some issues that need to be addressed prior to this modeling. As we mentioned in the introduction, the simplified setup of our model allows us to isolate the chemical outcomes of grain evolution, although the process of grain growth should probably have a more general influence on disk structure. The response of a disk to dust evolution has already been addressed a number of times, but with only an oversimplified approach to grain growth and/or sedimentation. Our modeling shows that dust evolution in a disk is highly non-uniform, both in the vertical and radial directions, which should be reflected in a disk physical properties.

In future disk models, one would need to at least calculate the processes of grain growth and sedimentation consistently with the description of the disk structure, as density and temperature distributions in the disk are controlled by opacities. Dust absorption is definitely affected by growth and sedimentation, but both these processes, in turn, depend on the disk structure. In this study, changes in the surface averaged grain size (and, hence, in the total grain surface area) are only minor, and even in model GS, where dust is evolved, the disk is relatively opaque to incoming radiation. This means that extra heating due to decreased opacity would mostly affect the upper disk, above the region where most molecules are concentrated. Because in this region molecular abundances are mostly controlled by photoprocesses, most column densities probably will not be strongly affected by the increased gas scale height or gas temperature in the upper disk. The exception is represented by abundant components that bind almost all CNO atoms in the molecular layer (CO, N$_2$, O). As we noted, the increase of their column densities in the inner disk in models GS and A4 relative to A5 is partially caused by the downward shift of the molecular layer to the denser disk region. If we would take the disk’s vertical expansion due to increased heating into account, the peak of relative abundance for these components would probably reside in the region of fewer density, thus suppressing the increase in column densities. This calls into question the ability of CO to be a tracer of dust evolution within the framework of our model. However, dust growth may affect not CO itself, but rather its isotopic ratios (Visser et al. 2009).

Another issue, which should be addressed properly in the future, is the possible interrelation between chemical and physical structures of a disk with evolving dust. This interrelation has already been discussed from the point of view of thermal balance in the disk (e.g., Jonkheid et al. 2007). However, dust evolution may also lead to significant changes in fractional ionization, which is an important dynamical parameter, especially if turbulence in disks is excited due to magnetorotational instability (Igner & Nelson 2008). All of this calls for more self-consistency, not only between disk structure and grain evolution, but also between these two factors and chemistry.

The next step is to include time dependence in the model. Two of the three ingredients of our model (disk structure and grain-ensemble properties) explicitly imply that the disk is in a steady state. The third ingredient (chemistry) is formally time dependent but produces steady-state abundances for most species. This is the reasonable outcome given that the other

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**Table 4**

| Species  | 10 AU | 100 AU | 550 AU |
|----------|-------|--------|--------|
|          | A5    | GS     | A5 GS  | A5 GS  |
| s-H$_2$O | 99.8  | 97.3   | 57.4   | 91.0   |
| s-NH$_3$ | 1.0   | 1.0    | 1.0    | 5.0    |
| s-C$_2$H$_2$ | ... | ... | ... | ... |
| s-C$_3$H$_2$ | ... | ... | 20.9 | 3.3 |
| s-C$_2$H$_3$ | ... | ... | 12.0 | ... |
| s-C$_3$H$_2$ | ... | ... | 5.0 | ... |
| s-C$_2$H$_4$ | ... | ... | 1.3 | ... |
| s-CO$_2$ | ... | ... | 2.0 | ... |
| s-H$_2$O$_2$ | ... | ... | ... | 1.5 |
| s-HCN | ... | ... | ... | 3.1 |
| s-HNCO | ... | ... | 1.0 | ... |
| s-H$_2$C$_{14}$ | ... | ... | 1.0 | ... |

**Note.** Only species with contribution of 1% or more are shown.
two ingredients are in equilibrium. Our results represent only a snapshot of the disk at an early (or even the earliest) stage of grain evolution. However, at some later stage, the grain growth timescale may become short enough to be comparable with the timescale of various chemical transformations. With the current model, we cannot say what impact on chemistry possible further grain growth, beyond what the Birnstiel model can currently calculate, would have, even though some hints are provided by model A4. In particular, we may expect higher molecular densities at the disk periphery, with the molecular layer extending down to the midplane. This confirms the earlier suggestion that observations of gas-phase CO and water molecules in a cold disk region can be explained by an increase in grain size. Further improvements in the dust growth model are also needed. This field now represents an area of active research, both theoretical and experimental, and there are certain indications that grain evolution is not limited to simply sticking and fragmenting (e.g., Zsom et al. 2010).

Another issue that may become more important with the grain ensemble containing large grains is the treatment of grain surface chemistry. Currently, in chemical modeling we consider grains of equal “effective mean size” instead of the real grain size distribution. We believe that this simplification does not dramatically affect results of this study. The average grain size defined according to Equation (9) is close to the size of grains that dominate the total grain surface area available for surface chemistry. In other words, most of the surface chemistry occurs on grains of similar sizes. Also, K. Acharyya & E. Herbst (2011, in preparation) constructed a chemical model with grains of several grain sizes in order to reproduce the grain size distribution. They found its results to be quite similar to those obtained with a single grain size. However, the problem may be more complicated, as the temperature of an individual grain depends on its size. For the smallest grains, stochastic heating becomes important, which makes it impossible to assign a single temperature to them. These questions are not trivial and are worth considering in a separate study. In this work, we do not have grains of extremely small radii ($R \leq 10^{-8}$ cm). So, the considerations above should be of only a limited importance here.

Finally, transport processes are an important evolutionary factor in an accretion disk. At least, some of the differences between models GS and A5, such as the enhanced depletion layer in model A5, are quite localized. One does need to account for possible gas mixing to check whether these differences can survive in a more dynamic medium. The radial motion of grains has to be included in a realistic treatment of disk evolution.

6. CONCLUSIONS

We investigated the chemical evolution of the PPD around a T Tauri star. The thermal and density structures of the disk were calculated with a (1+1)-dimensional α-viscosity model. The processes of grain coagulation, fragmentation, and sedimentation were modeled as described in Brauer et al. (2008) and Birnstiel et al. (2010). The initial dust ensemble was the standard MRN grain size distribution (Mathis et al. 1977). Using the final grain size distribution (at $t = 2$ Myr) and the (1+1)-dimensional disk structure, we calculated the vertical distribution of the dust in the disk, assuming stirring–settling equilibrium according to Dullemond & Dominik (2004). For this distribution, we calculated the approximate UV field in the disk and simulated the chemical evolution of the disk over 2 Myr. Results for three dust models were compared: (1) a classical dust model, with uniform spherical particles of 0.1 $\mu$m and a gas-to-dust mass ratio of 100 (model A5); (2) a simplified grain growth model, with larger grains of 1 $\mu$m (model A4); and (3) a detailed grain growth model (model GS). The main results of the work can be summarized as follows.

1. The fragmentation of grains due to collisions keeps a population of small dust particles in the disk that dominate the total grain surface area crucial for chemical evolution of the disk. This effect reduces the impact of grain growth on the chemical structure of the disk. Grain growth proceeds quickly in low-mass T Tauri disks at distances $\lesssim 20–50$ AU, where the steady-state grain size distribution is reached in a few thousand years. Outside this radius, up to $10^6$ yr are needed to reach steady state at $R \geq 100$ AU. Furthermore, grain coagulation is limited there, and increases the average grain size by no more than an order of magnitude in the midplane. After 2 Myr of evolution, the average grain size in the disk midplane varies between $10^{-8}$ cm at $R = 10$ AU and $2 \times 10^{-5}$ cm at $R = 550$ AU. The dust-to-gas mass ratios in the same distance range are confined between $\sim 10^{-6}$ and 0.02.

2. The net effect of the dust settling and grain growth are a reduction of the total grain surface and higher UV irradiation rates in the upper disk. The chemical structure of an evolved disk still has three layers, but the intermediate molecular layer gets wider and shifts closer to the midplane. Therefore, the abundances and column densities of many species are enhanced by a factor of 3–100, even for such moderate grain growth.

3. A simplified model of grain growth, in which the dust-to-gas mass ratio is kept constant and grain size is simply increased by one order of magnitude, is not sufficient to reproduce the chemical evolution of a disk with evolving dust. For example, the column density of $H_2$, which is proposed to be sensitive to grain growth (Aikawa & Nomura 2006), exhibits high sensitivity to grain growth in our simple model, but not in the model with a detailed treatment of grain growth and sedimentation.

4. Grain evolution suppresses the formation of organic molecules in icy mantles, but it also enhances gas-phase molecular abundances. In particular, water and CO abundances are enhanced in the cold midplane.

5. We propose a few observational tracers of the grain evolution process. These are the column densities of gas-phase molecules such as $C_2H$, $HC_2N$, and $H_2O$ for the inner disk. The abundance ratio of $C_2H_2/HCN$ may serve as a grain evolution tracer in the outer disk, as may the abundance of $CH_3OH$. The composition of the ice mantles of interstellar grains seen in scattered light in the intermediate disk layer (around $\tau = 1$) may also serve as a tracer of grain evolution.

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