CHEMICAL EVOLUTION OF TURBULENT PROTOPLANETARY DISKS AND THE SOLAR NEBULA

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ABSTRACT

We study the influence of transport processes on the chemical evolution of DM Tau-like protoplanetary disks. Turbulent transport of gases and ices is implicitly modeled in full two dimensions (2D), using the mixing-length approximation, along with the time-dependent chemistry. We find that turbulent transport enhances abundances and column densities of many gas-phase species and ices, particularly, complex ones. The influence of turbulent mixing on disk chemistry is more pronounced in the inner, planet-forming disk region where gradients of temperature and high-energy radiation intensities are steeper than in the outer region. The molecules that are unresponsive to transport include, e.g., C$_2$H, C+, CH$_4$, CN, CO, HCN, HNC, H$_2$CO, OH; as well as water and ammonia ice. Their column densities computed with the laminar and 2D mixing model differ by a factor of $\lesssim$2–5. Molecules whose vertical column densities in the laminar and dynamical models differ by up to two orders of magnitude include, e.g., C$_2$H$_2$, some carbon chains, CS, H$_2$CS, H$_2$O, HCO$^+$, HCOOH, HNCO, H$_2$N$^+$, NH$_3$, CO ice, H$_2$CO ice, CH$_3$OH ice, and electrons. Molecules whose column densities are altered by diffusion by more than two orders of magnitude include, e.g., C$_2$S, C$_3$S, C$_6$H$_6$, CO$_2$, O$_2$, SiO, SO, SO$_2$, long carbon chain ices, CH$_3$CHO ice, HCOOH ice, O$_2$ ice, and OCN ice. We indicate several observable or potentially detectable tracers of transport processes in protoplanetary disks and the solar nebula, such as heavy hydrocarbon ices, complex organics, CO$_2$, O$_2$, SO, SO$_2$, C$_2$S, C$_3$S compared to CO and water ice.

Key words: accretion, accretion disks – astrochemistry – molecular processes – protoplanetary disks – stars: individual (DM Tau) – turbulence

Online-only material: color figures

1. INTRODUCTION

One of the most exciting topics in astrophysics is the genesis of prebiotic molecules that served as life-building blocks in the solar system and are preserved in meteorites and comets. Protoplanetary disks are believed to be birth places of planetary systems, so we may expect prebiotic molecules to be the eventual outcome of the disk evolution. However, a detailed comparison with existing chemical models, needed to solidify this assertion, is still hampered by poor sensitivity and spatial resolution of available spectral data (e.g., Píetu et al. 2005; Dutrey et al. 2007b; Panić et al. 2009). Apart from CO and its isotopologs, and occasionally HCO$^+$, DCO$^+$, CN, HCN, DCN, CCH, H$_2$CO, and CS, the molecular content of protoplanetary disks remains largely unexplored (e.g., Dutrey et al. 1997; Kastner et al. 1997; Aikawa et al. 2003; Thi et al. 2004; Píetu et al. 2007; Qi et al. 2008; Henning et al. 2010). Still, some conclusions can be drawn even from these limited data (of course, with the promise of the Atacama Large Millimeter Array, ALMA, in mind).

Multi-molecule, multi-transition interferometric observations, coupled with line radiative transfer and chemical modeling, have already allowed constraining the disk sizes, kinematics, distribution of temperature, surface density, and molecular column densities (see reviews by Bergin et al. 2007 and Dutrey et al. 2007a). The measured line intensities are indicative of vertical temperature gradients in disks (e.g., Dartois et al. 2003; Qi et al. 2006). A significant reservoir of very cold CO, HCO$^+$, CN, and HCN gases has been found in the disk of DM Tau at temperatures $\lesssim$6–17 K, which cannot be explained by conventional chemical models without invoking a non-thermal desorption or transport mechanism (e.g., Semenov et al. 2006; Aikawa 2007; Hersant et al. 2009). Non-thermal broadening of emission lines of $\sim$0.1 km s$^{-1}$ has been reported (e.g., Bergin et al. 2007; Dutrey et al. 2007a; Hughes et al. 2011), which is likely due to subsonic turbulence driven by the magneto-rotational instability (Balbus & Hawley 1991).

Recently, with space-borne (Spitzer) and ground-based (Keck, Very Large Telescope (VLT), Subaru) infrared telescopes, molecules have been detected in very inner zones of planet-forming systems, at $r \lesssim$ 1–10 AU. Rotational-vibrational emission lines from CO, CO$_2$, C$_2$H$_2$, HCN, OH, and H$_2$O imply a rich chemistry driven by endothermic reactions or reactions with activation barriers and photoprocesses (Lahuis et al. 2006; Carr & Najita 2008; Salyk et al. 2008, 2011; Pontoppidan et al. 2008a; Pascucci et al. 2009; van der Plas et al. 2009). Also, through ISO and Spitzer infrared spectroscopy, abundant ices in cold disk regions consisting of water ice and substantial amounts ($\sim$1%–30%) of volatile materials such as CO, CO$_2$, NH$_3$, CH$_4$, H$_2$CO, and HCOOH have been detected (e.g., Pontoppidan et al. 2005; Terada et al. 2007; Zasowski et al. 2009).

The conditions of planet formation in the early solar system have been revealed by a detailed analysis of the chemical and mineralogical composition of meteoritic samples and cometary dust particles (e.g., Bradley 2005). The recent Stardust and Genesis space missions have brought back the first samples of pristine materials, likely of cometary origin, showing a complex structure of high-temperature crystalline silicates embedded in low-temperature condensates (Brownlee et al. 2004, 2008; Flynn et al. 2006). Comets have been assembled around or beyond Neptune and expelled gravitationally outward; however, the presence of Mg-rich crystalline silicates in cometary...
dust indicates annealing of amorphous presolar grains at temperatures above 800 K (Wooden et al. 1999, 2007). The presence of crystalline silicates in the outer regions of protoplanetary disks has also been revealed (e.g., van Boekel et al. 2004; Juhász et al. 2010).

An isotopic analysis of refractory condensates in unaltered chondritic meteorites shows strong evidence that the inner part of the solar nebula has been almost completely mixed during the first several megayears of its evolution (e.g., Boss 2004; Ciesla 2009). This mixing (either advective or turbulent), along with high-energy irradiation, could have also been important for fractionation in both gas-phase and solid compounds (e.g., Clayton 1993; Clayton & Mayeda 1996; Lee et al. 1998b; Hersant et al. 2001; Lyons & Young 2005). The rich variety of organic compounds in meteorites, including amino acids, suggests that these species have formed just prior to or during the formation of planets in heavily irradiated, warm regions of the solar nebula (e.g., Ehrenfreund & Charnley 2000; Busemann et al. 2006). Combustion and pyrolysis of hydrocarbons at high temperatures, coupled with outward transport, has been inferred to explain the omnipresence of kerogene-like (mainly aromatic) carbonaceous material in meteoritic and cometary samples (Morgan et al. 1991).

While most modern astrochemical models (Willacy & Langer 2000; Aikawa et al. 2002; Markwick et al. 2002; van Zadelhoff et al. 2003; Igner et al. 2004; Kamp & Dullemond 2004; Semenov et al. 2005; Aikawa & Nomura 2006; Tscharnuter & Gail 2007; Agúndez et al. 2008; Woods & Willacy 2009; Visser et al. 2009b; Walsh et al. 2010) of protoplanetary disks are still based on laminar disk models, evidence for mixing, mentioned above, calls for a more sophisticated treatment. A few such dynamical studies have been presented. Models of the early solar nebula with radial transport by advective flows have been developed (e.g., Morfill & Völk 1984; Gail 2001, 2002; Wehrstedt & Gail 2002; Boss 2004; Keller & Gail 2004). Igner et al. (2004) for the first time simultaneously modeled the influence of turbulent diffusion in the vertical direction and advection flows in the radial direction on the chemical composition of the inner disk region. They found that dynamical processes significantly affect the chemical evolution of sulfur-bearing species. Willacy et al. (2006) have shown that one-dimensional (1D) vertical mixing modifies chemical composition of the outer disk region and that results with mixing agree better with observations. Semenov et al. (2006, Paper I) and Aikawa (2007) have found that turbulent transport allows explanation of the presence of a large amount of cold (≤15 K) CO gas in the disk of DM Tau. Tscharnuter & Gail (2007) have used a 2D disk chemo-hydrodynamical model and showed that in the disk midplane matter moves outward, carrying out the angular momentum, while the accretion flows toward the star are located at elevated altitudes. Consequently, gas-phase species produced by warm chemistry in the inner nebula can be steadily transported into the cold outer region and freeze out. Tscharnuter & Gail (2007) have claimed that global radial advective flows dominate over diffusive mixing for the disk chemical evolution. A radial advection model has also been utilized by Nomura et al. (2009), who have demonstrated that inward radial transport enhances abundances of organic molecules (produced mainly on dust surfaces in cold outer regions). Woods & Willacy (2009) have elaborated a disk chemical model with improved heating and cooling balance and accurate modeling of the UV radiation field and found that the $^{12}$C/$^{13}$C fractionation in the solar system comets can be explained by the reprocessing of presolar materials in a warm nebular region. Hersant et al. (2009) have studied various mechanisms for retaining gas-phase CO in very cold disk regions. They concluded that efficient photodesorption in moderately obscured disk regions ($A_V < 5'$) greatly enhances gas-phase CO concentrations, while the role of vertical mixing is less important. Heinzeller et al. (2011) have investigated the disk chemical evolution with radial advection, vertical mixing, and vertical wind transport processes. They have found that disk wind has a negligible effect on disk chemistry, whereas the radial accretion alters molecular abundances in the cold midplane, and the vertical turbulent mixing affects the chemistry in the warm molecular layer. The abundances of NH$_3$, CH$_3$OH, C$_2$H$_2$, and sulfur-containing species are most enhanced by transport.

In this paper we continue the detailed study of chemo-dynamical interactions in the protoplanetary disk started in Paper I. The primary aim of this study is to characterize the importance of turbulent diffusion for the chemical evolution in various disk domains and for various chemical families. For the first time, we utilize a large-scale disk physical model along with an extended gas–grain chemical network coupled to 2D turbulent transport. A wide range of temperatures, densities, and X-ray/UV radiation intensities encountered in this dynamical model allows us to follow the formation and destruction of various molecules, possibly detectable with ALMA and Herschel. We argue that even though the overall efficiency of diffusive transport in the outer disk is dominated by vertical mixing, one has to consider vertical and radial mixing simultaneously in the planet-forming region. Many complex ices and their gas-phase counterparts are enhanced by turbulent diffusion, in particular sulfur-bearing and other heavy (complex) species.

The organization of the paper is as follows. In Section 2, we describe the adopted disk physical model and the chemical network. In Section 3.1, basic chemical and dynamical timescales in protoplanetary disks are outlined and discussed. A general scheme for estimating possible sensitivity of a given molecule to transport processes is presented in Section 3.2. The influence of the 2D turbulent diffusion on the chemical evolution of dominant ions as well as C-, O-, N-, S-bearing species and complex organic molecules is studied in detail in Sections 4.1–4.6. Detailed comparison with the previous studies and future improvements of chemo-dynamical models are discussed in Section 5.1. We discuss the importance of turbulent diffusion for the presence of cold gases in disk midplanes in Section 5.2. We verify the feasibility of our chemical and physical disk models by comparing the calculated and observed column densities in the DM Tau disk and abundances of cometary ices in the solar system (Section 5.3). Detected or potentially detectable molecular tracers of transport processes in protoplanetary disks are summarized in Section 5.4. Summary and conclusions follow in Section 6.

2. MODEL

2.1. Disk Structure

We focus on the DM Tau system because it is one of the most observationally studied and molecularly rich protoplanetary disks around a T Tauri star. The flaring disk structure adopted is based on a 1+1D steady-state α-model similar to the D’Alessio et al. (1999) model. The DM Tau is a single M0.5 dwarf ($T_{\text{eff}} = 3720$ K), with a mass of 0.65 $M_\odot$, and a radius of 1.2 $R_\odot$ (Mazzitelli 1989; Simon et al. 2000). The non-thermal...
FUV radiation field from DM Tau is represented by the scaled interstellar radiation field of Draine (1978), with unattenuated intensity at 100 AU of \( \chi_\text{FUV}(100) = 410 \) (e.g., Bergin et al. 2003). For the X-ray luminosity of the star we adopt a value of 10\(^{30}\) erg s\(^{-1}\), which is constrained by recent measurements with Chandra and XMM in the range of 0.3–10 keV (M. Gueld 2010, private communication).

The model disk has an inner radius \( r_0 = 0.03 \) AU (dust sublimation front, \( T \approx 1500 \) K), an outer radius \( r_1 = 800 \) AU, an accretion rate \( M = 4 \times 10^{-9} M_\odot\) yr\(^{-1}\) and a mass \( M = 0.066 M_\odot\) (Dutrey et al. 2007b; Henning et al. 2010). The DM Tau disk age is about 5–7 Myr (Simon et al. 2000), so we adopted 5 Myr as the limiting time in our chemical simulations. According to the Spitzer Infrared Spectrograph (IRS) observations (Calvet et al. 2005), the inner DM Tau disk is cleared of small dust (\( \lesssim 3 \) AU) and is already in a pre-transitional phase. Therefore, in the chemical simulations only a disk region beyond 10 AU is considered, where dust grain evolution seems to be slow and grain growth is moderate (Birnstiel et al. 2010). In chemical modeling, dust grains are assumed to be uniform 0.1 \( \mu \)m amorphous olivine particles (with density of \( \rho_d = 3 \) g cm\(^{-3}\)). Equal gas and dust temperatures are assumed. Gas becomes hotter than dust only in an upper, tenuous, and heavily irradiated disk layer, which often has negligible contribution to molecular column densities.

The turbulence in disks is likely driven by the magnetorotational instability (MRI), which is operative even in a weakly ionized medium, and is essentially a 3D phenomenon (e.g., Balbus & Hawley 1991). With modern computational facilities coupled chemo-MHD 3D models are manageable only for extremely limited chemical networks and a restricted disk domain (see, for example, Turner et al. 2007). We have followed the parameterization of Shakura & Sunyaev (1973), where turbulent viscosity \( v \) is related to local disk properties such as the characteristic (vertical) spatial scale \( H(r) \), the sound speed \( c_s(r, z) \), and the dimensionless parameter \( \alpha \):

\[
v(r, z) = \alpha c_s(r, z) H(r).
\]

From observational constraints \( \alpha \approx 0.001–0.1 \) (Andrews & Williams 2007; Guilloteau et al. 2011), similar to values obtained from MHD modeling of the MRI (e.g., Dzyurkevich et al. 2010). However, the magnitude of MHD viscous stresses changes throughout the disk, and thus in this simplistic parameterization, the \( \alpha \)-parameter should also be variable. Unfortunately, without detailed MHD studies it is hard to characterize \( \alpha \), so we adopt a constant value of 0.01. Since only a disk region beyond 10 AU is studied, a “dead zone” where effective \( \alpha \) can be very low, \( \lesssim 10^{-4}, \) is avoided.

Consequently, the diffusion coefficient is calculated as

\[
D_{\text{turb}}(r, z) = v(r, z)/\text{Sc},
\]

where \( \text{Sc} \) is the Schmidt number that describes the efficiency of turbulent diffusivity (see, e.g., Shakura & Sunyaev 1973; Schr"apler & Henning 2004). In our simulations, we assume that gas-phase species and dust grains are well mixed, and transported with the same diffusion coefficient. We treat diffusion of mantles materials similar to gas-phase molecules, without relating it to individual grain dynamics. Hence, two chemodynamical models are considered: (1) the high-efficiency mixing model with \( \text{Sc} = 1 \), and (2) the low-efficiency mixing model with \( \text{Sc} = 100 \). In the \( \text{Sc} = 1 \) model, the diffusion coefficient in outer disk regions is \( \sim 10^{18} \text{ cm}^2 \text{s}^{-1} \), similar to Willacy et al. (2006). The second model represents a hypothetical case where mixing of molecules occurs much slower than turbulent eddy turnover speeds, yet faster than in the pure laminar gas. The temperature and density structure, diffusion coefficient \( D_{\text{turb}} \), and vertical pressure scale height \( H(r) \) of the DM Tau-like disk model are shown in Figure 1.

2.2. Chemical Network

The adopted gas–grain chemical model is described in our recent papers on benchmarking of disk chemical models (Semenov et al. 2010b) and observations of CCH in DM Tau, LkCa 15, and MWC 480 (Henning et al. 2010). A brief summary is provided below. The chemical network is based on the osu.2007 ratefile, with recent updates to reaction rates.\(^4\) (Note that in Paper I, we used the UMIST 95 ratefile.) A new class of X-ray-driven reactions leading to the production of O\(^{++}\), C\(^{++}\), N\(^{++}\), S\(^{++}\), Fe\(^{++}\), and Si\(^{++}\) is added. Their neutralization reactions by electrons and charge transfer reactions with molecules are adopted from Stäuber et al. (2005). The photoionization cross sections are taken from Verner et al. (1993), as described in Maloney et al. (1996). Secondary electron impact ionization cross sections are taken from Meijerink & Spaans (2005).

To calculate UV ionization and dissociation rates, the mean FUV intensity at a given disk location is obtained by adding the stellar \( \chi_\text{FUV}(r) = 410 (r, \text{AU})/(100 \text{AU})^2 \) and interstellar \( \chi_0 \) components that are scaled down by the visual extinction in the vertical direction and in the direction to the central star (1D plane–parallel approximation). Several tens of photoreaction rates are updated using the new calculations of van Dishoeck et al. (2006), which are publicly available.\(^5\) The self-shielding of H\(_2\) from photodissociation is calculated by Equation (37) from

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\(^4\) See http://www.physics.osu.edu/~eric/research.html.

\(^5\) http://www.strw.leidenuniv.nl/ewine/photo/.
Table 1  

| Species | Desorption Energies (K) |
|---------|------------------------|
| C       | 800                    |
| C2      | 1600                   |
| C2H     | 2140                   |
| C2H2    | 2590                   |
| C2S     | 2700                   |
| C3      | 2400                   |
| C3H2    | 3390                   |
| C4H6    | 7590                   |
| C4H2    | 7390                   |
| CH2OH   | 5080                   |
| CH2CO   | 2200                   |
| CH3CHO  | 2870                   |
| CH4OH   | 5530                   |
| CH3     | 1300                   |
| CN      | 1600                   |
| CO      | 1150                   |
| CO2     | 2580                   |
| CS      | 1900                   |
| H        | 624                    |
| H2      | 552                    |
| H2S     | 2740                   |
| H2CO    | 2050                   |
| H2CS    | 2700                   |
| H2O     | 5700                   |
| HCN     | 2050                   |
| HOCO    | 5570                   |
| HNC     | 2050                   |
| HNCO    | 2850                   |
| HNO     | 2050                   |
| N       | 800                    |
| N2      | 1000                   |
| NH      | 2380                   |
| NH2     | 3960                   |
| NH3     | 5530                   |
| NO      | 1600                   |
| O       | 800                    |
| O2      | 1000                   |
| OCN     | 2400                   |
| OH      | 2850                   |
| S       | 1100                   |
| SO      | 2600                   |
| SO2     | 3400                   |

Draine & Bertoldi (1996). The shielding of CO by dust grains, H2, and its self-shielding are calculated using the precomputed table of Lee et al. (1996, Table 11).

We model the attenuation of cosmic rays (CRP) by Equation (3) of Semenov et al. (2004), using the standard CRP ionization rate $\dot{\zeta}_{\text{CRP}} = 1.3 \times 10^{-17}$ s$^{-1}$. Ionization due to the decay of short-living radionuclides is taken into account, $\dot{\zeta}_{\text{RN}} = 6.5 \times 10^{-19}$ s$^{-1}$ (Finocchi et al. 1997). The stellar X-ray radiation is modeled using observational results of Glassgold et al. (2005) and the approximate expressions (Equations (7)–(9)) from the 2D Monte Carlo simulations of Glassgold et al. (1997a, 1997b). The typical X-ray photon energy is 3 keV, and the X-ray-emitting source is located at 12 stellar radii above the midplane. The X-ray ionization rates exceed those of the CRPs in the disk regions above the midplane.

The gas–grain interactions include sticking of neutral species and electrons to uniformly sized dust grains with a 100% probability, release of frozen molecules by thermal, CRP-, and UV-induced desorption, dissociative recombination and radiative neutralization of ions on charged grains, and grain recharging. We do not allow H2 to stick to grains because the binding energy of H2 to pure H2 mantle is low, $\sim$100 K (Lee 1972), and it freezes out in substantial quantities only at temperatures below $\approx$4 K. Chemisorption of surface molecules is not considered. We considered various UV photodesorption yields between $10^{-5}$ and $10^{-3}$ (e.g., Greenberg 1973; Öberg et al. 2009b, 2009a) and found that in this range the exact yield value has negligible impact on the modeling results. To allow synthesis of complex (organic) molecules, an extended list of surface reactions, together with desorption energies and a list of photodissociation reactions of surface species, is adopted from Garrod & Herbst (2006). Desorption energies for assorted molecules are listed in Table 1. We assume that each 0.1 µm spherical olivine grain provides $\approx 2 \times 10^9$ surface sites, and that surface recombination proceeds solely through the Langmuir-Hinshelwood formation mechanism. Upon surface recombination, there is a 5% chance for the products to leave the grain. Following the interpretations of experimental results on the formation of molecular hydrogen on dust grains (Katz et al. 1999), we employ the standard rate equation approach to the surface chemistry without H and H2 tunneling either through the potential walls of the surface sites or through reaction barriers. As shown by Vasyunin et al. (2009), when surface recombination rates are slow, the stochastic effects are of no importance for the surface chemistry.

Overall, the disk’s chemical network consists of 657 species made of 13 elements and 7306 reactions. The “low metals” initial abundances of Lee et al. (1998a) are utilized (Table 2). The choice of initial abundances does not affect the resulting molecular abundances and column densities due to relatively high densities in long evolutionary timescales of protoplanetary disks, which essentially reset a chemical “clock” (e.g., Willacy et al. 2006).

2.3. Modeling Chemistry with Transport

The disk’s physical structure and the chemical model described above are used to solve chemical kinetics equations together with turbulent transport terms. We utilize the mixing approach of Xie et al. (1995), which is based on the Fickian diffusion laws:

$$\frac{dn_i}{dt}(r, z) = F_i(r, z) - L_i(r, z) - \nabla \cdot \left(D_{\text{mix}}(r, z) n_i(r, z) \nabla n_i(r, z)\right),$$

where $F_i(r, z)$ and $L_i(r, z)$ are the formation and destruction rates of the species $i$, and $D_{\text{mix}}(r, z)$ is the mixing coefficient.
Here, $n_i$ is concentrations of the $i$th species ($\text{cm}^{-3}$), $F_i$ and $L_i$ are formation and destruction (loss) terms. In the following, we will use relative abundances for the considered species $X_i = n_i/n_{\text{H}}$, where $n_{\text{H}}$ is the total hydrogen nucleus number density. In this formalism, the turbulence mixing rate for a certain species depends on its chemical gradient.

The stiff equations of chemical kinetics are integrated simultaneously with the diffusion terms in the Eulerian description, using a fully implicit 2D integration scheme. As boundary conditions for mixing, we assume that there is no inflow and outward diffusion across the boundaries of the disk domain, and that there is no flux through the midplane. We do not employ approximate, operator-splitting integration schemes, in which transport and chemical processes are treated separately, and instead integrate the partial differential equation (PDE) system directly. All the equations are solved on a nonuniform staggered grid consisting of 41 radial points (from 10 to 800 AU) and 91 vertical points. This resolution is found to be optimal for mixing problems in a protoplanetary accretion disk, keeping the computation tractable and still providing enough accuracy for the analysis.

Our main set of chemical simulations consists of three runs: (1) the laminar disk chemical model (no transport processes are taken into account), (2) the fast 2D mixing model ($Sc = 1$), and (3) the slow 2D mixing transport model ($Sc = 100$). The chemical evolutionary time span is 5 Myr.

### 3. WHEN TURBULENCE AFFECTS DISK CHEMISTRY?

Before drilling into complex numerics, it is reasonable to analyze the general conditions at which turbulent diffusion may affect the chemical evolution in a protoplanetary disk.

#### 3.1. Chemical and Dynamical Timescales

In computational fluid dynamics with reacting flows the Damköhler number $Da$ is often used as a measure of the influence of dynamical processes on chemical evolution. This number is simply the ratio of a physical timescale to a chemical timescale:

$$Da = \frac{\tau_{\text{phys}}}{\tau_{\text{chem}}}.$$  (4)

When $Da \lesssim 1$, chemical evolution of a molecule is slow and therefore may be sensitive to changes in physical conditions due to the flow. In contrast, when $Da \gg 1$, chemical evolution is fast and is not affected by transport processes.

The physical (or dynamical) timescale is often written as $\tau_{\text{phys}} = L/V$, where $V$ is a characteristic value of velocity fluctuations set by turbulence and $L$ is their correlation length.

### (e.g., Cant & Mastorakis 2008). For our $\alpha$-disk model, the characteristic physical timescale is a turbulent mixing timescale:

$$\tau_{\text{phys}}(r, z) = H(r)^2/D_{\text{turb}}(r, z).$$  (5)

The distribution of $\tau_{\text{phys}}(r, z)$ in the adopted disk model is shown in Figure 2 (first panel). In the outer disk region, $r \sim 100–800$ AU $\tau_{\text{phys}}$ exceeds $10^5$ yr, while in the Jovian planet-forming zone the mixing timescale is faster, $\lesssim 10^4$ yr. Due to the vertical temperature gradient this timescale is slightly shorter in the superheated disk upper region (see Figure 1, first panel). Further, we compare the mixing timescale with timescales of key chemical processes.

The typical timescale of a first-order kinetics reaction (e.g., photodissociation) with rate $k$ is $\tau_{\text{chem}} \sim k^{-1}$. For a second-order reaction involving species $A$ and $B$ with rate $k_{AB}$, the reaction timescale for the species $A$ is $\tau_{\text{chem}} \sim 1/k_{AB}n_B$. We assess the characteristic timescale of ion–molecule (IM) chemistry in disks, using HCO$^+$ as an example. The IM reactions are rapid even at very cold temperatures and usually have no barriers (e.g., Smith et al. 2004; Woodall et al. 2007; Wakelam 2009). We assume that the HCO$^+$ evolution is governed by the following formation and destruction reactions, CO $+ \text{H} \rightarrow \text{HCO}^+$ $+ \text{H}_2$ ($k_1 = 1.61 \times 10^{-9}$ cm$^3$ s$^{-1}$) and dissociative recombination $\text{HCO}^+ + e^- \rightarrow \text{CO} + \text{H}$ ($k_2 = 2.4 \times 10^{-7}$ (T/300) $^{-0.09}$ cm$^3$ s$^{-1}$). Then, the corresponding HCO$^+$ IM chemistry timescale can be estimated as

$$\tau_{\text{IM}} \sim (k_1 n_{\text{CO}} n_{\text{H}}/n_{\text{HCO}} - k_2 n_{\text{HCO}})^{-1}.$$  (6)

The IM timescale distribution in the disk is shown in Figure 2 (second panel), where we take $n_{\text{CO}} = 6 \times 10^{-5}n_{\text{H}}$, $n_{\text{H}} = 10^{-10}n_{\text{H}}$, and $n_{\text{HCO}} = 10^{-9}n_{\text{H}}$. As can clearly be seen, IM chemistry is very rapid, with a typical timescale of $\lesssim 10^3$ yr even in low-density disk regions. This is also true for neutral–neutral reactions without barriers or with small barriers, involving radicals and open-shell species. They have comparable timescales even in the outer cold disk region (Smith et al. 2004). In the warm ($T > 50–100$ K) inner disk region, other neutral–neutral reactions with considerable barriers of $\gtrsim 1000$ become competitive. Overall, IM and neutral–neutral reactions without large barriers proceed faster than turbulent transport.

Chemical evolution in upper disk layers is determined by photochemistry, which is driven by intense high-energy stellar (UV, X-rays) and interstellar (UV, CRP) radiation. The corresponding timescale is primarily set by rates of the UV dissociation and X-ray ionization processes,

$$\tau_{\text{UV}} \sim 1/(k_{\text{rad}}^{\text{UV}} + k_{\text{ion}}^{\text{X}}).$$  (7)
For a CO-like molecule and without shielding, the UV and X-ray photorates are $k_{\text{ph}} = 2 \times 10^{-10} (\exp^{-1.7T/H_{\text{vis}}} \chi_s + \exp^{-1.7T/H_{\text{vis}}})^{-1}$ and $k_{\text{ph}}^X = 3(\chi_s + \chi_{\text{CRP}})$, respectively. The calculated photochemistry timescale is presented in Figure 2 (third panel). Photochemistry is fast ($\lesssim 1$ yr) in the disk atmosphere (faster than turbulent transport) and becomes slow ($\gtrsim 10^6$ yr) in dense dark disk regions close to the midplane.

The next important process in disk chemistry is the freeze-out of neutral species onto dust grain surfaces in cold and dense regions ($T \lesssim 20-120$ K). The inferred substantial depletions of observed gas-phase molecules in disks compared to the ISM are generally interpreted as a combined action of photodissociation and freeze-out processes (e.g., Bergin et al. 2007; Dutrey et al. 2007a; Semenov et al. 2010a). The adsorption (AD) timescale is

$$\tau_{\text{AD}} \sim k^{-1}_{\text{AD}} = 1/(\pi a_{\text{gr}}^2 V_{\text{th}} n_d),$$

where $a_{\text{gr}}$ is the grain radius (cm), $V_{\text{th}}$ is the kinetic velocity of molecules (cm s$^{-1}$), and $n_d$ is the grain concentration (cm$^{-3}$). The freeze-out timescale for CO in our disk model is depicted in Figure 2 (fourth panel). This value is mostly determined by density (assuming homogeneous dust and gas mixture) and only slightly by the temperature and mass of a molecule. It varies between $\lesssim 1$ and $10^3$ yr around the midplane. At higher, less dense disk regions, $\tau_{\text{AD}}$ is longer, up to $\sim 10^5-10^6$ yr, though at such conditions the evaporation rate will be much shorter. The adsorption timescale is in general shorter than the mixing timescale in the disk regions favorable for freeze-out.

A process, competitive to adsorption, is the evaporation of icy mantles in warm and/or irradiated disk regions. The evaporation timescale in disks is a combination of thermal desorption, CRP-induced desorption, photodesorption, and possibly other non-thermal desorption mechanisms (e.g., explosive desorption; Shalabiea & Greenberg 1994). Thermal desorption will prevail in warm viscously heated midplane regions ($r \sim 1-5$ AU) and across intermediate molecular layers, whereas CRP desorption operates in the coldest, dark outer disk midplanes, and photodesorption becomes competitive in the upper disk layers. Thus, evaporation timescale can be written as

$$\tau_{\text{des}} \sim 1/(k_{\text{UV}} + k_{\text{CRP}} + k_{\text{th}}),$$

where

$$k_{\text{UV}} = 10^{-3} \pi a_{\text{gr}}^2 (\exp^{-2.3T/H_{\text{vis}}} \chi_s + \exp^{-2.3T/H_{\text{vis}}}),$$

$$k_{\text{CRP}} = 2.4 \times 10^{-2} \chi_{\text{CRP}} \nu_0 \exp^{-\gamma/T_{\text{CRP}}},$$

and

$$k_{\text{th}} = \nu_0 \exp^{-\gamma/T}.$$
\[ \tau_{\text{chem}} \sim 10^5 - 10^6 \text{ yr}, \] determining the chemical timescales in the midplane, \( z/H_t \lesssim 0.8 \) (here \( H_t \) is the pressure scale height). In the warm inner midplane, \( r \lesssim 20 \text{ AU} \), the characteristic chemical timescales are large because not only H and H\(_2\) but also heavy radicals become mobile at abundances below \( 10^{-25} \) this timescale is assumed to be 1 yr. Within the plotted timescale greater than 5 Myr do not reach an equilibrium in a considered time interval.

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

\[ \tau_{\text{chem}} \sim 10^4 - 10^5 \text{ yr}, \] in this region, and are governed by gas–grain interaction rates. Above the cold and dark midplane, at \( \approx 1 \) pressure scale height, where a warm molecular layer is located, the characteristic chemical timescales are shorter, \( \lesssim 10^5 \) yr, since thermal desorption and photodesorption begin to prevail there over surface chemistry and accretion. Within the inner \( \approx 200 \) AU of the molecular layer, lukewarm temperatures and elevated X-ray ionization enable slow photodestruction of well-bound ices. In the upper disk region, \( \gtrsim 1.5 \) pressure scale height, where molecules are effectively destroyed by high-energy UV and X-ray photons, photochemistry coupled to slow neutral–neutral reactions set chemical timescales that increase outward from \( \sim 10^3 \) yr until \( \gtrsim 1 \) Myr. The outward decrease of the gas density in this region makes recombination rates slower (as these scale down as density squared), whereas the stellar UV and X-ray fluxes also decrease with the radial distance from the star. Note that chemical timescales are shorter in the CO molecular layer and, in particular, for C\(^+\), which is abundant in the disk atmosphere at \( z/H_t \lesssim 1.8 - 2 \), while \( \tau_{\text{chem}} \) is long and comparable to the dynamical timescales in regions where CO\(_2\), CH\(_3\)OH ice, and SO\(_2\) are produced (see Figure 3). As we shall see later, indeed chemical evolution of these (and many others) species is affected by the turbulent diffusion.

3.2. Mixing Importance Measure

Considerations presented in the previous subsection provide some clues on the mixing sensitivity for various species. However, it would be instructive to find some general quantitative measure of this sensitivity. We suggest a new mixing importance measure (MIM) to find necessary conditions for sensitivity of column densities of a given molecule to the turbulent mixing, based on results of the laminar model. This quantity comes in three varieties, namely, a local value

\[ \text{MIM}_{r,z} = \frac{1}{\text{Da}(r, z)} \frac{n(r, z)}{\mathcal{N}(r)}, \] (13)

a vertically integrated value

\[ \text{MIM}_r = \int_{z}^{z_{\text{out}}(r)} \text{MIM}_{r,z}dz, \] (14)

and a global value

\[ \text{MIM} = \frac{1}{(r_1 - r_0)} \int_{r_0}^{r_1} \text{MIM}_r dr, \] (15)
where \( Da(r, z) \) is the Damköhler number (Equation (4)), \( N(r) \) is the total vertical column density (cm\(^{-2}\)) of a given species at radius \( r \), \( n(r, z) \) (cm\(^{-3}\)) is its number density at disk location \((r, z)\), \( z_{\text{max}}(r) \) is the disk height at radius \( r \), and \( r_0 \) and \( r_1 \) are the disk inner and outer radii, respectively. The characteristic physical timescale is the diffusion timescale given by Equation (5), and the characteristic chemical timescale of a molecule is its quasi-steady-state timescale defined above (see Figure 3). By definition, the MIM for a molecule allows localizing those disk regions where the chemical evolution is slow and which contribute most to the vertical column density (a typical observationally inferred quantity). Thus, the larger the MIM, the stronger the possible changes in vertical column densities of a considered species due to turbulent transport. However, the straightforward expression (13) is not a sufficient criterion for making reliable estimates on the magnitude of such changes. For example, in the absence of relative abundance gradients even very slow chemistry (resulting in large MIM) leads to the same column densities as the non-mixing (laminar) disk model. On the other hand, if MIM is small everywhere in the disk, mixing will not alter resulting column densities. The local (Equation (13)), vertically integrated (Equation (14)), and disk-averaged (Equation (15)) MIMs for several species are shown in Figure 4 (log\(_g\)) scale.

The MIM values for \( \text{C}^+ \) become relatively large at elevated disk heights, \( \sim 1-2 H_z \), where the \( \text{C}^+ \) concentration is high, and photochemistry is relatively slow yet efficient, especially on ices (see Figure 2). The importance of turbulent mixing to its chemical evolution is low (\( \log(\text{MIM}) = 0.23 \)) compared to the other species, particularly, in the outer disk region at \( r \gtrsim 300 \) AU. Two other species with similarly low global MIM values of \( \log(\text{MIM}) = 0.22 \) and \( \log(\text{MIM}) = -0.28 \) are CO and \( \text{NH}_3 \), respectively. The MIM distribution for CO has a distinct peak around the inner disk midplane at \( r \lesssim 30 \) AU, where temperatures are appropriate for its surface conversion to \( \text{CO}_2 \), and where the gas-phase CO concentration is high. Another region where the CO chemistry may be affected by the turbulent processes is located at the upper CO molecular layer, at \( \sim 2 H_z \), in the inner disk zone. There, the UV photodissociation of CO is slow due to self-shielding and mutual-shielding by \( \text{H}_2 \) and dust, and X-ray ionization of He leads to slow destruction of CO by \( \text{He}^+ \) at late times, \( t \sim 10^5-10^6 \) yr.

In contrast to CO and \( \text{C}^+ \), the MIM for \( \text{CO}_2 \), \( \text{NH}_3 \), and \( \text{SO}_2 \) chemistry exhibits a somewhat similar pattern (Figure 4). The most likely dynamically sensitive regions are the warm molecular layers, where photoprocessing is activated, and the inner part of the disk midplane, where surface heavy C-, O-, and N-bearing radicals become mobile. This is also probably true for S-bearing radicals, but our surface network includes only a very limited sulfur chemistry; therefore, the MIM for \( \text{SO}_2 \) does not reach its maximum in the inner midplane, and peaks within the \( \text{SO}_2 \) molecular layer. The MIM for \( \text{CH}_3\text{OH} \) ice is the largest in the disk midplane, where solid methanol is produced by surface hydrogenation of CO and by \( \text{CH}_3 \) reacting with OH. The disk-averaged MIM values are relatively high for \( \text{CO}_2 \) (\( \log(\text{MIM}) = 0.56 \)) and especially for \( \text{SO}_2 \) (\( \log(\text{MIM}) = 0.74 \)) and solid \( \text{CH}_3\text{OH} \) (\( \log(\text{MIM}) = 0.87 \)). Below we will reveal that their column densities are enhanced by the turbulent diffusion by more than an order of magnitude, unlike those of \( \text{C}^+ \), CO, and \( \text{NH}_3 \).
4. RESULTS OF NUMERICAL MODELING

As already mentioned, we present results for three models. In the laminar model no diffusion is taken into account. In the fast diffusion model $Sc = 1$ is assumed, while in the slow diffusion model we use $Sc = 100$. In Figure 5, the disk-averaged MIMs (Equations (13)–(15)) are plotted versus the column density ratios (CDRs) for fast mixing and laminar cases and for all species potentially observable with ALMA (with maximum column densities above $10^{11}$ cm$^{-2}$) in the laminar case. The corresponding linear correlation coefficient is also shown. The red line shows the corresponding mean and its 1σ error bars.

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

Figure 5. Dependence of the ratio of the molecular column densities integrated over the disk radius and computed with the 2D mixing and laminar models ($t = 5$ Myr) vs. MIM. Shown are the molecules whose peak column densities exceed $10^{11}$ cm$^{-2}$ in the laminar case. The corresponding linear correlation coefficient is also shown. The red line shows the corresponding mean and its 1σ error bars.

The individual families of primal ions, C-, O-, N-, S-bearing and complex (organic) species, are depicted in Figures 7–12 and discussed in detail below. The major influence of turbulent transport on the disk chemical evolution can be summarized as follows. First, 2D mixing behaves as a combination of vertical and radial mixing processes, that have to be considered simultaneously. Vertical mixing is more important as it affects the evolution of gas-phase and surface species of any kind, whereas the effect of radial mixing is pronounced mostly for the evolution of ices (e.g., CO$_2$ ice produced from OH and CO ices). The reason is that the radial temperature gradient is weaker, and thus is only relevant for the evolution of polyatomic ices formed via surface reactions. On the other hand, steep vertical gradients of temperature and high-energy radiation intensity cause much sharper transitions from the ice-dominated chemistry in the disk midplane to the oasis of the gas-phase chemistry in the warm molecular layer.

Second, the inefficient diffusion in the slow mixing model leads to molecular abundances and column densities that are close to those calculated with the laminar (non-mixing) model for most molecules.

We divide all the considered species into three groups. Species with fast chemistry (faster than the diffusion timescale) are rather insensitive to turbulent transport. Further, we call them *steadfast* species (Table 5). These include simple radicals and ions (e.g., C$^+$, Mg$^+$, CO, OH, C$_2$H, H$_3$O$^+$, HCN, N$_2$), and few abundant ices (e.g., water and ammonia ices). Their column densities calculated with the laminar model and the fast mixing model differ by no more than a factor of 3–5, which is comparable to intrinsic uncertainties in molecular concentrations caused by uncertainties in the reaction rates (e.g., Vasyunin et al. 2008).

Abundances of many polyatomic species, in particular complex (organic) molecules and their ices produced (at least partially) on dust grain surfaces (e.g., CO$_2$, HCOOH, CH$_3$CHO ice, carbon chain and cyanopolyiyne ices, O$_2$ ice, SO, SO$_2$), are significantly altered by diffusion. These species are included in “sensitive” and “hypersensitive” groups. Column densities of *sensitive* species (Tables 6) are altered by diffusion by up to two orders of magnitude, and are even stronger for a *hypersensitive* group (Table 7). Mixing steadily transports ice-coated grains in warmer regions, allowing more efficient surface processing due to enhanced hopping rates of heavy radicals. In the warm intermediate layer, these “rich” ices eventually evaporate, and in the inner disk they can also be photodissociated by CRP/ X-ray-induced UV photons. The importance of mixing is higher
in an inner, planet-forming disk zone, where thermal, density, and high-energy radiation gradients are stronger than those in the outer region. We note that even efficient 2D transport in the fast mixing model cannot completely erase the layered chemical structure in the disk, leaving the midplane a gas-phase molecular “desert.”
The charged species sensitive to mixing include, e.g., atomic ions and a few simple molecular ions, e.g., C+, Mg+, Fe+, He+, H+ (e.g., C+, Mg+, Fe+, He+, H+ (by less than a factor of three; see Table 5). The charged species sensitive to mixing include, e.g., hydrocarbons, electrons, H+, O+, S+, N2H+, and HCO+ (their column densities are altered by factors of ~3–50; Table 6). Only a few ions are hypersensitive to mixing, e.g., N+, OH+, H2O+ (CDRs are ~100; Table 7).

In Figure 7, we show distributions of molecular abundances and column densities at 5 Myr of several major ions and the disk

**Figure 9.** Same as in Figure 7 but for the O-containing species. Results are shown for CO, CO ice, CO2, CO2 ice, H2O, O, O2, and H2CO.

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

**Figure 10.** Same as in Figure 7 but for the N-containing species. Results are shown for CN, HCN, HNC, NO, HNO, OCN, HC5N, and HC5N ice.

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

4.1. Major Atomic and Molecular Ions

Turbulent diffusion does not affect column densities of most atomic ions and a few simple molecular ions, e.g., C+, Mg+, Fe+, He+, H+, CH3+, NH2+ (by less than a factor of three; see Table 5). The charged species sensitive to mixing include, e.g.,
ionization degree calculated with the laminar and the mixing models. The global ionization structure has a layered pattern similar to that of photon-dominated regions (PDRs; see also, e.g., Semenov et al. 2004; Bergin et al. 2007; Röllig et al. 2007): (1) heavily irradiated and ionized, hot atmosphere where the dominant ions are C\(^+\) and H\(^+\), (2) partly UV-shielded, warm molecular layer where carbon is locked in CO and major charged species are X-ray-produced H\(^+\) and polyatomic ions like HCO\(^+\).
Table 5
Species Steadfast to Turbulent Mixing

| Molecule | log (MIM) | log (CDR) | log (N_{\text{max}}^{\text{disk}}) |
|----------|-----------|-----------|----------------------------------|
| C        | 0.23      | 0.48      | 16.79                            |
| C₂       | 0.25      | 0.68      | 14.41                            |
| C₃H      | 0.40      | 0.64      | 14.29                            |
| C₂H₂     | 0.67      | 0.68      | 12.36                            |
| CH       | 0.30      | 0.37      | 12.91                            |
| CH₂      | 0.33      | 0.45      | 12.73                            |
| CH₃⁺     | 0.69      | 0.57      | 12.22                            |
| CH₅⁺     | 0.34      | 0.66      | 13.48                            |
| Fe⁺      | -0.17     | 0.21      | 13.95                            |
| CN       | 0.12      | 0.56      | 14.41                            |
| CO       | 0.22      | 0.43      | 18.67                            |
| FeH      | 0.31      | 0.45      | 11.31                            |
| FeH⁺     | -0.62     | 0.19      | 13.69                            |
| H₂O      | 0.22      | 0.68      | 12.16                            |
| grain(0) | -0.21     | 0.35      | 12.29                            |
| H₂       | -1.08     | 0.02      | 24.30                            |
| H₂CN⁺    | 0.13      | 0.49      | 13.06                            |
| H₂CO     | 0.32      | 0.44      | 13.91                            |
| H₂CO⁺    | 0.78      | 0.44      | 11.23                            |
| H₂S      | 0.11      | 0.44      | 13.23                            |
| H₂⁺      | -0.68     | 0.52      | 14.81                            |
| H₂CO⁺    | 0.58      | 0.37      | 11.62                            |
| H₂O⁺     | 0.12      | 0.64      | 13.43                            |
| HCN      | -0.00     | 0.65      | 14.50                            |
| HCS      | 0.27      | 0.61      | 11.28                            |
| He⁺      | 0.07      | 0.51      | 15.07                            |
| HNC      | -0.04     | 0.66      | 14.24                            |
| Mg       | -1.67     | 0.12      | 12.06                            |
| Mg⁺      | -1.38     | 0.10      | 13.91                            |
| MgH₂     | -1.38     | 0.20      | 13.27                            |
| N₂       | 0.19      | 0.43      | 17.61                            |
| Na       | -1.62     | 0.10      | 11.84                            |
| NH₂      | -0.59     | 0.35      | 14.18                            |
| NH₂⁺     | -0.00     | 0.53      | 12.17                            |
| OH       | 0.09      | 0.32      | 14.92                            |
| Si       | 0.69      | 0.42      | 13.06                            |
| SiH      | 0.49      | 0.35      | 11.21                            |
| SiH₃     | -0.59     | 0.38      | 11.05                            |
| C       | 1.03      | 0.50      | 16.00                            |
| C₂H₆      | 0.18     | 0.62      | 13.91                           |
| CH₃N      | 1.26     | 0.67      | 15.54                           |
| FeH      | -1.47     | 0.02      | 16.04                           |
| H       | -1.00     | 0.37      | 18.55                           |
| H₂       | 1.15      | 0.43      | 17.08                           |
| H₂CS     | 0.34      | 0.52      | 16.29                           |
| H₂O      | 0.06     | 0.09      | 20.84                           |
| H₂S      | -0.98     | 0.05      | 17.54                           |
| HCN      | 0.27     | 0.65      | 19.43                           |
| HCSi     | -0.00     | 0.54      | 12.50                           |
| HS       | 1.01     | 0.38      | 15.54                           |
| MgH₂     | -1.29     | 0.01      | 16.64                           |
| NaH      | -1.78     | 0.01      | 15.96                           |
| NH₂      | -0.08     | 0.11      | 19.84                           |
| Si       | 0.96     | 0.57      | 15.50                           |
| S₂       | 0.74     | 0.42      | 11.45                           |
| SiC      | 0.88     | 0.39      | 13.85                           |
| SiCH₂     | 0.94    | 0.23      | 12.95                           |
| SiH₂     | -0.11     | 0.08      | 16.59                           |

Notes. Column 2: the MIM integrated over the disk (in log scale). Column 3: the ratio of the vertical column density at $t = 5$ Myr computed with the 2D mixing and the laminar chemical models, averaged over the radius (in log scale). Column 4: the maximal vertical column density for a given molecule at 5 Myr in the laminar model.

* Listed are the molecules in which vertical column densities in the disk exceed $10^{11}$ cm$^{-2}$.

and H₂⁺, and (3) dark, dense, and cold midplane where most of molecules are frozen out onto dust grains and the most abundant charged species are dust grains and H₅⁺.
| Molecule | log (MIM) | log (CDR) | log ($N_{\text{max}}^{\text{stat}}$) |
|----------|-----------|-----------|-------------------------------|
| HCO$^+$  | 0.48      | 1.35      | 13.98                         |
| HNCO     | 0.95      | 1.96      | 12.14                         |
| HNO      | 0.18      | 1.48      | 13.67                         |
| HNSi     | 0.47      | 1.99      | 11.29                         |
| HS       | 0.79      | 1.37      | 11.60                         |
| HS$_2$   | 0.97      | 1.67      | 11.21                         |
| N        | 0.52      | 0.84      | 17.78                         |
| N$_2$H$^+$| 0.47      | 1.47      | 12.39                         |
| NH       | 0.09      | 1.13      | 13.36                         |
| NH$_2$CN | 0.62      | 1.07      | 12.40                         |
| NH$_3$   | $-0.28$   | 0.75      | 14.74                         |
| NH$_3^+$ | 0.34      | 0.89      | 11.43                         |
| NO       | 0.36      | 1.43      | 14.57                         |
| NO$_2$   | 0.66      | 0.89      | 11.23                         |
| O        | 0.08      | 0.73      | 18.65                         |
| O$_2$    | 0.80      | 1.52      | 12.24                         |
| O$_2^+$  | 0.58      | 1.98      | 16.91                         |
| OCN      | 0.86      | 1.10      | 13.41                         |
| P        | 0.26      | 0.73      | 12.53                         |
| P$_2$    | 0.73      | 1.56      | 12.89                         |
| S        | 0.60      | 1.23      | 14.73                         |
| S$_2$    | 0.68      | 1.13      | 15.52                         |
| Si       | 0.69      | 1.25      | 14.12                         |
| SiH$_4$  | 0.32      | 0.87      | 12.07                         |
| SO       | 0.59      | 1.11      | 12.00                         |
| C$_{10}$ ice | 1.04   | 1.19      | 15.00                         |
| C$_2$ ice | 0.96      | 1.91      | 15.28                         |
| C$_2$H ice | 0.94     | 1.91      | 15.22                         |
| C$_2$H$_5$ ice | 1.34    | 1.89      | 12.79                         |
| C$_3$ ice | 0.96      | 1.80      | 15.81                         |
| C$_3$H$_5$ ice | 0.78    | 1.77      | 16.39                         |
| C$_4$ ice | 0.70      | 1.20      | 19.66                         |
| C$_4$S ice | 0.92      | 1.52      | 12.84                         |
| C$_5$S ice | 1.30      | 1.70      | 12.84                         |
| C$_6$H$_5$ ice | 1.30    | 1.86      | 13.18                         |
| C$_7$H$_5$ ice | 0.84    | 1.74      | 14.43                         |
| C$_8$H$_5$ ice | 1.28    | 1.85      | 12.74                         |
| C$_9$H$_5$ ice | 0.79    | 1.89      | 18.06                         |
| C$_{10}$H$_5$ ice | 0.67   | 1.75      | 14.78                         |
| C$_{11}$H$_5$ ice | 1.16    | 1.10      | 12.84                         |
| C$_{12}$H$_5$ ice | 0.77    | 1.54      | 18.73                         |
| C$_{13}$H$_5$ ice | 0.61    | 1.34      | 18.59                         |
| C$_{14}$H$_5$ ice | 1.06    | 1.99      | 13.81                         |
| C$_{15}$H$_5$ ice | 0.67    | 1.62      | 17.95                         |
| C$_{16}$H$_5$ ice | 0.70    | 1.82      | 18.44                         |
| C$_{17}$H$_5$ ice | 0.58    | 1.04      | 18.06                         |
| CCL$_2$ ice | 1.06    | 0.98      | 11.76                         |
| CH$_2$ ice | 0.93      | 1.20      | 16.16                         |
| CH$_3$ ice | 0.79      | 1.37      | 17.73                         |
| CH$_3$CO ice | 1.36    | 1.37      | 15.26                         |
| CH$_3$NH ice | 1.37    | 1.45      | 13.37                         |
| CH$_3$NH$_2$ ice | 1.37   | 1.76      | 12.95                         |
| CH$_4$ ice | 0.40      | 1.34      | 17.77                         |
| CH$_3$CN ice | 0.71    | 1.78      | 14.65                         |
| CH$_3$OH ice | 1.38    | 1.70      | 12.95                         |
| CH$_3$O$_2$ ice | 0.87    | 1.70      | 16.08                         |
| CH$_3$S$_2$ ice | 0.26    | 1.51      | 19.95                         |
| CL$_2$ ice | 0.63      | 0.88      | 15.20                         |
| CN$_2$ ice | 0.58      | 1.00      | 15.53                         |
| CO$_2$ ice | 0.92      | 0.85      | 19.51                         |
| CS$_2$ ice | 0.66      | 1.87      | 14.93                         |
| H$_2$C$_2$N$_2$ ice | 1.33   | 1.71      | 13.25                         |
| H$_2$CO ice | 1.03      | 0.93      | 16.73                         |

Notes. Column 2: the MIM integrated over the disk (in log scale). Column 3: the ratio of the vertical column density at $t = 5$ Myr computed with the 2D mixing and the laminar chemical models, averaged over the radius (in log scale). Column 4: the maximal vertical column density for a given molecule at 5 Myr in the laminar model.

* Listed are the molecules in which vertical column densities in the disk exceed $10^{11}$ cm$^{-2}$.

Turbulent diffusion lowers abundances of electrons and some atomic ions such as $S^+$ and $H^+$, by up to three orders of magnitude, mainly in the inner molecular layer ($r \lesssim 100$ AU, $\sim 1-2H_2$). Consequently, their column densities within $\sim 100$ AU are decreased by factors $3-\sim 100$. The effect is exactly the opposite for $H_3O^+$, $HCO^+$, and $N_2H^+$. Their column densities and abundances are enhanced by mixing in this region, albeit by only up to an order of magnitude. Mixing remarkably expands their inner molecular layers that are rather confined in the laminar case (particularly, for $N_2H^+$). The abundance distribution of $H_3^+$ shows similar expansion due to mixing as other polyatomic ions, while its column density is slightly decreased at $r \lesssim 30$ AU. Overall, fast turbulent stirring makes chemical gradients of key ionized species stronger compared to the laminar disk model. The slow mixing model does not differ significantly from the laminar model (compare the first and second panels in Figure 7).

The most important reactions responsible for the time-dependent net change of the electron, $H^+$, $C^+$, $HCO^+$, $H_3O^+$,
Table 7
Species Hypersensitive to Turbulent Mixing

| Molecule | log (MIM) | log (CDR) | log (N\(\text{max}_{\text{stat}}\)) |
|----------|-----------|-----------|-------------------------------|
| C\(_1\)O | 1.18      | 2.01      | 12.09                         |
| C\(_2\)S | 0.71      | 2.27      | 11.80                         |
| C\(_2\)H\(_3\) | 1.12 | 2.64      | 11.39                         |
| C\(_2\)H\(_4\) | 1.03 | 3.31      | 11.89                         |
| C\(_2\)S \(_2\) | 1.00 | 2.31      | 11.35                         |
| C\(_2\)N | 1.12      | 2.57      | 11.58                         |
| CH\(_2\)C\(_2\)H | 1.10 | 2.18      | 11.21                         |
| CO\(_2\) | 0.56      | 2.23      | 14.94                         |
| H\(_2\)O\(_2\) | 0.95 | 2.09      | 12.53                         |
| H\(_2\)O\(_2\) | 0.91 | 2.53      | 13.54                         |
| H\(_2\)C\(_4\)N | 1.13 | 2.34      | 11.34                         |
| HCOOH | 0.81      | 2.07      | 12.36                         |
| HSIO\(_4\) | 0.75 | 2.75      | 11.38                         |
| N\(_2\) | 0.67      | 2.00      | 11.51                         |
| N\(_2\)O | 0.44 | 2.92      | 12.30                         |
| NO\(_2\) | 0.85 | 2.26      | 12.06                         |
| O\(_3\) | 0.05      | 2.02      | 15.06                         |
| OH\(_2\) | 1.00 | 2.68      | 12.86                         |
| SiO | 0.76 | 3.33      | 13.17                         |
| SO | 0.74 | 3.23      | 13.33                         |
| SO\(_2\) | 0.81 | 3.83      | 12.45                         |
| C\(_3\)H\(_4\) ice | 0.99 | 2.61 | 16.71 |
| C\(_3\)H\(_6\) ice | 0.86 | 6.37 | 18.21 |
| C\(_3\)S ice | 0.95 | 2.79 | 12.86 |
| C\(_3\)H\(_6\)N ice | 1.14 | 2.04 | 11.92 |
| C\(_3\)H\(_4\) ice | 1.00 | 5.65 | 19.05 |
| C\(_5\)S ice | 1.28 | 5.24 | 12.63 |
| C\(_5\)H\(_6\) ice | 1.00 | 3.67 | 13.38 |
| C\(_5\)H\(_4\) ice | 1.57 | 7.39 | 14.81 |
| C\(_5\)O ice | 1.33 | 4.78 | 12.51 |
| C\(_5\)H\(_4\) ice | 0.91 | 3.77 | 13.08 |
| C\(_7\)H\(_4\) ice | 1.10 | 2.21 | 14.51 |
| C\(_7\) ice | 1.39 | 5.34 | 12.22 |
| C\(_7\)H\(_4\) ice | 1.11 | 3.93 | 12.65 |
| C\(_7\)H\(_6\) ice | 1.53 | 8.73 | 13.81 |
| C\(_8\)H\(_4\) ice | 1.32 | 4.65 | 12.72 |
| C\(_8\)H\(_4\) ice | 1.01 | 2.83 | 13.24 |
| C\(_8\)H\(_4\) ice | 1.53 | 9.24 | 14.19 |
| C\(_9\)H\(_4\) ice | 1.35 | 4.83 | 12.79 |
| C\(_9\)H\(_4\) ice | 1.14 | 3.52 | 13.60 |
| C\(_9\)H\(_6\) ice | 1.54 | 10.09 | 13.83 |
| C\(_9\)H\(_8\) ice | 1.30 | 2.74 | 11.47 |
| C\(_9\)H\(_8\) ice | 1.54 | 6.99 | 12.26 |
| C\(_9\)H\(_8\)N ice | 1.37 | 2.18 | 13.23 |
| C\(_9\)H\(_8\)H ice | 1.04 | 2.01 | 14.79 |
| C\(_9\)H\(_8\) ice | 1.14 | 2.13 | 13.66 |
| C\(_9\)H\(_8\)CHO ice | 1.17 | 3.26 | 13.15 |
| CO\(_2\) ice | 1.03 | 3.60 | 19.62 |
| CP ice | 1.12 | 2.66 | 14.68 |
| Fe ice | 1.27 | 3.14 | 13.35 |
| H\(_2\)CO\(_2\) ice | 1.34 | 2.96 | 15.94 |
| H\(_2\)O\(_2\) ice | 1.40 | 2.20 | 16.97 |
| H\(_2\)C\(_3\)N\(_2\) ice | 1.55 | 7.22 | 13.16 |
| HCCP ice | 1.41 | 2.85 | 11.08 |
| HCL ice | 0.64 | 2.86 | 15.60 |
| HCOOH ice | 1.32 | 3.47 | 16.71 |
| HCP ice | 1.21 | 3.21 | 14.22 |
| HNC\(_3\) ice | 0.91 | 2.76 | 11.09 |
| HNO ice | 0.81 | 2.38 | 17.90 |
| HPO ice | 1.37 | 5.45 | 13.28 |
| Mg ice | 1.66 | 7.32 | 12.74 |
| MgH\(_2\) ice | 1.25 | 4.25 | 14.39 |
| N\(_2\) ice | 0.86 | 4.24 | 18.37 |
| N\(_2\)H\(_2\) ice | 0.76 | 2.62 | 16.65 |
| Na ice | 1.35 | 5.44 | 12.99 |

Table 7 (Continued)

| Molecule | log (MIM) | log (CDR) | log (N\(\text{max}_{\text{stat}}\)) |
|----------|-----------|-----------|-------------------------------|
| NO\(_2\) ice | 1.25 | 2.84 | 13.20 |
| NS ice | 1.19 | 2.37 | 14.27 |
| O\(_2\) ice | 0.99 | 2.25 | 17.31 |
| O\(_2\)H ice | 1.35 | 2.79 | 11.28 |
| O\(_3\) ice | 0.91 | 2.58 | 18.07 |
| PN ice | 1.30 | 2.25 | 13.69 |
| PO ice | 1.09 | 3.05 | 14.17 |
| SiH ice | 1.44 | 2.24 | 12.99 |
| SiS ice | 1.30 | 2.14 | 11.63 |
| C\(_5\)H\(_3\) ice | 1.40 | 6.40 | 11.31 |

Notes. Column 2: the MIM integrated over the disk (in log scale). Column 3: the ratio of the vertical column density at \(t = 5\) Myr computed with the 2D mixing and the laminar chemical models, averaged over the radius (in log scale). Column 4: the maximal vertical column density for a given molecule at 5 Myr in the laminar model.

* Listed are the molecules in which vertical column densities in the disk exceed \(10^{11}\) cm\(^{-2}\).
converged to atomic hydrogen via fast IM reactions involving OH$^+$ and H$_2$O$^+$ (e.g., H$_2$O$^+ + H_2 \rightarrow H_2O^+ + H$; Table 8). In turn, these ions become abundant due to a steady release of elemental oxygen from water, which begins from the photodissociation of water ice. H$_2^+$ is rapidly converted to H$_3^+$ that protonates abundant radicals (e.g., CO, N$_2$), forming various polyatomic ions (e.g., HCO$^+$, N$_2$H$^+$). Thus, abundance distribution of the polyatomic ions are peaked along a narrow stripe, 0.5 $H_\odot$, where both H$_2^+$ and progenitor molecules are abundant. The molecular ion layers are vertically expanded in the outer disk at $r \gtrsim 200$ AU, where the surface density is so low that the disk becomes partly transparent to the interstellar UV radiation. N$_2$H$^+$ is destroyed by reactions with abundant CO and, hence, the N$_2$H$^+$ layer is particularly thin (see Figure 7). N$_2$H$^+$, HCO$^+$, and H$_3$O$^+$ layers are rather sharp-edged from below where their parent molecules are locked in dust icy mantles, whereas the H$_3^+$ layer extends more toward the cold region as H$_3$O$^+$ does not deplete. The formation of polyatomic ions is balanced out by dissociative recombination with $e^-$, and within $\sim 10^4$ yr (inner disk) and $\sim 10^5$ yr (outer disk) a chemical quasi-steady state is reached. This equilibrium timescale is mainly set by the slow X-ray-driven destruction of H$_2$ that is needed to produce H$_3^+$, and is $\sim 2 \times 10^3-10^5$ yr. Thus, the characteristic chemical timescales exceed those due to mixing, making the ionization state of the inner molecular layer vulnerable to turbulent transport. The dominant charged species in the warm molecular layer are H$^+$ as well as HCO$^+$, H$_2$O$^+$, and C$^+$, with abundances of $10^{-10}$–$10^{-5}$. The resulting ionization fraction is $\sim 10^{-8}$–$10^{-5}$, which is sufficient for the MRI to be operational (e.g., Fromang et al. 2002).

In the cold, dark midplane X-ray ionization rates further decrease, and the cosmic-ray ionization becomes important ($\zeta_{CR} = 1.3 \times 10^{-17}$ s$^{-1}$). Except for H$_2$, majority of molecules severely deplete within $\lesssim 10^3$ yr, leaving only a tiny fraction in the gas (see Figure 2, fourth panel, and Figure 8). Electron sticking to grains is efficient, and negatively charged grains play an important role as charge carriers and reactants of dissociative recombination (e.g., HCO$^+$ + grain(–) $\rightarrow CO + H +$ grain(0); see Table 8). The fractional ionization drops as low as $\lesssim 10^{-12}$–$10^{-9}$, and a “dead” zone for the MRI-driven accretion may develop. Characteristic timescales of the evolution of the fractional ionization in the disk midplane are $\sim 5 \times 10^3$–$10^5$ yr, after which a quasi-steady state is reached. These values are smaller than the mixing timescale in the midplane (Figure 2), and the influence of turbulent transport on ionization chemistry should be negligible.

### Table 8

| Reaction | $\alpha$ (cm$^3$ s$^{-1}$) | $\beta$ | $\gamma$ (K) | $t_{\text{min}}$ (yr) | $t_{\text{max}}$ (yr) |
|----------|-----------------|---------|--------------|-------------------|-------------------|
| H$_2$ + X-rays $\rightarrow e^-$ + H$_2^+$ | 0.93$\chi$ | 0 | 0 | 1.00 | 1.20 (4) |
| H$_2$ + C.R.P. $\rightarrow e^-$ + H$_2^+$ | 0.93$\chi$ | 0 | 0 | 1.00 | 5.00 (6) |
| H + X-rays $\rightarrow H^+ + e^-$ | 0.46$\chi$ | 0 | 0 | 1.00 | 5.00 (6) |
| C$^+$ + X-rays $\rightarrow$ C$^{++} + e^-$ | 0.5$\chi$ | 0 | 0 | 1.00 | 5.00 (6) |
| S$^+$ + X-rays $\rightarrow$ S$^{++} + e^-$ | $\chi$ | 0 | 0 | 1.00 | 5.00 (6) |
| H$_2$ + X-rays $\rightarrow e^-$ + H + H$^+$ | 0.02$\chi$ | 0 | 0 | 1.00 | 5.00 (6) |
| C + UV $\rightarrow e^-$ + C$^+$ | 0.31 ($-$9) | 0 | 3.33 | 1.00 | 55.90 |
| H$_2$CO + UV $\rightarrow$ HCO$^+$ + H + e$^-$ | 0.48 ($-$9) | 0 | 3.21 | 4.18 (2) | 1.20 (4) |
| H$_2$ + UV $\rightarrow$ H$^+ + H$ | 0.57 ($-$9) | 0 | 2.37 | 1.00 | 55.90 |
| H$_2$ + UV $\rightarrow$ H$^+ + H_2$ | 0.20 ($-$7) | 0 | 1.80 | 1.00 | 5.00 (6) |
| H$^+$ + O $\rightarrow$ O$^+$ + H | 0.70 ($-$9) | 0 | 2.32 (2) | 1.00 | 5.00 (6) |
| H$^+$ + O$_2$ $\rightarrow$ O$_2^+$ + H | 0.12 ($-$8) | 0 | 0 | 1.00 | 5.00 (6) |
| H$^+$ + S $\rightarrow$ S$^+$ + H | 0.13 ($-$8) | 0 | 0 | 1.00 | 5.00 (6) |
| He$^+$ + CO $\rightarrow$ C$^+$ + O + He | 0.16 ($-$8) | 0 | 0 | 1.00 | 5.00 (6) |
| C$^+$ + H$_2$ $\rightarrow$ CH$_4$ | 0.40 ($-$15) | $-$0.20 | 0 | 1.00 | 5.00 (6) |
| S$^+$ + H$_2$ $\rightarrow$ H$_2$S$^+$ | 1.00 ($-$17) | $-$0.20 | 0 | 1.00 | 5.00 (6) |
| H$_2$O$^+$ + H$_2$ $\rightarrow$ H$_2$O$^+$ + H | 0.61 ($-$9) | 0 | 0 | 1.00 | 5.00 (6) |
| N$_2$$^+$ + H$_2$ $\rightarrow$ N$_2$H$^+$ + H | 0.17 ($-$8) | 0 | 1.00 | 5.00 (6) |
| NH$^+$ + H$_2$ $\rightarrow$ H$_3$N$^+$ + N | 0.23 ($-$9) | 0 | 0 | 1.96 | 5.00 (6) |
| C$^+$ + S $\rightarrow$ S$^+$ + C | 0.15 ($-$8) | 0 | 0 | 1.00 | 5.00 (6) |
| H$_3$ + CO $\rightarrow$ HCO$^+$ + H$_2$ | 0.16 ($-$8) | 0 | 0 | 1.00 | 5.00 (6) |
| H$_3$ + N$_2$ $\rightarrow$ N$_2$H$^+$ + H$_2$ | 0.17 ($-$8) | 0 | 0 | 1.00 | 5.00 (6) |
| HS$^+$ + H $\rightarrow$ S$^+$ + H$_2$ | 0.11 ($-$9) | 0 | 0 | 1.00 | 5.00 (6) |
| N$_2$H$^+$ + CO $\rightarrow$ HCO$^+$ + N$_2$ | 0.88 ($-$9) | 0 | 0 | 1.00 | 5.00 (6) |
| NH$_2$ + N $\rightarrow$ N$_2$H$^+$ + H | 0.91 ($-$10) | 0 | 0 | 1.00 | 5.00 (6) |
| O$^+$ + H $\rightarrow$ H$^+ + O$ | 0.70 ($-$9) | 0 | 0 | 7.48 | 5.00 (6) |
| OH$^+$ + N$_2$ $\rightarrow$ N$_2$H$^+$ + O | 0.36 ($-$9) | 0 | 0 | 2.34 (4) | 5.00 (6) |
| S$^+$ + O$_2$ $\rightarrow$ SO$^+$ + O | 0.20 ($-$10) | 0 | 0 | 1.00 | 5.00 (6) |
| S$^+$ + OH $\rightarrow$ SO$^+$ + H | 0.46 ($-$8) | $-$0.50 | 0 | 1.00 | 5.00 (6) |
| S$^+$ + NH$_3$ $\rightarrow$ NH$_3^+$ + S | 0.16 ($-$8) | $-$0.50 | 0 | 1.00 | 5.00 (6) |
| S$^+$ + e$^-$ $\rightarrow$ S | 0.39 ($-$11) | $-$0.63 | 0 | 4.18 (2) | 5.00 (6) |
| HCO$^+$ + e$^-$ $\rightarrow$ CO + H | 0.24 ($-$6) | $-$0.69 | 0 | 1.00 | 5.00 (6) |
| N$_2$H$^+$ + e$^-$ $\rightarrow$ NH + N | 0.64 ($-$7) | $-$0.51 | 0 | 1.00 | 5.00 (6) |
| H$_2$O$^+$ + e$^-$ $\rightarrow$ OH + H | 0.26 ($-$6) | $-$0.50 | 0 | 1.00 | 5.00 (6) |
| e$^-$ + grain(0) $\rightarrow$ grain(–) | 1.00 | 0 | 0 | 1.00 | 5.00 (6) |
| HCO$^+$ + grain(–) $\rightarrow$ CO + H + grain(0) | 1.00 | 0 | 0 | 1.00 | 5.00 (6) |
Indeed, as can be clearly seen in Figure 7 (compare first and third panels), turbulent diffusion most strongly affects abundances of ions in the inner warm molecular layer, at $r \lesssim 200$ AU, $H\theta \approx 1–2$, where the characteristic diffusive mixing timescale ($\sim 10^3 \text{yr}$) is shorter than the chemical timescale ($\sim 10^4 \text{yr}$) regulated by the slow X-ray-driven destruction of $H_2$ and radiative recombination and association processes involving $C^+$. The diffusion timescale is relatively short in the inner disk because of stronger gradients of density and ionization rates, elevated temperatures, and short distances for transport (see Figures 1 and 2). The vertical uptake of molecular hydrogen from the inner midplane to the inner intermediate layer allows production of more $H^+$, while simultaneously lowering ionization fraction and abundances of $H^+$ and $C^+$ due to their enhanced neutralization via radiative association, charge exchange, and IM reactions (e.g., $C^+ + H_2 \rightarrow CH_2^+$; Table 8). The increased abundances of $H^+$ in the inner molecular layer leads to more efficient production of polyatomic ions through protonation reactions, which lead to remarkable peaks in abundances of HCO$^+$, N$_2$H$^+$, H$_2$O$^+$, and other molecular ions. The chemistry of OH$^+$, H$_2$O$^+$, and N$^+$ ions is most sensitive to the X-ray-driven, partly surface, processes (similar results were obtained by Aresu et al. 2011). Naturally, OH$^+$, H$_2$O$^+$, and N$^+$ are most sensitive to mixing in our model.

### 4.2. Carbon-bearing Molecules

There are only several steadfast light hydrocarbons, including four neutral diatomic and triatomic species (e.g., CH, CH$_2$, and C$_2$H$_4$), four ions (e.g., CH$^+_2$ and CH$^+_3$), and C$_2$H$_2$ ice. Turbulence-sensitive hydrocarbons include 28 neutral molecules (e.g., CH$_3$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_5$,..., C$_9$H$_2$), eight ions (e.g., C$_2$H$_3^+$, C$_3$H$_2^+$, and C$_4$H$_2^+$), and 22 ices (e.g., CH$_4$, C$_2$, C$_2$H, C$_3$H$_2$,..., C$_9$H$_2$). For 25 hypersensitive hydrocarbons the turbulent diffusion changes column densities by up to a factor of $10^{10}$ (for the C$_9$H$_4$ ice). These species include four neutral hydrocarbons (e.g., C$_{10}$, C$_{12}$H, and CH$_2$C$_2$H), and 21 ices (e.g., C$_2$H$_6$, C$_3$H$_4$, C$_5$, C$_7$H$_4$, C$_9$H, C$_9$H$_5$). A rough trend shows that heavier and more saturated hydrocarbons are more strongly affected by turbulent transport than lighter species, and that abundances and column densities of hydrocarbon ices are more strongly altered compared to their gas-phase counterparts. Overall, frozen hydrocarbons are among the species most sensitive to mixing in our chemical model.

In Figure 8, distributions of abundances and column densities of CH$_2^+$, CH$_4$, C$_2$H, C$_2$H$_2$, C$_2$H$_3$, C$_2$H$_4$ ice, C$_6$H$_6$ ice, and C$_8$H$_4$ ice calculated with the laminar and mixing models are presented. Hydrocarbon abundances show a three-layer structure similar to that of the polyatomic ions, with rather narrow molecular layers of 0.2–0.5 $H\theta$ at $z \approx 1$ $H\theta$, and typical values of $\sim 10^{-10}$–$10^{-7}$. Note that abundances of hydrocarbon ices are also high in the warm molecular layer ($X \sim 10^{10}$–$10^{11}$). The hydrocarbons are fragile to the UV and X-ray irradiation and thus are absent in the disk atmosphere, apart from the photostable ethynyl radical (C$_2$H) and CH$^+_2$ ion that are abundant in the lower disk atmosphere, at $z \sim 2$ $H\theta$. In the midplane the gas-phase hydrocarbons are depleted, whereas their ices are moderately abundant. Turbulent mixing expands and enhances molecular layers of gas-phase hydrocarbons at almost all radii. For the ices, there is no such clear trend. As a rule, abundances of carbon chains that serve as intermediate products to surface hydrogenation are lowered by turbulent transport, e.g., C$_6$H$_6$ ice, whereas more saturated hydrocarbons show increased abundances, e.g., C$_6$H$_6$ ice (Figure 8). Note that turbulent transport affects gas-phase and solid abundances of heavy hydrocarbons (like C$_9$H$_2$) in an opposite way, enhancing the concentration of a gas-phase species and reducing its solid-state abundances. We attribute such a behavior to the particularly slow evaporation of frozen heavy carbon chains that is comparable to or longer than the dynamical timescale, $\lesssim 1$ Myr, even in the warm molecular layer.

Most important reactions responsible for the time-dependent evolution of hydrocarbons in the midplane, the molecular layer, and the atmosphere at 10 and 250 AU are presented in Table 9. The list contains the top 25 reactions for CH$_2^+$, CH$_4$, C$_2$H$_2$, C$_2$H$_3$, C$_2$H$_4$ ice, C$_6$H$_6$ ice, and C$_8$H$_2$ ice per region (midplane, molecular layer, atmosphere) for the entire 5 Myr time span, with all repetitions removed.

The chemical evolution starts with the production of light hydrocarbons in the gas phase by the radiative association of C$^+$ with H$_2$, followed by hydrogen addition reactions: C$^+$ → CH$_2^+$ → CH$_3^+$ → CH$_4$. An alternative route is the radiative association reaction between C and H$_2$, leading to CH$_2$, that can be further converted to CH$_3$ by the addition of C. The protonated methane reacts with electrons, O, CO, C, OH, etc., forming CH$_4$. Methane undergoes reactive collisions with C$^+$, producing C$_2$H$_3^+$ and C$_3$H$_4^+$. All these primonial hydrocarbons dissociatively recombine on electrons or negatively charged grains (in the inner dark midplane), which leads to simple neutral species such as CH, C$_2$H, and C$_2$H$_2$. The neutral hydrocarbons readily react with ionized and neutral atomic carbon, forming other, heavier hydrocarbons, e.g., C$_8$H$_2$ + C → C$_9$H$_2$ + H and C$_9$H$_2$ + O → C$_9$H$_3$ + HCO$. The growth rate of chemical complexity of carbon chains is regulated by IM and neutral–neutral exothermic reactions with atomic oxygen that lead to the formation of CO, e.g., O + C$_2$H$_2$ → C$_2$H + CO (see also Figure 7 in Henning et al. 2010 and Figure 4 in Turner et al. 2000). The associated chemical timescales are $\lesssim 10^3–10^4$ yr, see Figure 2 and Tables 3 and 4, except for the disk atmosphere at $z \approx 2$ $H\theta$, where the chemical evolution of CH$_3$ and its daughter species, C$_2$H and CH$_3$, is subject to the evolution of H$_2$ and O. As discussed in the previous subsection, at these high altitudes slow destruction of molecular hydrogen, water, and CO by He$^+$ locally sets long evolutionary timescales ($\lesssim 10^5$ yr) for many species, e.g., ethynyl, CH$_2$, and CH$_3$ radicals.

To enhance the production of hydrocarbons in the gas, particular physical conditions have to be satisfied. The heavy carbon-bearing compounds can be produced at high densities and $T \gtrsim 800$ K by pyrolysis of precursor hydrocarbons (e.g., Morgan et al. 1991) or in a Fischer–Tropsch-like process involving CO, H$_2$, and catalytic surfaces (Tscharnuter & Gail 2007). These conditions are met at sub-AU radii in the very inner disk midplane which is not examined in the present study. Another possibility for the gas-phase production of hydrocarbons is to bring elemental carbon locked in CO back to the gas, while simultaneously maintaining low oxygen abundances. Due to self-shielding and mutual-shielding by H$_2$, the UV photodissociation of CO is only important in dilute disk atmosphere (e.g., van Dishoeck 1988; Visser et al. 2009a). However, in the lower part of the inner warm molecular layer ($r \lesssim 200$ AU, $z \approx 1$ $H\theta$), He$^+$ ions produced by the X-ray ionization slowly destroy CO, restoring gas-phase concentrations of C$^+$ and O on the timescale of $\sim 5 \times 10^3$ yr. Relatively high densities ($\rho_{HI} \sim 10^8–10^9$ cm$^{-3}$) and lukewarm temperatures ($T \sim 30–75$ K) in this region (Figure 1) allow rapid conversion of released oxygen into water. Thus, locally in the inner regions of the X-ray-irradiated disks, the gas-phase
C/O ratio may revert from the Solar value of $\approx 0.43$ to a $\gtrsim 1$ value typical of carbon-rich AGB shells (D. Hollenbach 2009, private communication), which facilitates gas-phase formation of heavy hydrocarbons.

An efficient alternative route to accumulate complex hydrocarbons in disks is surface chemistry coupled to the destruction of hydrocarbon ices and other C-bearing species. In cold disk regions ($T < 20$ K), it is mainly the hydrogenation of species such as $\text{C}_n\text{H}_m$ ($n = 2–9$, $m \leq 2$), as at low dust temperatures mostly hydrogen is mobile to scan the grain surface (e.g., d’Hendecourt et al. 1985; Hasegawa & Herbst 1993; Katz et al. 1999). Ultimately, this process leads to the formation of saturated ices, e.g.,
CH₄ and C₂H₄. In the inner disk midplane (r ≲ 20 AU) warmed up by the accretion to the temperatures of ~40–50 K, the desorption of CH₄ dominates over its sticking to grains, forming an oasis of abundant gas-phase methane. At these elevated temperatures heavier radicals such as C, O, and OH become more mobile (e.g., Garrod & Herbst 2006; Garrod et al. 2008; Herbst & van Dishoeck 2009). However, the surface growth of hydrocarbons by the addition of atomic carbon is still not as efficient as the surface hydrogenation and the gas-phase chemistry, and accounts for only a few percent of their total surface production rate. The most favorable conditions for active surface hydrocarbon chemistry are met in the warm molecular layer, where atomic hydrogen is plentiful in the gas, and its accretion rate is fast even in comparison with rapid desorption. More importantly, complex ices are slowly destroyed by X-ray/CRP-driven photons as well as by partly absorbed stellar (inner disk) and interstellar UV (outer disk) photons, producing various reactive radicals. For example, C₃H is produced by the photodestruction of C₂H₂ ice, followed by evaporation (Table 9). In the outer disk partly transparent to the IS UV radiation, these surface photo-processes become important even in the midplane (see the C₂H₂ panel in Figure 8).

As already discussed in Section 3.1, the surface chemistry timescales are the longest in the disk, typically exceeding several Myr (see Tables 3 and 4). Photoprocessing of ices on dust grains has similar timescale in the molecular layer and the disk midplane, τchem ≲ 10⁶ yr (Figure 2). The overall pace of the surface chemistry is also dependent on the number of involved surface processes. Thus, typical chemical timescales for hydrocarbons are beyond 1 Myr, particularly for the heaviest and saturated ones (e.g., C₃H₄). Not surprisingly, mixing strongly affects the hydrocarbon chemistry in disks. The evolution of the heaviest carbon chains with more than six carbon atoms is so far from a steady state that it is sensitive to transport processes even in the slow mixing model (see, e.g., the C₃H₂ ice in Figure 8). Vertical transport brings up dust grains from the midplane to the upper, more irradiated and warmer disk regions, allowing more efficient photoprocessing of ices, photodesorption of frozen hydrocarbons, and their photodissociation. These processes increase abundances of gas-phase hydrocarbons by up to several orders of magnitude. In turn, downward vertical transport allows retention of newly formed hydrocarbon radicals in icy mantles and facilitates their slow hydrogenation. The radial mixing does not play a major role in the hydrocarbon chemistry. Consequently, abundances of saturated hydrocarbon ices are increased by vertical mixing, in particular in the inner disk with the shortest dynamical timescales (e.g., benzene ice), whereas the intermediate products become less abundant (e.g., C₃H₂ ice). Note also that mixing allows CH₂ and C₂H to be more efficiently formed in the outer disk atmosphere, where second layers of their high abundances are developed. This is caused by upward turbulent transport of molecular hydrogen, which is otherwise slowly destroyed in the atmosphere by X-rays and cosmic-ray particles.

4.3. Oxygen-bearing Molecules

In this subsection, we focus on simple neutral molecules that are composed of O, C, H only, and consider complex organics in a separate subsection.

There are four steadfast neutral O-bearing molecules (CO, OH, H₂CO, and the water ice), and three steadfast ions (H₂CO⁺, H₃CO⁺, and H₂O⁺; Table 5). Among the species sensitive to turbulent transport (Table 6) there are five molecules (C₂O, H₂O, HCO, O, O₂), three ions (HCO⁺, O⁺, O₂⁺), and four solid species (CO, H₂CO, O, OH ices). Hypersensitive O-bearing species (Table 7) include three molecules (CO₂, H₂O₂, O₃), two ions (OH⁺, H₂O⁺) and five ices (CO₂, H₂O₂, O₂, O₃, O₂). Turbulent diffusion alters their column densities by up to a factor of 4000 (CO₂ ice). Apparently, neutral species with a large number of oxygen atoms (e.g., ozone) affected more strongly by the turbulent mixing than the molecules containing a single O atom (e.g., CO). Similar to the hydrocarbon chemistry, abundances and column densities of O-bearing ices are more strongly altered by turbulent diffusion compared to gas-phase molecules. Once again this is an indication that the chemical evolution of multi-oxygen molecules in protoplanetary disks is at least partly governed by slow chemical processes (surface recombination, photodissociation of ices, etc.).

In Figure 9 distributions of relative molecular abundances and column densities at 5 Myr of CO, CO ice, CO₂, CO₂ ice, H₂O, O, O₂, and H₂CO calculated with the laminar and the 2D mixing models are presented. The abundance distribution of atomic oxygen shows a two-layer structure, with a maximum of relative concentrations (X(O) ≈ 1.5 × 10⁻²⁻) in the disk atmosphere and in the upper part of the molecular layer, and strong depletion in the midplane (X(O) ≲ 10⁻¹¹). On the other hand, CO and CO₂ ices are concentrated in the midplane and a lower part of the molecular layer (at r ≲ 1 H₉), with typical relative abundances of ≲10⁻⁵. The CO₂ ice abundance is particularly high in the inner warm midplane (r ≲ 20 AU). Its distribution is also two layered. Consideration of the remaining O-molecules shows a three-layer abundance structure similar to that of the polyatomic ions and hydrocarbons. The carbon monoxide spreads over a wide range of heights in the disk due to self-shielding and low desorption energy (z ≲ 1–2.5 at r = 10 AU and z ≈ 0.8–2 at r = 800 AU, with a typical abundance of 7.6 × 10⁻⁵). The tip of low CO abundances in the inner low atmosphere at 2 H₉ is due to enhanced X-ray-driven dissociation in this region (see also Section 3.1). Note that gas-phase CO in the laminar model is partially produced in the very inner disk midplane (r < 20 AU). Water is also widespread throughout the disk, though due to photodissociation and rapid freeze-out at T ≲ 120 K its peak abundances of 10⁻⁸–10⁻⁷ are confined to the bottom of the molecular layer, with a maximum in the outer disk region at r ≥ 200 AU (Figure 9). Gas-phase water comprises less than 0.01% of the total water abundance that are locked in dust mantles in the midplane. The O₂ abundance distribution has almost the same pattern as that of gas-phase water, with maximum values of X(O₂) ≈ 10⁻⁷–3 × 10⁻⁵. The peak CO₂ relative abundances are narrow and rather low, ~10⁻¹⁰–10⁻⁸, and restricted to the very outer disk (r ≥ 400 AU). In contrast, the H₂CO has a radially uniform, narrow (=0.3 H₉) molecular layer, with maximum abundances of ~10⁻¹⁰–10⁻⁹ at z ≈ 0.8–1 H₉.

Turbulent mixing does not considerably affect column densities of H₂CO and CO in gas and solid phases, although it populates the viscously heated inner midplane with carbon monoxide, and slightly widens their molecular layers upward (Figure 9). Unlike atomic ions, mixing softens the vertical gradient of the atomic oxygen abundances, and lowers its column density. Turbulent diffusion transports solid CO₂ from the inner midplane radially and vertically outward, enhancing its column densities and abundances by more than three orders of magnitude at r ≥ 30 AU. Column densities of gas-phase CO₂, H₂O, and O₂ are increased by the turbulence by factors of 10–1000, with
their molecular layers enriched and vertically expanded up to \( \sim 1.2–2 \, H_\odot \) and more homogeneously distributed in the radial direction.

Most important reactions responsible for the evolution of CO, CO ice, CO\(_2\), CO\(_2\) ice, H\(_2\)O, O, O\(_2\), and H\(_2\)CO abundances at 10 and 250 AU are presented in Table 10. The list contains the top 25 reactions per region (midplane, molecular layer, and atmosphere) for the entire 5 Myr time span.

The chemical evolution of these species is governed by a limited set of reactions. Atomic oxygen is present in the disk atmosphere and converted to CO, CO\(_2\), and H\(_2\)O in the midplane and the molecular layer. The rate of its conversion in the molecular layer is partly regulated by the evolution of H\(_2\)O and hydrocarbons, which is in turn determined by the slow X-ray irradiation of H\(_2\) (Section 4.1) and the slow release of O from CO by X-ray-ionized helium in the inner disk (Section 4.2), and the surface chemistry of O-bearing species. The resulting chemical timescale of \( \gtrsim 1 \, \text{Myr} \) exceeds the transport timescale in the molecular layer (Tables 3 and 4).

Water ice forms on dust grain surfaces via accretion of gas-phase water in disk regions with \( T \lesssim 120 \, \text{K} \), and via surface hydrogenation of frozen atomic oxygen and hydroxyl (minor route). The destruction pathways for water ice are thermal or photoevaporation (major route), and further hydrogenation to hydrogen peroxide ice (very minor route). In the gas, water formation begins by production of OH\(^+\) from O and H\(_2\)\(^+\), followed by subsequent hydrogen abstraction reactions with H\(_2\) until H\(_2\)O\(^+\) is created. The protonated water dissociatively recombines with electrons or negatively charged grains into H\(_2\)O (25\%) or OH (74\%) or O (1\%), or de-protonates by IM reactions with other abundant neutral molecules (CH\(_4\), CO, etc.).

The gas-phase formation of water is assisted by a slow radiative association reaction between H and OH, and photoe vaporation of water ice in the warm molecular layer. The gas-phase removal channels for H\(_2\)O include photodissociation, charge transfer reactions with H\(^+\) followed by dissociative recombination, freeze-out, and reactions with He\(^+\) (minor route). The solid water is a terminal species that serves as one of the sinks of the elemental oxygen in the disks. Thus, the key chemical processes leading to the evolution of water are fast, \( \tau_{\text{chem}} \lesssim 1–10^2 \, \text{yr} \), in the atmosphere and the midplane, whereas in the molecular layer it is regulated by the late-time evolution of H\(_2\)\(^+\) due to the X-ray ionization (\( \tau_{\text{chem}} \gtrsim 10^5 \, \text{yr} \); see Section 4.1).

Molecular oxygen is produced in the gas by neutral–neutral exothermic reactions of OH and O, and destroyed in IM and neutral–neutral combustion reactions with various radicals (mostly dehydrogenated hydrocarbons, e.g., C and C\(_3\)), by photodissociation and IM reactions of O\(_2\) with H\(_2\)\(^+\) and ionized C and H, followed by dissociative recombination of O\(_2\) into atomic oxygen. On dust surfaces molecular oxygen is produced either directly from the recombination of oxygen atoms at conditions when surface O becomes mobile (\( T \gtrsim 30 \, \text{K} \); the inner disk midplane and the warm molecular layer), or via surface oxidation reactions; O (ice) + OH (ice) \( \rightarrow \) O\(_2\)H (ice) and O (ice) + O\(_2\)H (ice) \( \rightarrow \) O\(_2\) (ice) + OH (ice). The surface O\(_2\) can be further converted to O\(_3\) ice. The characteristic chemical timescale for O\(_2\) is set by the slow surface chemistry timescale (\( \tau_{\text{chem}} \gtrsim 10^6 \, \text{yr} \)).

CO molecules serve as a sink of almost all elemental carbon and about half of elemental oxygen in disks. Carbon monoxide is formed essentially in the gas-phase via reactions of atomic oxygen with CH, CH\(_2\), and C\(_2\), and other abundant hydrocarbons (see the previous subsection and Table 9). The removal pathway of CO in the gas include freeze-out onto the grain surfaces (major channel), and the slow IM reaction with He\(^+\) (minor channel). In the upper, heavily UV-irradiated and dilute disk atmosphere CO is also UV-photodissociated (\( z \gtrsim 2.5 \, H_\odot \)). At \( T \lesssim 30 \, \text{K} \), in the outer midplane CO sticks to grains and is partly converted to H\(_2\)CO and CH\(_3\)OH ices via hydrogenation reactions, whereas in the warm midplane (\( r \lesssim 30 \, \text{AU}, T_{\text{gas}} \sim 30–40 \, \text{K} \)) CO is transformed into CO\(_2\) in a slightly endothermic reaction between the CO and OH ices (with a barrier of 80 K). The chemistry of CO gas reaches a steady state in the molecular layer and the cold outer midplane within fewer than \( 10^2–10^3 \, \text{yr} \) (see Figure 3).

The quasi-equilibrium CO chemistry in the molecular layer is restricted to the protonation of CO molecules by H\(_2\)\(^+\) into HCO\(^+\), balanced by dissociative recombination. In the disk atmosphere, CO chemistry is controlled by the photodissociation slowed down by self- and mutual-shielding by H\(_2\) (\( \tau_{\text{chem}} \lesssim 10^3–10^6 \, \text{yr} \)). In the inner warm midplane, the surface conversion of CO into CO\(_2\) leads to a very long timescale of \( \lesssim 1 \, \text{Myr} \).

Carbon dioxide is a daughter molecule of CO, and is mainly produced in the gas phase via oxidation of HCO (O + HCO \( \rightarrow \) CO\(_2\) + H), slow combustion of C\(_3\) and C\(_2\)H, slow endothermic reaction of CO and OH with a barrier of 176 K, and desorption of CO\(_2\) ice at \( T \gtrsim 60 \, \text{K} \) or UV photodesorption. The main removal gas-phase pathways include photodissociation, IM reactions with C\(^+\) and H\(^+\) (forming CO\(^+\) and HCO\(^+\), respectively), and accretion to dust grains. Solid CO\(_2\) is mainly produced via endothermic reaction of surface CO and OH in the disk inner midplane and the lower part of the entire molecular layer, and through accretion of the gas-phase carbon dioxide. CO\(_2\) ice is destroyed by the X-ray/CRP-induced UV photons in the inner midplane, and via thermal and UV desorption. Thus, the CO\(_2\) chemistry has a particularly long timescale associated with the surface reaction of CO and OH, and slow photoprocessing of CO\(_2\) ice (\( \tau_{\text{chem}} \gtrsim 1 \, \text{Myr} \)).

In the gas-phase, the H\(_2\)CO molecule is mostly produced through the reaction of C\(_2\)H\(_3\) with oxygen atoms, and desorption of formaldehyde ice. The major gas-phase removal routes are sticking to dust in the disk regions with \( T \lesssim 40–50 \, \text{K} \), photodissociation, reactions with ionized atomic C and H, oxidation by O (into CO, OH, and H), and protonation by H\(_2\)\(^+\) followed by dissociative recombination back to either H\(_2\)CO (33\%), CO (33\%), or HCO (33\%). The surface evolution of H\(_2\)CO is governed by accretion and desorption processes, and a sequence of surface hydrogenation of CO into CH\(_2\)OH where formaldehyde ice is an intermediate product. The timescale of key evolutionary processes for formaldehyde, namely, oxidation of CH\(_3\) and H\(_2\)CO, as well as accretion and evaporation, is fast, \( \lesssim 10^2–10^3 \, \text{yr} \).

As a result, the column density of formaldehyde is not significantly influenced by turbulent transport (see Figure 9). The same is true for the most abundant gas-phase CO and the H\(_2\)O ice. Their global chemical evolution is only slightly controlled by the surface chemistry, and the CRP/X-ray irradiation is important only in the upper regions that do not contribute to the resulting column densities. 2D mixing enables more efficient production of formaldehyde in the atmosphere (at \( \approx 1–2 \, H_\odot \)) thanks to enhanced abundances of CH\(_3\) (see Section 4.2). The turbulent diffusion lowers the column density of atomic oxygen, and increases the column density of gas-phase water, carbon dioxide in all phases, and molecular oxygen. The rate of conversion of atomic oxygen into other O-bearing species is partly governed by H\(_2\)\(^+\), which is sensitive to transport (see the discussion in Section 4.1). The gas-phase water production involves
slow desorption, and thus gas-phase water is sensitive to mixing. Abundances of CO₂ and O₂ (and other multi-O species) are at least partly determined by slow surface reactions. This also makes them sensitive to mixing.

4.4. Nitrogen-bearing Molecules

There are four steadfast neutral N-bearing molecules (CN, HCN, HNC, NH₂), two ions (H₂CN⁺ and NH⁺; Table 5). Sensitive nitrogen species include 19 molecules (e.g., C₃N, C₃N₃, C₆N, HC₅N), six ions (e.g., NO⁺, N₂H⁺, and CNC⁺), and 22 solid species (e.g., CH₃C₃N, HCN, H₃C₅N, CN, and NO; Table 6). The N-bearing hypersensitive species are four molecules (C₂N, HCN, N₂O, and NO₂), N⁺, and eight ices (e.g., CH₃C₃N, HNO, N₂, and NO₂), see Table 7. The turbulent diffusion alters their column densities by up to seven orders of magnitude (H₅C₅N ice). Similar to hydrocarbons and oxygen-containing molecules, complex chains with multiple N, C, or H atoms are more strongly affected by turbulent transport than simpler species, though the trend is not that clear (e.g., NO₂, HNCO, N₂, N₂O are the outliers). As Vasyunin et al. (2008) have found, nitrogen chemistry in disks involves a larger number of key reactions, including many exothermic neutral–neutral reactions, surface processes, compared to chemistries of O- and C-containing species. We have selected several most interesting nitrogen species for detailed chemical analysis. In Figure 10, distributions of relative molecular abundances and column densities of CN, HCN, NO, HNO, OCN, HC₅N, and HC₅N ice calculated with the laminar and the
2D mixing models are presented. Relative abundance distributions of all the considered species show a three-layer structure, with peak concentrations in the molecular layers at ~0.8–1 H₉, and typical values of 10⁻1⁰–10⁻⁸. Molecular layers of N-bearing molecules are narrow, ~0.2–0.5 H₉, similar to those of hydrocarbons, HCO⁺ and H₂CO (see Figures 8 and 9). The photostable CN radical has a second molecular layer in the outer disk atmosphere, at z ~ 1.8 (r > 200 AU), though it does not contribute much to the total CN column density. HC₅N ice is also concentrated in the molecular layer, at H₉ ~ 1.

Turbulent mixing does not affect column densities of CN, HCN, and HNC species (see the fourth panels in Figure 10). Nonetheless, their molecular layers are broadened by diffusion, and the second, upper molecular layer of CN becomes more prominent (compare first and third panels). NO, HNO, OCN, HC₃N, and HC₅N ices are sensitive to mixing, with their column densities increased by 2D turbulent diffusion by up to a factor of 40 (cyanodiacetylene; Table 6). The corresponding abundance distributions are vertically extended over ~0.5–1.5 of H₉, and enhanced by transport by up to several orders of magnitude.

Most important reactions responsible for the time-dependent evolution of CN, HCN, HNC, NO, HNO, OCN, HC₃N, and the surface HC₅N abundances are presented in Table 11. The list contains the top 20 reactions per region.

The evolution of cyanopolyyne ice is tightly connected to the evolution of carbon chains discussed in Section 4.2. Their major production pathways in the gas include evaporation from icy mantles, neutral–neutral reaction of N with Renner–Teller hydrocarbons (C₃H), slow or slightly endothermic reaction of CN with Cₙ⁻H₂ (e.g., C₄H₂ → C₅H₃N), and (at later times) dissociative recombination of their protonated analogs formed by the IM reactions with H⁺. The main removal pathways are the freeze-out at temperatures ≤70–170 K, UV photodissociation, and reactive collisions with C, H, and He ions. On dust surfaces, cyanopolyne ice forms either via addition of N to frozen Renner–Teller hydrocarbons or through hydrogenation of C₅N ices. The major destruction routes for the cyanopolyne ice are photoevaporation, photoprocessing by X-ray- or CRP-driven UV photons (e.g., HC₅N ice + hᵥCRP → C₆H ice + CN ice), and surface conversion to even more complex species (e.g., HC₃N ice + H → H₂C₅N ice + H). In turn, dehydrogenated carbon chains with attached nitrogen atom are produced in gas and on dust surfaces by rapid neutral–neutral reactions of N with the C₄H species, and dissociation of complex molecules with multiple C and N atoms (e.g., CH₃C₅N ice + hᵥCRP → C₆N ice + CH₃ ice). Obviously, as in the case of complex carbon chains, characteristic timescales of the cyanopolyne chemical evolution are regulated by the slow surface processes with τₜₕₑₘ exceeding a million years.

In contrast, chemical histories of CN, HCN, and HNC are closely related and governed by a small set of reactions. The production and destruction of CN proceeds entirely in the gas phase. The primal formation pathways are photodissociation of hydrogen cyanide and isocyanide, rapid barrierless neutral–neutral reactions of N with CH, C₂, and C₄N, and NO with C (rate coefficients are ~10⁻¹¹–6 × 10⁻¹⁰ cm³ s⁻¹), and dissociative recombination of HCNH⁺ at later times (t > 10⁵–10⁶ yr). Another, less important formation pathway for CN is the neutral–neutral reaction between C and OCN, leading to CN and CO. The destruction of CN is mostly caused by photodissociation, fast neutral–neutral reactions with N, O, OH, and O₂, and freeze-out in the disk midplane at T ≤ 35–40 K. In the atmosphere CN reacts with H⁺, forming CN⁺, which is converted back to CN by charge transfer with atomic hydrogen. The fact that CN chemistry involves only gas-phase routes implies its relatively short characteristic timescale, ~10⁴ yr (Tables 3 and 4). Only in the outer atmosphere τₜₕₑₘ(CN) > 10⁵ yr, because CN evolution there depends on the slow evolution of C₂H (see Figure 8 and the discussion in Section 4.2).

The key production route for gas-phase HCN and HNC is the reaction of nitrogen atoms with CH₂ and dissociative recombination of HCNH⁺. The more energetically favorable isomer, HCN, is produced in reactive collisions of ionized hydrogen with hydrogen isocyanide. Minor formation channels in the disk midplane include direct surface recombination of atomic hydrogen and the cyanogen radical, which leads to gas-phase HCN and H (with 5% probability), and charge transfer between H and CN⁺. Due to their relatively large binding energies, thermal desorption of HCN and HNC does not occur until temperatures of T > 40 K are reached. The major destruction routes for gas-phase HCN and HNC include accretion onto dust grains, charge transfer reaction with H⁺, IM reaction with C⁺ leading to CNC⁺ or C₂N⁺, and protonation reaction with H₂⁺, HCO⁺, and H₂O⁺. Another important destruction channel for hydrogen (iso)cyanide in the upper disk layers at ~1.5–2 scale heights is photodissociation. The characteristic timescales of the HCN and HNC evolution in the molecular layer are ~10⁴–10⁵ yr. In the midplane their chemical timescales exceed 10⁵–10⁶ yr, as their evolution is partly controlled by the slow surface formation. Evolution is comparably slow in the inner upper molecular layer/low atmosphere subject to slow X-ray-driven dissociation of H₂ and release of oxygen from water and CO.

The evolution of NO, HNO, and OCN, similar to that of CN, HCN, and HNC, is also governed by a set of rapid exothermic neutral–neutral reactions. Major formation pathways for nitrogen monoxide comprise reactive collisions of atomic nitrogen with hydroxyl, reactive collisions of atomic oxygen with NH, gas-phase destruction of HNO by atomic oxygen, and, in the inner midplane, surface destruction of HNO by O, CH₂, and CH₃, with products, in particular NO, directly injected into gas. In the disk atmosphere NO is produced by photodissociation of HNO. In the inner disk midplane, a source of NO gas is thermal desorption of NO ice. The major removal processes for NO include photodissociation in the atmosphere, accretion onto dust grains in disk regions with T ≤ 30–35 K, neutral–neutral reactions with atomic carbon and nitrogen (leading to CO and N₂), and charge transfer reactions with H⁺ and C⁺. The characteristic timescale for NO is ~10⁴–10⁵ yr in the molecular layer, and ~10⁵–10⁶ yr in the midplane, where its evolution is partly controlled by surface processes. In the upper molecular layer at r ~ 100 AU, the NO chemical timescale is again long, ~1 Myr, since it is related to the evolution of atomic oxygen which is slow at those disk heights.

The chemical evolution of nitric acid (HNO) is very similar to that of NO. The major production terms for HNO are neutral–neutral reaction of atomic oxygen with nitrogen dioxide, and, in the warm molecular layer and the inner midplane, via surface hydrogenation of NO directly to the gas phase. The evaporation of solid HNO plays only a minor role in the production of gas-phase HNO (in the laminar model). The major destruction terms for HNO include photodissociation in the atmosphere, accretion onto dust grains in disk regions with T ≤ 40–50 K, neutral–neutral reactions with atomic hydrogen and oxygen (leading to NO), and IM reaction with H⁺.
(forming ionized NO and H₂). The distribution of the characteristic timescale for HNO over the disk is close to that of NO.

The chemical evolution of cyanate (OCN) is more diverse than that of NO and HNO. The key formation routes comprise neutral–neutral reactions of CN with OH and O₂, N and HNO, and oxidation reactions with abundant cyanopolymers, e.g., C₇N + O → OCN + C₆. It can also be produced by direct surface recombination in O and CN ices. Similar to HNO, desorption of solid OCN is not a key formation process for gas-phase cyanate (in the laminar model). The key removal routes include photodissociation in the atmosphere, sticking to dust grains in disk regions with T ≲ 50–60 K, neutral–neutral reactions with atomic oxygen and carbon (leading to NO or CO), slow combustion reaction with O₂ (producing CO₂ and NO), and IM reaction with C⁺ (forming ionized CO and CN). The characteristic timescale of the OCN evolution is ≤10³–10⁴ yr in the molecular layer, and ≥10⁵–10⁶ yr in the inner and outer midplane, where its evolution is partly controlled by surface processes. In the atmosphere the OCN chemical timescale

### Table II

| Reaction                           | α (cm³ s⁻¹) | β (K) | μ (yr⁻¹) | tmin (yr) | tmax (yr) |
|-----------------------------------|-------------|-------|----------|-----------|-----------|
| HC₃N ice + hvCRP → C₄H ice + CN ice | 1.75 (3)    | 0     | 0        | 1.00      | 5.00 (6)  |
| HCN + UV → CN + H                 | 0.16 (−8)   | 0     | 2.69     | 1.00      | 5.00 (6)  |
| HNC + UV → CN + H                 | 0.55 (−9)   | 0     | 2.00     | 1.00      | 5.00 (6)  |
| HNO + UV → NO + H                 | 0.17 (−9)   | 0     | 0.53     | 1.00      | 5.00 (6)  |
| OCN + UV → O + CN                 | 1.00 (−11)  | 0     | 2.00     | 1.00      | 5.00 (6)  |
| CN + grain → CN ice               | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| HCN + grain → HCN ice             | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| HNC + grain → HNC ice             | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| HNO + grain → HNO ice             | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| NO + grain → NO ice               | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| OCN + grain → OCN ice             | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| HC₃N + grain → HC₅N ice           | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| H ice + CN ice → HCN              | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| H ice + C₃N ice → HC₅N ice        | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| H ice + C₅N ice → HC₅N ice        | 1.00        | 0     | 28.60    | 1.00      | 5.00 (6)  |
| H ice + NO ice → HNO              | 1.00        | 0     | 0        | 1.00      | 5.00 (6)  |
| C₃H₂N + C + H → HCCN + CH₄⁺       | 0.20 (−7)   | −0.50 | 0        | 3.82      | 5.00 (6)  |
| HCN + H⁺ → HCN⁺ + H               | 0.40 (−7)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| HCN + H⁺ → HCN + H⁺               | 0.28 (−7)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| HNC + H⁺ → HCN + H⁺               | 0.25 (−7)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| HCN⁺ + H → HCN + H⁺               | 0.37 (−10)  | 0     | 0        | 1.00      | 5.00 (6)  |
| NO + C → CN + O                   | 0.60 (−10)  | −0.16 | 0        | 1.00      | 5.00 (6)  |
| OCN + C → CN + CO                 | 1.00 (−10)  | 0     | 0        | 1.00      | 5.00 (6)  |
| CN + O₂ → OCN + O                 | 0.24 (−10)  | −0.60 | 0        | 1.00      | 5.00 (6)  |
| HNO + O → NO + OH                 | 0.38 (−10)  | 0     | 0        | 1.00      | 5.00 (6)  |
| NH₂ + O → HNO + H                 | 0.80 (−10)  | 0     | 1.00     | 5.00 (6)  |
| C₆N + O → OCN + C₆                | 0.40 (−10)  | 0     | 0        | 1.00      | 5.00 (6)  |
| CN + OH → OCN + H                 | 0.70 (−10)  | 0     | 0        | 1.00      | 5.00 (6)  |
| HNO + H → NO + H₂                 | 0.45 (−10)  | 0.72  | 3.29     | 1.00      | 5.00 (6)  |
| N + CH → CN + H                   | 0.17 (−9)   | −0.09 | 0        | 1.00      | 2.56 (5)  |
| N + CH₂ → HNC + H                 | 0.40 (−10)  | 0.17  | 0        | 1.00      | 5.00 (6)  |
| N + HCO → OCN + H                 | 1.00 (−10)  | 0     | 0        | 1.00      | 5.00 (6)  |
| N + NO → N₂ + O                   | 0.30 (−10)  | −0.60 | 0        | 1.00      | 5.00 (6)  |
| N + OH → NO + H                   | 0.75 (−10)  | −0.18 | 0        | 1.00      | 5.00 (6)  |
| C₃H₂N⁺ + e⁻ → HNC + C₂H           | 0.75 (−7)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| C₃H⁺N⁺ + e⁻ → HCN + C₂            | 0.30 (−6)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| C₃H₂N⁺ + e⁻ → HCN + H             | 0.15 (−6)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| C₃H⁺N⁺ + e⁻ → HCN + H₂            | 1.00 (−6)   | −0.30 | 0        | 7.48      | 5.00 (6)  |
| C₃H₂N⁺ + e⁻ → HCN + CH₃           | 1.00 (−6)   | −0.30 | 0        | 1.00      | 5.00 (6)  |
| CH₃CN⁺ + e⁻ → HCN + CH            | 0.30 (−6)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| H₂CN⁺N⁺ + e⁻ → HCN + H            | 0.19 (−6)   | −0.65 | 0        | 1.00      | 5.00 (6)  |
| H₂CN⁺N⁺ + e⁻ → HNC + H            | 0.19 (−6)   | −0.65 | 0        | 1.00      | 5.00 (6)  |
| H₂NO⁺ + e⁻ → HNO + H              | 0.15 (−6)   | −0.50 | 0        | 1.00      | 5.00 (6)  |
| H₂CN⁺ + e⁻ → CN + H + H           | 0.92 (−7)   | −0.65 | 0        | 1.00      | 5.00 (6)  |
increases from $10^4$ to $10^6$ yr, similar to the CO$_2$ timescale shown in Figure 3.

Column densities of CN, HCN, and HNC are not much affected by diffusion as their key evolutionary processes in their molecular layers are rapid (Figure 10). As for many molecules in the model, turbulent transport expands their layers in the vertical direction. Since the chemistry of CN involves C$_2$H, and its abundance is increased by mixing in the atmosphere at $z \lesssim 2$ $H$, (see Figure 8 and the discussion in Section 4.2), in the 2D mixing case ($Sc = 1$) the second molecular layer of CN is formed. Similarly, the hydrogen cyanide and isocyanide evolution is related to the evolution of CH$_2$, which is sensitive to transport in the same upper disk region, though not as strong as C$_2$H. The chemistry of NO-containing species (e.g., NO, HNO, and OCN) is sensitive to mixing as it depends on the evolution of O and O$_2$, which is in turn influenced by transport, and as their production involves minor slow surface routes. Thermal evaporation of these heavy species is inefficient, and thus photoevaporation of their ices becomes an important production pathway for their gas-phase counterparts. Vertical mixing allows more efficient evaporation of NO, HNO, and OCN ices in the warm molecular layer, enhancing their gas-phase abundances. Due to utter importance of surface chemistry for the chemical evolution of cyanopolyynes, their abundances and column densities are increased by mixing, albeit not as strongly as for some heavy hydrocarbons.

4.5. Sulfur-bearing Molecules

The chemistry of sulfur-bearing molecules is least understood in astrochemistry. Therefore, results in this subsection should be interpreted with special care. So far there are only two sulfur-containing molecules detected in disks, namely, CS (e.g., Dutrey et al. 1997) and, recently, SO (Fuente et al. 2010). Thus, we restrict ourselves to the discussion of neutral species only.

There are two steadfast neutral S-bearing molecules (H$_2$S and HCS), five ices (HS, H$_2$S, H$_2$CS, S, and S$_2$), and no ions (Table 5). The sensitive sulfur-bearing species include seven gas-phase molecules (e.g., CS, H$_2$CS, H$_2$S$_2$, HS, S), two ions ($S^+$ and $SO^+$), and seven ices (e.g., CS, C$_2$S, C$_3$S, H$_2$S$_2$, SO; Table 6). Among hypersensitive species (Table 7) there are four gas-phase molecules (C$_2$S, CS, SO, and SO$_2$), two ions, and three ices (C$_2$S, NS, and SiS). The turbulent diffusion alters their column densities by up to a factor of 7000 (SO$_2$ ice). Similar to hydrocarbons and oxygen-bearing molecules, complex S-chains with multiple carbon or oxygen atoms are more strongly affected by turbulent transport than simpler species. Unlike C- and N-bearing species, there is no evidence that concentrations of sulfur-bearing ices are more strongly altered by transport than abundances of their gas-phase counterparts.

In Figure 11, distributions of abundances and column densities of CS, C$_2$S, C$_3$S ice, C$_2$S ice, H$_2$S, OCS, H$_2$CS, and SO$_2$ calculated with the laminar and the 2D mixing models are shown. In the laminar model, abundance distributions of gas-phase species show a three-layer structure, with peak concentrations in the molecular layers at $\approx 0.8 - 1$ $H$. In contrast, C$_2$S and C$_3$S ices are more concentrated toward the disk midplane and the bottom of the molecular layer, with typical abundances of $10^{-12} - 10^{-10}$. The molecular layers of gas-phase sulfur-bearing molecules have various thicknesses, from $\approx 0.05$ $H$ for C$_2$S to $\approx 2$ $H$ for CS, and are not as pronounced as for carbon-, oxygen-, and nitrogen-bearing species (see Figures 8–10). Their typical peak abundances are only $10^{-12} - 10^{-10}$, though in the outer molecular layer H$_2$S abundances are as high as $\approx 10^{-8}$.

Among the listed molecules, only H$_2$S is steadfast (see fourth panels in Figure 11). Mixing enhances H$_2$S concentration in the upper molecular layer at $z \gtrsim 1.3$ $H$, that does not contribute to the total column density (compare first and third panels). CS, C$_2$S, C$_3$S ice, C$_2$S ice, OCS, H$_2$CS, and SO$_2$ are sensitive and hypersensitive to mixing. The corresponding molecular layers are vertically broadened up to $\approx 2$ $H$, and enhanced by several orders of magnitude.

Most important reactions responsible for the time-dependent evolution of CS, C$_2$S, C$_3$S ice, C$_2$S ice, H$_2$S, OCS, H$_2$CS, and SO$_2$ abundances are presented in Table 12, both for the inner and outer disk regions. The list contains the top 20 reactions per region (midplane, molecular layer, and atmosphere).

The chemical evolution of hydrogen sulfide in the atmosphere begins with the radiative association of ionized sulfur and H$_2$, leading to H$_2$S$^+$ that slowly radiatively recombines into H$_2$S. The major destruction reactions in the atmosphere are photodissociation, rapid IM reaction with C$^+$, and charge transfer reaction with H$^+$. In the molecular layer and midplane, hydrogen sulfide is initially produced as in the atmosphere, but after 1–100 yr its top formation pathway is a direct surface recombination of HS and H ices. HS radical is formed via neutral–neutral reaction of S with OH, and also via direct surface recombination of H and S. The major destruction pathways for H$_2$S in the molecular layer and midplane are accretion onto dust grains, IM reactions with HCO$^+$ and H$_3^+$, and charge transfer reaction with H. The characteristic timescale of the H$_2$S evolution is short in the midplane and molecular layer, $\approx 10^{-10}$ yr, since its initial production and freeze-out are relatively fast. Later, accretion is balanced out by the direct surface recombination, while desorption of H$_2$S is not significant. In the atmosphere H$_2$S reaches a quasi-steady state within $10^5 - 10^6$ yr, which is determined by the slow evolution of H$_2$, H$_3^+$, and H$_2^+$ (see the discussion in Section 4.1).

The chemical evolution of CS proceeds entirely in the gas phase. It is synthesized in the dissociative recombination of HCS$^+$, C$_2$S$^+$, C$_3$S$^+$, HOC$^+$, and HCS$^+$ on electrons or negatively charged grains in the inner midplane, and via desorption of CS ice at $T \gtrsim 35 – 40$ K. The major destruction pathways are photodissociation in the atmosphere, depletion in the molecular layer and the midplane, slow endothermic oxidation reaction (CS + O $\rightarrow$ CO + S), charge transfer with ionized hydrogen atoms, and IM reactions with primal ions, e.g., HCO$^+$, H$_3^+$, and H$_2^+$. The steady state for CS is attained at about $10^{-10}$ yr in the lower molecular layer/upper midplane, and later in other disk parts. While the CS chemistry does not include surface processes directly, it is related to the evolution of C$_2$S$^+$, C$_3$S$^+$, HOC$^+$, and HCS$^+$, and, thus, their chemical “parents,” namely C$_2$S, C$_3$S, and OCS. The latter molecules are partially synthesized via surface reactions, making their evolution slow in the cold midplane.

The chemical evolution of all the C$_n$S species in the model ($n \leq 4$) is well coupled. For example, as in the case of CS, major formation channels for gas-phase C$_2$S include dissociative recombination of C$_2$S$^+$, C$_3$S$^+$, HCS$^+$, and HC$_2$S$^+$ on negatively charged grains in the inner midplane and electrons. The binding energy adopted for C$_2$S is $2.700$ K, and higher for more massive carbon chain sulfides, which precludes effective thermal desorption of their ices in the disk midplane and the molecular layer beyond 10 AU. The major destruction channels for C$_2$S are photodissociation, accretion onto dust grains, charge transfer reactions with H$^+$ and C$^+$, and protonation by abundant polyatomic ions. The evolution of the C$_2$S ice is significantly simpler. It involves only three major processes: accretion of the
gas-phase C$_2$S, surface reaction of frozen atomic carbon with the C$_2$S ice producing the C$_3$S ice, and photodissociation of the C$_2$S ice by the CRP/X-ray-induced UV photons (leading to C and CS ices). The evolution of the C$_3$S ice includes its surface synthesis from C$_2$ and C, accretion of gas-phase C$_3$S, and photodestruction to the C$_2$ and CS ices. Consequently, the characteristic chemical timescales for gas-phase and, particularly, surface C$_3$S molecules are long, $t_{\text{chem}} \gtrsim 10^6$ yr.

Thioformaldehyde, H$_2$CS, like CS and H$_2$CO, is synthesized in the gas. Its major production routes consist of neutral–neutral reaction between S and CH$_3$, and dissociative recombination of protonated H$_2$CS at later times. The key destruction routes are photodissociation, accretion onto dust grains at $T \lesssim 45–50$ K, charge transfer reaction with H$^+$, IM reaction with C$^+$, and proton addition in reactive collisions with HCO$^+$, H$_2^+$, etc. Distribution of the H$_2$CS characteristic timescale over the disk closely resembles that of $t_{\text{chem}}$(CS).

The chemical evolution of carbonyl sulfide (OCS) begins with its formation in oxidation of HCS and radiative association of S and CO. At later times, OCS is also produced by direct
surface recombination of S and CO ices, and the CS and O ices. The destruction of OCS involves photodissociation in the disk atmosphere, accretion onto dust in the molecular layer and the midplane, and IM reactions with C and H. The protonation of OCS by the polyatomic ions leads to HOC+S, which dissociatively recombines into OCS and H (50%) or CS and H (50%). The characteristic timescale for carbonyl sulfide is \( \lesssim 10^2-10^4 \) yr in the disk midplane, \( \sim 10^3-10^4 \) yr in the lower molecular layer, and \( \gtrsim 10^5-10^6 \) elsewhere in the disk.

Sulfur dioxide (SO2) is synthesized by exothermic neutral–neutral reaction between SO and OH, slow radiative association of SO and O, and the same reaction catalyzed by dust grains, with SO2 directly desorbed back to the gas with a 5% probability. Its major removal channels are photodissociation, freeze-out in disk regions with \( T \lesssim 60-80 \) K, neutral–neutral reaction with atomic carbon (leading to SO and CO), and IM reaction with C (producing SO and CO). Later a quasi-equilibrium cycling of SO2 prevails, which includes protonation of sulfur dioxide by abundant polyatomic ions (H+, HCO+) followed by dissociation recombination back to SO2 with a 66% probability. In turn, sulfur monoxide (SO) is produced by slow combustion of S, neutral–neutral reactions between S and OH and O with HS, and direct surface reaction of HS and O ices. Consequently, the characteristic chemical timescale of SO2 is governed by the slow evolution of molecular oxygen (see Section 4.3), and exceeds 1 Myr in the disk midplane, and \( 10^3-10^5 \) yr in the molecular layer.

Since chemical network for S-bearing species, especially complex chains, in our model is more limited than that for the N- and C-containing molecules, turbulent transport enhances abundances and column densities even for transient S-species. All species considered above either formed via surface reactions or their synthesis involved surface-produced radicals. Thus, their chemical evolution proceeds slower than mixing (see Figure 11). Complex S-ices are more readily produced in the mixing case as their formation is based on heavy radicals, which become mobile at \( T \gtrsim 20-40 \) K. Also, in the mixing model photodissociation of these ices is more effective (see the peak in the relative abundances of C2S ice at \( r \sim 100 \) AU, \( z \sim 1.5 H_H \)). Diffusive transport strongly increases the concentration of SO2 molecules by producing more molecular oxygen needed for its synthesis. For SO2, its radial distribution becomes sensitive to transport. The least affected species is H2S (along with HCS, and ices of S, HS, and H2S) as its characteristic evolutionary timescale is shorter than the mixing timescale in the disk region where it is most abundant (see Tables 3 and 4).

### 4.6. Complex Organic Molecules

For the purpose of the current discussion we consider organic polyatomic neutral molecules consisting of at least several H, C, and O atoms, and heavier elements.

There is a single organic species insensitive to the turbulent diffusion, namely, formaldehyde (see Section 4.3). Transport-sensitive organic species include two gas-phase molecules (CH2CO and HNCO) and five ices (CH2CO, HNCO, CH3OH, H2CO, and NH2CHO; Table 6). One gas-phase molecule (HCOOH) and three ices (HCOOH, H2C5O, and CH3CHO) are among the hypersensitive species in Table 7. Turbulent diffusion alters their column densities by up to a factor of 3000 (solid formic acid). The chemical evolution of all the considered organic species is influenced by transport as their major production and removal routes require surface processes.

In Figure 12, distributions of abundances and column densities of HCOOH, HCOOH ice, CH3OH, HNCO, HNCO ice, CH3CHO, CH3CHO ice, and CH2CO calculated with the laminar and the 2D mixing models are presented. In the laminar model the relative abundance distributions of the gas-phase species show a three-layer structure, with very narrow molecular layers located at \( \approx 0.8-1 H_H \), HCOOH, HNCO, and CH3CO molecular layers are wider beyond \( \sim 200 \) AU, and have higher abundances. Abundance distributions of complex ices are maximum either at the bottom of the molecular layer (HNC ice and HCOOH ice) or in the inner warm midplane (CH3CHO ice and HCOOH ice). The overall trend can be easily explained as heavy ices are hard to evaporate thermally, so photoevaporation is necessary, while gas-phase organic molecules are rather photofragile. For the efficient production of heavy ices surface mobility of radicals (O, C, CH, etc.) is required, which necessitates warm temperatures (\( T \gtrsim 30 \) K) and/or photoprocessing of precursor molecules by the X-ray/CRP-induced UV photons.

The most important reactions responsible for the time-dependent evolution of HCOOH, HCOOH ice, CH3OH, HNCO, HNCO ice, CH3CHO, CH3CHO ice, and CH2CO abundances are presented in Table 13. The list contains the top 25 reactions per region (midplane, molecular layer, and atmosphere).

The chemical evolution of formic acid (HCOOH) starts with a single production channel via dissociative recombination of CH3O2 either on electrons or negatively charged grains. In turn, protonated formic acid is produced by radiative association of HCO+ and H2O, and by the IM reaction of methane with ionized molecular oxygen. The primal removal channels for HCOOH are photodissociation and photoionization, depletion onto dust grains at \( T \lesssim 100-120 \) K, charge transfer with ionized atomic hydrogen, and protonation by abundant polyatomic ions (HCO+, H3+, H2O+). HCOOH ice is mainly produced by accretion of gas-phase formic acid, and destroyed by primary and secondary UV photons in the disk midplane and molecular layer. The surface as well as gas-phase formation of HCOOH via a neutral–neutral reaction of OH and H2CO is only a minor channel in the laminar model. Consequently, evolutionary timescales for gas-phase and surface HCOOH are similar and typically exceed \( 10^5 \) yr.

Gas-phase methanol (CH3OH) is produced by direct surface recombination of frozen H and CH2OH as well as frozen OH and CH3. evaporation of methanol ice, dissociative recombination of protonated methanol, and dissociative recombination of H2C2O2 (minor route). Its key removal pathways are surface accretion in the disk regions with \( T \lesssim 100-120 \) K, photodissociation and photoionization, and protonation by the dominant polyatomic ions. On dust surfaces methanol is produced via a sequence of hydrogenation reactions, starting from CO ice, and is photodissociated by UV radiation. The characteristic chemical timescale for methanol is fully controlled by the slow surface chemistry (\( \tau_{\text{chem}} \gtrsim 10^5 \) yr).

The chemical evolution of isocyanic acid (HNCO) is also dominated by surface processes. In the gas-phase it is produced either by evaporation of HNCO ice at \( T \lesssim 50-60 \) K or by direct surface recombination of surface H and OCN. The major gas-phase destruction pathways are accretion onto grains in the midplane and the molecular layer, and IM reaction with H+. HNCO ice is produced by a surface reaction involving H and OCN, accretion of HNCO gas, and is destroyed by UV photons. Their characteristic timescales are like those of HCOOH and methanol.

The chemistry of acetaldehyde (CH3CHO) involves gas-phase production by reactive collisions between O and C2H5,
accretion to dust grains at $T \lesssim 50$–$60$ K, and desorption at $T \lesssim 60$ K, and removal via charge transfer reactions with C$^+$ and IM reactions with C$^+$, H$^+$, and H$_3$O$^+$. At later times, acetaldehyde is reproduced from its protonated analog by dissociative recombination (albeit with low probability). The frozen acetaldehyde is synthesized by accretion of gas-phase CH$_3$CHO, via surface recombination of CH$_3$ and HCO ices, and destroyed by the UV dissociation. As for other complex organics, the chemical timescale for acetaldehyde is typically longer than 1 Myr.

Gas-phase ethene (CH$_2$CO) is produced via oxidation of C$_2$H$_2$, direct surface recombination of the H and H$_2$O ices, and dissociative recombination of protonated ethene. Thermal evaporation of ethene ice is effective when dust temperatures exceed $\sim 100$ K. Key removal channels include photodissociation and photoionization, freeze-out in the midplane and the molecular layer, charge transfer reaction with C$^+$ and H$^+$, and, at later times, protonation by polyatomic ions. The chemical timescale for CH$_3$CO exceeds $10^5$–$10^6$ yr.

Not surprisingly, turbulent mixing enhances the abundances and column density of these organic species, given their long evolutionary timescales governed by surface reactions and photodissociation of ices by the CRP- and X-ray-induced secondary UV radiation field. HCOOH and HCOOH ices are more abundant since water ice and HCO$^+$ abundances are increased by mixing, leading to more efficient production of the parental ion, CH$_3$O$^+$. Radial transport is important for both the gas-phase and solid formic acid. The effect is less pronounced for HNCO, as its precursor species, OCN, is enhanced by transport by less than an order of magnitude. HNCO ice, produced in the lower part of the molecular layer, is transported by diffusion to the cold midplane where it cannot be synthesized.
otherwise. Relative abundance of gas-phase acetaldehyde is greatly enhanced by disk mixing in the middle of the molecular layer (\(z \approx 1.5 H_\star\)), within the inner 100 AU. As its synthesis proceeds via surface recombination of CH₃ and HCO, in the laminar model appropriate conditions are only met in the very inner midplane/molecular layer. In the fast mixing model, larger quantities of solid acetaldehyde can be accumulated as more icy grains reach the warm disk regions. Vertical mixing brings CH₃CHO ice in the inner midplane to the molecular layer, where it photovaporizes, and is then radially transported to larger distances. The ethene abundances are vertically broadened by mixing, and moderately increased as the ethylene ice production is enhanced by mixing.

5. DISCUSSION

5.1. Comparison with Previous Studies and Future Developments

In this section we discuss the results and drawbacks of our model in context of other studies of the chemo-dynamical evolution of protoplanetary systems.

Models of the inner solar nebula: the role of advective transport. The ability of turbulent or advective transport to cause radial mixing of materials in the inner early solar system has been proposed and investigated by Morfill (e.g., Morfill 1983; Morfill & Völk 1984), with a simple 1D analytical disk model and passive tracers. In a similar manner, 2D radial mixing of materials in the inner early solar system has been proposed and investigated by Morfill (e.g., Morfill 1983; Morfill & Völk 1984), with a simple 1D analytical disk model and passive tracers. In a similar manner, 2D radial mixing of gaseous and solid water in the inner nebula has been studied by Cyr et al. (1998). In a series of papers, the group of Prof. H.-P. Gail (Heidelberg University) has investigated various aspects of the chemo-dynamical evolution of the inner protosolar nebula (1–10 AU), progressing from stationary accretion disk models and crude gas-phase chemistry toward a self-consistent 2D radiative-hydrodynamical model with the coupled C-, H-, O- gas-phase chemistry (e.g., Bauer et al. 1997; Finocchi et al. 1997; Gail 1998, 2001, 2002; Wehrstedt & Gail 2002; Gail 2004; Keller & Gail 2004; Tscharnuter & Gail 2007). In Bauer et al. (1997), the gas-phase C-, H-, N-, and O-chemistry driven by dust destruction and evaporation of ices in the presence of slow radial transport has been modeled, utilizing the semi-analytical one-zone disk model of Duschl et al. (1996). The major finding is that radial transport enriches the outer, \(r > 10\) AU nebular regions with methane and acetylene produced by oxidation of carbon dust at \(r \lesssim 1\) AU, as observed in comets such as Hyakutake and Hale-Bopp. When a self-consistent 2D description of advective transport and turbulent diffusion is used, quasi-stationary accretion flows develop a 2D structure such that in the disk midplane gas moves outward, carrying out the angular momentum, whereas inward mass accretion proceeds through the surface layers. The radial advection dominates the diffusive mixing in outer disk regions at \(r > 5\) AU. Thus, chemical species produced by the “warm” chemistry in the inner nebula can reach its outer region, where they are intermixed by turbulence with surrounding matter and freeze-out. The H₂ and CO evolution is insensitive to transport, while abundance distributions of, e.g., O, O₂, CO₂ are altered by the disk dynamics within 300 yr of the evolution.

Our modeling is related to outer nebular regions beyond 10 AU and does not include advective transport. However, in the presence of a steep chemical gradient for a molecule, radial diffusive mixing is able to transport it from 100 AU to 1 AU within about \(1–2 \times 10^6\) yr, and from 1 AU to 10 AU within about \(\lesssim 3 \times 10^5\) yr, which is still smaller than a typical disk lifetime of several Myrs. Calculated H₂ and CO column densities are also not sensitive to the diffusive mixing in our model, similar to that was found by Tscharnuter & Gail (2007). In agreement with Gail et al.’s results, we show that the synthesis of hydrocarbons, including CH₄ and C₂H₂, is intensified by mixing, particularly in the zone of comet formation around 10–20 AU (Figure 8). CO₂ ice, which is produced via surface reactions in the warm inner midplane and can be considered as an example of a “warm” species, is transported outward by 2D turbulent mixing.

Models of protoplanetary disks: the role of advective transport. Some disk models have been used to simulate chemical evolution of protoplanetary disks in the astrophysical context. Aikawa et al. (1999) have utilized an isothermal \(\alpha\)-disk model of Lynden-Bell & Pringle (1974) with \(M = 10^{-5} M_\odot\ yr^{-1}\) and calculated its density structure assuming hydrostatic equilibrium in the vertical direction. They have modeled the chemical evolution in the presence of steady inward accretion, using both atomic and molecular initial abundances, and found similar results. We also find that the difference in the calculated abundances between the adopted “low metals” atomic initial abundances and those from a molecular cloud is negligible in our model. Aikawa et al. (1999) have concluded that radial transport leads to higher concentrations of heavy hydrocarbons at \(\lesssim 20\) AU, whereas methane is the dominant hydrocarbon in the outer disk region. In our laminar model, methane prevails over heavier hydrocarbons in the entire disk, while in the presence of radial and vertical mixing a substantial fraction of CH₄ is converted into heavy carbon chains (especially at 10–50 AU; see Figure 8). Aikawa et al. (1999) have concluded that radial transport leads to simultaneous existence of the reduced (e.g., CH₄) and oxidized (e.g., CO₂) ices, as observed in comets, and as found by our modeling. They have studied in detail chemistries of O-, N-, and C-bearing species and found that H₂O and He produce e.g., CO₂, CH₄, and NH₃ from CO and N₂, and that grain properties and ionization rate are crucial factors for molecular evolution. This is consistent with our findings, but with an additional notion that X-rays further strengthen He⁺ and H⁺ influence on the chemical evolution of turbulent protoplanetary disks.

Later, Woods & Willacy (2007) have investigated the genesis of benzene in protoplanetary disks at \(r \lesssim 35\) AU. They used a D’Alessio-like flaring \(\alpha\)-disk model and considered a passage of a gas parcel from \(>35\) AU onto the central star. They have found that radial transport results in efficient production of benzene at \(\lesssim 3\) AU, mostly due to IM reactions between C₃H₃ and C₄H₄, followed by grain dissociative recombination. These results are very sensitive to the adopted value of C₆H₆ binding energy. Similarly, we find that benzene is produced via the same IM reaction because the surface network is limited for heavy hydrocarbons and does not include surface routes to C₆H₆, whereas the gas-phase production is efficient. Nevertheless, as suggested in Woods & Willacy (2007), C₆H₆ abundances and column densities in the inner disk at 10–30 AU are increased by vertical turbulent diffusion in our model by up to two orders of magnitude (Figure 8).

Nomura et al. (2009), using a disk model with radial advection, studied the evolution of the inner disk region (\(\lesssim 12\) AU). The chemical evolution of gas parcels following various inward trajectories has been calculated. They found that the abundances are sensitive to the transport speed, and that fast transport allows gaseous molecules to reach disk regions where they would
otherwise be depleted. They have concluded that dynamical disk model facilitates synthesis of methanol, ammonia, hydrogen sulfide, acetylene, etc., and predicted the observability of a $J = 3_0-2_0$ methanol line at 145 GHz with ALMA. As we have shown above, our 2D mixing model follows the same trend, with transport enriching the disk with complex species.

**Models of protoplanetary disks: the role of turbulent transport.** Now we compare our results to more closely related studies of disk chemical evolution with turbulent mixing. Ilgner et al. (2004) have investigated the influence of 1D vertical mixing and radial advection on the chemistry of a steady α-disk model, adopting Xie et al. (1995) description of diffusion and Lagrangian description for advective transport (trajectories from 10 to 1 AU). Their key findings are that vertical mixing smoothes vertical abundance gradients, and that local changes in species concentrations due to mixing can be radiatively transported by advection. Ilgner et al. (2004) have concluded that diffusion has a limited effect on the disk regions dominated by gas–grain kinetics, though it enhances abundances of atomic oxygen and thus alters the evolution of related species (SO, SO$_2$, CS, etc.).

Our model, despite being limited to outer disk regions (beyond 10 AU), confirms their results that oxygen abundances are increased by diffusion (Figure 9), further propagating into the chemistry of many related species, particularly sulfur-bearing species such as SO and SO$_2$. We find that turbulent mixing either steepen or soften chemical gradients (e.g., for atomic ions and most of molecules, respectively), and it definitely affects strongly the evolution of species produced via gas-surface kinetics. This result is linked to the adopted set of surface photo- and recombination processes. Obviously, the extended surface reaction network is needed for disk studies, as some conclusions, especially those related to complex organics, do depend on the complexity of the adopted surface chemistry model.

Willacy et al. (2006) have utilized a steady-state α-disk model similar to that of Ilgner et al. (2004) and used the Xie approach to account for disk viscosity. They have studied the impact of 1D vertical mixing on the chemical evolution of the outer disk ($r > 100$ AU). It was found that vertical transport can increase column densities by up to two orders of magnitude. The three-layer disk structure is preserved in the mixing model, albeit depths of many molecular layers are increased. Our results confirm these general findings with the chemical network, which is about three times larger and based on recently updated reaction rates. In contrast to the results of Willacy et al. (2006), we found that the evolution of the ionization degree, ammonia and N$_2$H$^+$ are sensitive to mixing, whereas column densities of CO, H$_2$CO, CN, C$_2$H are steadfast (Tables 5–7). This is because in our model the X-ray irradiation of the disk, production of reactive radicals by photodissociation of ices, and UV photodesorption are taken into account. In the absence of photoevaporation, in the model of Willacy et al. (2006) CO production becomes sensitive to transport of ices from the midplane and atomic C and O from the atmosphere, whereas in our model this is true only for heavy ices with large binding energies ($\lesssim 3000–5000$ K), such as hydrocarbons. Also, our study supports their conclusion that column densities of complex molecules like methanol are greatly enhanced by disk dynamics.

Ilgner & Nelson (2006) have investigated in detail the ionization chemistry in disks at $r < 10$ AU and its sensitivity to various physical and chemical processes, like X-ray flares from a young T Tauri star, vertical mixing, abundances of gas-phase metals, and variations in chemical networks. They found that mixing has no effect on $X(e^-)$ if metals are absent in the gas since recombination timescales are fast, whereas at $X(\text{Me}) \lesssim 10^{-10} – 10^{-8}$ $t_{\text{chem}} > t_{\text{max}}$, and diffusion drastically reduces the size of the “dead” zone. Our extended disk chemical model shows that ionization degree and abundances of charged atoms and molecules are sensitive to transport in disk regions with $r \lesssim 100–200$ AU, and that polyatomic ions are important charge carriers in the disks (see also Semenov et al. 2004). Also, the role of X-ray photons is crucial for the disk ionization fraction and its molecular composition (see also Schreyer et al. 2008; Henning et al. 2010).

Recently, Heinzel et al. (2011) investigated the chemical evolution of a protoplanetary disk along with radial viscous accretion, vertical mixing, and vertical wind transport. The steady-state disk model with $\alpha = 0.01$, $M = 10^{-9}M_\odot$ yr$^{-1}$, and $L_X = 10^{30}$ erg s$^{-1}$ has been adopted.

Heinzel et al. (2011) used the gas–grain RATE06 (Woodall et al. 2007) network, no surface reactions apart from the H$_2$ formation, and the X-ray and UV photochemistry (375 species and about 4350 reactions). They concluded that diffusive mixing smoothes chemical gradients and that abundances of NH$_3$, CH$_3$OH, C$_2$H$_2$ and sulfur-containing species are the most enhanced. This has been related to increased ammonia abundances in the transport model, in which NH$_3$ is effectively produced via gas-phase reactions with more abundant oxygen. In our simulations, temperatures are usually well below 200 K, but we also see that sulfur-bearing molecules are among the most sensitive species to disk dynamics, along with complex organics (such as methanol), hydrocarbons (such as acetylene), and other species (such as ammonia). This is due to their dependence on slow surface processes and evaporation (for heavy gaseous species).

**Future directions of development for disk chemical models.** Overall, there is considerable progress over the last decade in the construction of feasible chemo-dynamical models of the early solar nebula and other protoplanetary disks. It will gain further momentum in light of forthcoming ALMA. In the following, we surmise possible future directions for the development of nebular and protoplanetary disks chemical models.

The inner, planet-forming disk regions accessible to ALMA and subject to disk–planet(s) interactions (gaps, spiral waves, shocks) may well be far from the axial symmetry and require 3D modeling (e.g., Wolf et al. 2002; Fukagawa et al. 2004; Piétu et al. 2005). Full 3D chemo-MHD models of the entire disk evolution within 1–5 Myr are beyond possible even with modern computational resources. Only local 3D models with radically reduced chemistry and a short evolutionary time span of 1000–10,000 yr or semi-analytical models of the entire disk with extended chemistry and $t \sim 1$ Myr will be feasible in the foreseeable future. However, there is still great potential in properly improved simple models.

Similarly, the steady-state disk physical model adopted in the present study needs to be converted to an evolutionary model with consistent calculations of grain evolution (e.g., Birnstiel et al. 2010; Fogel et al. 2011; Vasyunin et al. 2011), photoevaporation (e.g., Gorti et al. 2009), and accurate gas temperature (e.g., Gorti & Hollenbach 2004; Woitke et al. 2009). The accurate opacities of dust and gas covering a wide range of temperatures, densities, gas composition, and dust topological and mineralogical properties will have to be developed (e.g., Semenov et al. 2003; Helling & Lucas 2009) for that purpose. The grain coagulation, fragmentation, and sedimentation lead to redistribution of the total dust surface area, higher ionization rates, and thus to the shift of molecular layers.
toward the midplane, with significant increase of molecular column densities in the intermediate layer and decrease of their depletion zones (Fogel et al. 2011; Vasyunin et al. 2011). In the evolutionary disk models the total disk mass and size, and thus its density, thermal, and ionization structures, change with time, altering conditions in which chemical processes proceed both in the gas phase and on surfaces (Gorti et al. 2009). In evolutionary models covering formation and buildup disk phases, a large amount of gas and dust materials experience heating, cooling, recondensation, annealing, and varying irradiation intensities (e.g., Gail 2002, 2004; Visser et al. 2009b).

A more realistic 2D or full 3D prescription of the X-ray and UV radiation transfer modeling with scattering has to be included. The accurately calculated UV spectrum with the L$_\alpha$ line is vital to compute realistic photodissociation and photoionization rates, and shielding factors for CO and H$_2$ (see, e.g., van Zadelhoff et al. 2003; Bethell et al. 2007; Visser et al. 2009a). The realistic (maybe, variable) stellar X-ray spectrum is required to calculate gas temperature in the disk atmosphere, and for modeling disk ionization structure and IM chemistry (e.g., Glassgold et al. 2005; Meijerink et al. 2008; Aresu et al. 2011). At densities $\lesssim 10^4 - 10^6$ cm$^{-3}$, gas temperature decouples from that of dust, which affects the chemical and dynamical evolution in the upper disk layers (e.g., Kamp & Dullemond 2004; Owen et al. 2011). The dissipation of Alfvenic waves generated by MHD processes inside the disk can also heat gas in the disk atmosphere (e.g., Hirose & Turner 2011).

In comparison to the status of the disk physical structure where many key issues have been realized and partly solved, the advances in modeling disk chemistry are less straightforward. First of all, chemical studies employ various networks fully or partly based on astrochemical ratefiles that have been developed to model distinct astrophysical environments. It is hoped that this will be relieved with the advent of the Kinetic Database for Astrochemistry (KIDA)$^6$ that includes state-of-the-art rate data (Wakelam et al. 2010b). Unfortunately, intrinsic uncertainties in gas-phase reaction rates hamper the accuracy of chemical predictions both on abundances and column densities (see, e.g., Wakelam et al. 2006; Vasyunin et al. 2008; Wakelam et al. 2010a). The pace at which these quantities are measured in laboratories or calculated by quantum chemical models precludes the rapid progress of thousands of astrochemically relevant processes (Savin et al. 2011).

In the inner ($\lesssim 5$ AU) disk regions with $T \gtrsim 100$–300 K and densities exceeding $10^{12}$ cm$^{-3}$ three-body processes, many reverse reactions, and neutral–neutral reactions with large barriers are activated, and have to be fully taken into account (e.g., Aikawa et al. 2002; Tscharnuter & Gail 2007; Harada et al. 2010). The X-ray-driven ionization and dissociation of molecules other than H$_2$ are poorly understood, but important for disk chemistry (e.g., Glassgold et al. 2009). In the upper disk regions, an excess of energy upon gas-phase or surface recombination or ionization/dissociation may translate into (ro-)vibrational excitation of a product molecule, which may then react differently with other species (e.g., Pierce & A'Hearn 2010). This aspect has so far been almost completely neglected in astrochemical models.

In the cool outer disk regions, gas–grain interactions and surface reactions are essential, yet the latter are often disregarded in disk models. The same is true for nuclear-spin-dependent chemical reactions involving ortho- and para-states of key species, such as H$_3^+$, H$_2$, and H$_2$O (e.g., Pagani et al. 1992, 2009; Crabtree et al. 2011). Usually weak physisorption of molecules is considered in chemical models, while molecules can also form chemical bonds with dust surfaces, leading to heterogeneous surface chemistry active both in cold and hot regions, particularly on PAHs and carbonaceous grains (e.g., Fraser et al. 2005; Cazaux et al. 2005; Cuppen & Hornkeær 2008). Despite recent laboratory efforts to measure binding energies of key molecules such as CO, N$_2$, and water to various astrophysical ices and their photodesorption yields, many of these values still lack accurate estimates (Bisschop et al. 2006; Öberg et al. 2009b, 2009a). The dynamics, reactivity, photodissociation, and desorption of ices embedded into dust mantles are hard to measure or to model, and even harder to interpret (see, e.g., results for the water ice; Andersson et al. 2006; Andersson & van Dishoeck 2008; Bouwman et al. 2011). For example, sub-surface diffusion may increase desorption efficiency in the case of well-mixed ices within the H$_2$O ice matrix. Along with thermal, UV-, CRP- and X-ray-triggered desorption (Leger et al. 1985; Najita et al. 2001; Walsh et al. 2010), typically considered in disk chemical studies, other non-thermal mechanisms, such as grain–grain destruction and explosive desorption (Shalabiea & Greenberg 1994) can be operative. The surface recombination on porous grain surfaces or within heterogeneous ices is also non-trivial to accurate modeling (e.g., Cuppen et al. 2009; Fuchs et al. 2009; Ioppolo et al. 2011). The surface chemistry can be restricted to several uppermost monolayers of a grain, while often in chemical models the corresponding rates are calculated assuming it is active everywhere in an ice mantle (e.g., Hasegawa & Herbst 1993). In addition, the presence of large, photostable PAHs in the gas assists synthesis of polyatomic molecules by providing the surface area for surface recombination, ability to re-radiate energy released upon non-destructive ion-PAH recombination, and due to the combustion chemistry in the inner disk region (e.g., Wakelam & Herbst 2008; Kress et al. 2010; Perez-Becker & Chiang 2011). Calculated molecular concentrations depend on the adopted set of elemental abundances, which may vary from region to region, and underlying assumptions about depletion of heavy elements from the gas phase (e.g., Wakelam et al. 2010a).

5.2. Cold Molecules in DM Tau

Even with all the deficiencies listed above, it is instructive to check the feasibility of the present study by comparing our results to available observations of diagnostic molecules and ices in protoplanetary disks and the solar system.

The kinetic temperature distributions have been measured in nearby disks of DM Tau, LkCa 15, MWC 480, and AB Aur by Dartois et al. (2003); Piétu et al. (2005, 2007) and Henning et al. (2010), using the Plateau de Bure Interferometer and (1–0) and (2–1) emission lines of CO isotopologs, HCO$^+$, and C$_2$H. These lines have different optical depths and thus sample gas temperature at various heights above the disk equatorial plane (see Dartois et al. 2003).

In the bright, large 800 AU disk around DM Tau, very cold CO temperatures of $\approx 15$ K at 100 AU have been reported by Dartois et al. (2003), based on the analysis of the PdBI $^{13}$CO (1–0) spectral map. In the later study by Piétu et al. (2007) even lower temperatures of 8 and 15 K probed by the (1–0) and (2–1) transitions of $^{13}$CO, and $T_{\text{kin}} = 14 \pm 2$ K probed by the HCO$^+$ (1–0) line have been derived for the outer DM Tau disk. In contrast, in the same disk, optically thick $^{12}$CO lines give a

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6 http://kida.obs.u-bordeaux1.fr.
kinetic temperature of about 25 K. Henning et al. (2010) found a very low kinetic temperature of ≈7 K for C2H in the DM Tau system, using the CCH (1–0) and (2–1) PdBI data. In E. Chapillon et al. (2011, submitted) similar low values for the CN (1–0) temperatures have been inferred. The presence of gaseous molecules at such low temperatures is puzzling. Evaporation temperatures for CO, C2H, and CN are about 20, 30, and 40 K, respectively, and in dense, dark midplane (T ≈ 10–20 K) they should be rapidly depleted, τacc ≲ 10^3–10^4 yr (Tables 3 and 4).

In Paper I (Semenov et al. 2006), we have tackled the problem of the cold CO gas reservoir in the DM Tau disk using the 1+1D flaring disk model of D’Alessio et al. (1999) with the 2D radial–vertical turbulent diffusion. We have found that the CO column density of about 10^{16} cm^{-2} is required in the disk midplane to explain the puzzling observations of cold CO in DM Tau. Such CO column densities in the disk region with T < 25 K have been obtained in the model with vertical and radial mixing at all radii, while in the laminar model these values only appeared at r ≳ 500 AU. The CO molecules are transported from the warm molecular layer to the cold disk midplane, maintaining large concentration of CO even at late times, t ≳ 10^7–10^8 yr.

Aikawa (2007) used a steady-state α-disk structure and a 1D vertical mixing model to show that the warm CO gas from the intermediate layer can be transported down to the cold midplane at a rate that can be competitive with the CO adsorption rate. The efficiency of this process has been found particularly pronounced for the disk model when moderate grain growth is allowed, with grain sizes ≲ 1 μm.

Later, Hersant et al. (2009), using a disk model with 1D vertical mixing, concluded that the UV desorption of CO and other ices prevails over their upward transport by vertical mixing, leading to large amount of gaseous CO, HCO+, HCN in the midplane even in the laminar model. This is due to the adopted high UV desorption yield of ∼0.1% (e.g., Oberg et al. 2009b) and assumed high UV penetration efficiency caused by the UV scattering onto small dust grains in the disk atmosphere.

In Figure 13, we show the column densities of CO, HCO+, CN, HCN, C2H, and CS at 5 Myr in the disk regions with T < 20 K (odd rows) and T > 20 K (even rows) calculated with the laminar, the slow 2D-, and the fast 2D mixing models. Note that in the inner region at r ≲ 30 AU, kinetic temperatures are higher than 20 K even in the midplane (Figure 1, first panel).

As can be clearly seen, turbulent transport does enhance molecular abundances and column densities in the DM Tau disk midplane for all species except for CS. CO column densities in the midplane region (T < 20 K) are increased by diffusive mixing by two orders of magnitude, to values between 10^{15} and 10^{16} cm^{-2}, but in the laminar model these are also relatively high, ≳ 10^{14} cm^{-2}. As in the study of Hersant et al. (2009), powerful CRP-induced and UV desorption keeps some molecules in the gas phase even in the midplane. Column densities of “warm” CO are much higher, ≳ 10^{18} cm^{-2} and are not affected by the disk dynamics. The amount of cold CO in the mixing model is hardly sufficient for explaining the 13CO PdBI observations of DM Tau. On the other hand, there is enough warm CO to explain the presence of the T ≈ 26 K CO gas derived from the optically thick 12CO data tracing the disk upper region.

HCO+ shows an increase of midplane column densities by up to a factor of 100 in the mixing case, while in the molecular layer its column densities are enhanced by a factor of ≲ 30. The ratio of column densities of warm and cold HCO+ is large, and nearly the same for both the laminar and 2D mixing models, a factor of ≳ 30 and 10–100, respectively. With a typical column density of 10^{13}–10^{14} cm^{-2} at r ≳ 100 AU, the HCO+ (1–0) line
remains optically thin in the outer disk, sampling both the disk midplane and the warm molecular layer.

The critical density for the HCO+ $J = 1$–0 excitation is $\approx 1.5 \times 10^6$ cm$^{-3}$. The region where densities exceed $10^6$ cm$^{-3}$ extends vertically up to $\lesssim 3$ and $1 H_2$ in the inner and outer disks, respectively, and covers the midplane and the molecular layer (see Figure 1). Thus, HCO+ (1–0) emission would originate from the $T > 20$ K disk region, and the resulting temperature derived from this transition would likely exceed 15 K obtained from interferometric observations by Piétu et al. (2007).

The behavior of C$_2$H, CN, and HCN is similar as their chemical evolution is tightly linked (Section 4.4). Their vertical column densities are not much altered by mixing, having a typical value of $\approx 3 \times 10^{13}$–$10^{14}$ cm$^{-2}$ at 100 AU. Since absolute concentrations of C$_2$H, CN, and HCN are highest in the molecular layer where chemical timescales are relatively short, their $T > 20$ K column densities are not strongly increased by diffusion, in fact less than by a factor of three. In contrast, column densities in the midplane ($T < 20$ K) are raised due to transport by an order of magnitude for CN and HCN and by two orders of magnitude for C$_2$H. Resulting column densities through the midplane are $\gtrsim 10^{13}$ cm$^{-2}$. Thus, in the fast 2D mixing model column densities of warm and cold C$_2$H, CN, and HCN differ by only a factor of a few, which further decreases outward. Optically thin 1–0 rotational lines of C$_2$H, CN, and HCN are excited at densities of about $4$–$8 \times 10^6$ cm$^{-3}$. Consequently, in the presence of strong turbulent mixing low-lying transitions of C$_2$H, CN, and HCN likely trace the cold midplane of DM Tau, in agreement with observational evidence.

Turbulent transport decreases CS column densities in the midplane region by a factor of $\lesssim 4$, simultaneously increasing it in the $T > 20$ K zone by up to two orders of magnitude. The chemistry of sulfur-bearing molecules is among the most altered by mixing due to slow surface processes associated with these heavy species (see Section 4.5). However, even in the laminar model, column densities of cold ($T < 20$ K) CS are lower than those of warm ($T > 20$ K) CS by an order of magnitude. The overall CS column densities in the outer disk are $\approx 3 \times 10^{13}$–$3 \times 10^{12}$ cm$^{-2}$, and the low-J CS lines are optically thin. The critical densities of the excitation for the (2–1) and (3–2) CS transitions at 98 and 147 GHz are $\approx 5 \times 10^6$ and $2 \times 10^6$ cm$^{-3}$, respectively. Therefore, kinetic temperatures derived from low-lying CS emission lines should be above 20 K in the DM Tau disk.

Clearly our modeling shows potential for turbulent transport to be a cause for the presence of molecules in the cold midplanes in T Tauri disks. However, the increase in concentrations of cold gases in our 2D mixing model is not strong enough to set aside other explanations. First of all, more accurate modeling of UV scattering toward the midplane would result in faster photoevaporation of ices in the lower molecular layer and upper midplane (van Zadelhoff et al. 2003; Hersant et al. 2009). Second, as mentioned in Aikawa (2007), moderate grain growth beyond 1 $\mu$m in disk central regions lengths the depletion time for molecules so that the gas-phase CO abundances may remain high even after 1 Myr of the evolution. Indeed, Vasyunin et al. (2011) and Fogel et al. (2011) have modeled chemical evolution in disks taking grain evolution into account and found that the grain growth substantially decreases the depletion zones of molecules. From the analysis of the SED slopes in millimeter and centimeter wavelengths, large grain sizes of 1 mm have been inferred for many young systems in various star-forming regions, including the Taurus-Auriga association (e.g., Rodmann et al. 2006; Lommen et al. 2010; Ricci et al. 2010). Recently, Guilloteau et al. (2011) have used high-resolution, multi-frequency interferometric PdBI observations to discern more accurately dust emissivity slopes at millimeter wavelengths in a sample of young stars. Their analysis has indeed shown that the outer disk of DM Tau contains large grains with sizes $\gtrsim 1 \mu$m. We advocate for a combined action of turbulent transport and grain growth as a mechanism for maintaining a sizable reservoir of cold gases in the DM Tau system.

### 5.3. Comparison with Observations

**Molecules in protoplanetary disks.** Some previous studies of the laminar disk chemistry have reported reasonable quantitative agreement with observationally inferred column densities (e.g., Aikawa et al. 2002; Semenov et al. 2005; Dutrey et al. 2007b; Schreyer et al. 2008). On the other hand, radial profiles of column densities derived from high-resolution interferometric data have not been fully reproduced by conventional disk models. In the 1D vertical mixing study of Willacy et al. (2006), the modeling results have been compared with single-dish and interferometric observations of several molecules in the disks around DM Tau, LkCa 15, and TW Hya. The good agreement between theoretical and observed column densities for the mixing model has been inferred from the single-dish data, whereas the interferometric data have not been reproduced. Calculating infrared emission lines for the disk model with radial advective and vertical mixing transport, Heinzel et al. (2011) have shown that it improves agreement with the Spitzer observations of the inner disks around AA Tau, DR Tau, and AS 205, compared to predictions of the laminar chemical model.

We compile column densities at 250 AU derived from the analysis of high-quality PdBI interferometric observations and compare them with the results of our laminar, slow, and fast 2D mixing models in Table 14. Calculated column densities have intrinsic uncertainties of a factor of $\approx 3$–5, caused by reaction rate uncertainties (Vasyunin et al. 2008), whereas observational data suffer from calibration inaccuracies ($\approx 10$–20%), distance uncertainties (10%–20%), etc. Therefore, we assume that the agreement is good when observed and modeled values differ by a factor of $\lesssim 4$. The disk total surface density cannot be accurately derived from the continuum data, as these suffer from poorly known dust opacities at (sub-)millimeter wavelengths that can vary by factors of a few (Semenov et al. 2003). Instead, the observed CO column density distribution can be used as a proxy to the disk gas density structure. The problem in this case is that the $^{12}$CO rotational lines are optically thick and thus probe a limited disk region, whereas from optically thin CO isotopolog lines total CO column densities can only be recovered if $^{12}$C/$^{13}$C or $^{16}$O/$^{18}$O isotope ratios are known. We use $^{13}$CO and $^{12}$CO column densities obtained for the outer DM Tau disk from interferometric observations by Piétu et al. (2007) and adopt a total CO column density at 250 AU of $\approx 3 \times 10^{17}$ cm$^{-2}$. The corresponding theoretical value is almost the same as in the laminar and mixing models, $N$(CO) $\approx 10^{18}$ cm$^{-2}$ (Figure 9). To match this value, modeled column densities in Table 14 were renormalized accordingly.

All the considered models match quite well the observed column densities, apart from the CS data. CS column densities are underpredicted by factors of $\approx 7$–50, though the situation is considerably better for the fast 2D mixing model. A. Dutrey et al. (2011) have observed SO, H$_2$S, and CS in
DM Tau, LkCa 15, and MWC 480 with the IRAM 30 m and PdBI interferometer. They have derived upper limits for H$_2$S and SO in the DM Tau disk at 300 AU, namely, $N$(H$_2$S) $\lesssim 2 \times 10^{11}$ cm$^{-2}$ and $N$(SO) $\lesssim 8 \times 10^{11}$ cm$^{-2}$, whereas CS has been firmly detected with a column density of $N$(CS) $\lesssim 3.5 \times 10^{12}$ cm$^{-2}$. Dutrey et al. have found that the sulfur content of the three disks cannot be explained by modern chemical models as these predict higher abundances for H$_2$S and SO compared to the CS abundances, as is the case in our modeling. While having too little CS, our disk models overproduce column densities of sulfur monoxide and hydrogen sulfide. The reason for such a disagreement, as we discussed in Section 4.5, is that the sulfur chemistry is hampered by poorly known reaction data and may lack key reactions. Depletion of elemental sulfur from the gas is also poorly constrained.

Generally, the fast 2D mixing model produces more molecules per CO compared to the laminar disk chemistry, and overproduces HNC with respect to the observations. The utilized chemical network leads to the synthesis of hydrogen cyanide and isocyanide with almost equal probability in all the disk models, so that their computed ratio does not exceed 1.2. On the other hand, the observed column density of HCN is higher than that of HNC by a factor of $\lesssim 3$. The HCN/HNC ratios are typical for dark, dense cores (Tennekes et al. 2006; (6) Henning et al. 2010). The recent non-detection of cold water vapor in the DM Tau disk by the Herschel/HIFI has been reported by Bergin et al. (2010). They have inferred disk-averaged water column densities $\sim 5 \times 10^{12}$–$3 \times 10^{13}$ cm$^{-2}$. Our calculated disk-averaged H$_2$O column densities are $5 \times 10^{14}$ cm$^{-2}$ and $2 \times 10^{15}$ cm$^{-2}$ in the laminar and fast mixing models, respectively. Therefore, all our models overestimate abundance of gaseous water in DM Tau by a factor of at least 15. Similarly, large values have been obtained in studies of disk chemistry with grain evolution by Vasyunin et al. (2011) and Vogel et al. (2011). Bergin et al. (2010) concluded that to calculate UV penetration utilized in our current disk model make UV opacities too high in the molecular layer that results in HCN/HNC $\sim 1$.

Column densities or upper limits have also been reported for other species. Using the IRAM 30 m antenna, Dutrey et al. (1997) have not been able to detect molecular lines of SiO, SiS, HCN, C$_3$H$_2$, CH$_3$OH, CO$^+$, SO$_2$, HNCS, HCOOCH$_3$ in DM Tau. Among these species, only SiO, C$_3$H$_2$, and SO$_2$ have large modeled column densities (between $10^{12}$ and $10^{13}$ cm$^{-2}$) at 250 AU. SO$_2$ ro-vibrational lines are excited at $T \gtrsim 50$–100 K, so that its emission arises only in an inner disk region ($r \lesssim 5$–10 AU). The linear isomer H$_2$CCC has a large dipole moment of about 4 D and rotational spectrum starting at cm wavelengths. However, the IRAM 30 m observations of TMC1 and IRC +10216 by Cernicharo et al. (1991) have revealed that its abundance is only $\sim 1\%$ of a cyclic isomer. The cyclic isomer has rich ro-vibrational spectrum, with emission lines at (sub-)millimeter wavelengths that are excited at $n_{\text{hit}} \sim 10^6$ cm$^{-3}$ (Schöier et al. 2005). However, due to energy partition the individual lines are not as strong as in the case of HCO$^+$, making them hard to detect. SiO has a dipole moment of 3.1 D and strong rotational lines at (sub-)mm, excited at $\sim 10^6$ cm$^{-3}$ (Schöier et al. 2005). The calculated column density of SiO at 250 AU is $4 \times 10^{12}$ cm$^{-2}$ in the laminar model and $10^{13}$ cm$^{-2}$ in the fast 2D mixing model. These values are sensitive to the abundance of the elemental silicon remaining in the gas and may not be representative of DM Tau in the “low metals” set of initial abundances of Lee et al. (1998a) adopted in our modeling.

The recent non-detection/tentative detection of cold water vapor in the DM Tau disk by the Herschel/HIFI has been reported by Bergin et al. (2010). They have inferred disk-averaged water column densities $\sim 5 \times 10^{12}$–$3 \times 10^{13}$ cm$^{-2}$. Our calculated disk-averaged H$_2$O column densities are $5 \times 10^{14}$ cm$^{-2}$ and $2 \times 10^{15}$ cm$^{-2}$ in the laminar and fast mixing models, respectively. Therefore, all our models overestimate abundance of gaseous water in DM Tau by a factor of at least 15. Similarly, large values have been obtained in studies of disk chemistry with grain evolution by Vasyunin et al. (2011) and Vogel et al. (2011). Bergin et al. (2010) concluded that...
most water ice is trapped in large dust grain aggregates that sedimented toward the DM Tau midplane and thus cannot be easily photodesorbed. However, if this were the case, other molecules such as CO and CN would be depleted from the gas phase much more severely, and should not be present in molecules such as CO and CN would be depleted from the sedimented toward the DM Tau midplane and thus cannot be present in

| Species        | Relative Abundance | Ref. | 10 AU | 20 AU | 30 AU |
|---------------|-------------------|------|-------|-------|-------|
| H$_2$O        | 100               | 100  | 100   | 100   |       |
| CO            | 5–30              | (1, 2, 3, 4) | <0.01 | 0.7   | 1.6   |
| CO$_2$        | 3–20              | (1, 4) | 10    | 20    | 0.6   |
| H$_2$CO       | 0.04–1            | (1, 2, 3, 4) | 0.02  | 0.015 | <0.01 |
| CH$_3$OH      | 2                 | (2, 3, 4) | <0.01 | <0.01 |
| HCOOH         | 0.06–0.09         | (3, 4) | 0.02  | 0     | 0     |
| HCOOCH$_3$    | 0.06–0.08         | (3, 4) | 0     | 0     | 0     |
| CH$_4$        | 0.6–5             | (1, 3, 4) | 0    | 40    | 30    |
| C$_2$H$_2$    | 0.1–0.5           | (3, 4) | 0     | 0     | 0     |
| C$_2$H$_6$    | 0.3–0.4           | (3, 4) | 0.07  | 0     | 0     |
| NH$_3$        | 0.1–2             | (1, 3, 4) | 33   | 20    | 15    |
| HCN           | <0.25             | (1, 2, 3, 4) | 12    | 3.6   | 0.5   |
| HNC           | 0.01–0.04         | (4, 4) | 0.5   | 0.02  | 0     |
| HNCO          | 0.06–0.1          | (3, 4) | 0     | 0     | 0     |
| N$_2$         | ~0.02             | (1)   | 0     | 0     | 0     |
| CH$_3$CN      | 0.01–0.02         | (3, 4) | 0     | 0     | 0     |
| H$_2$CN       | 0.02              | (3, 4) | 0.003 | 0     | 0     |
| NH$_2$CHO     | 0.01–0.02         | (3, 4) | 0     | 0     | 0     |
| H$_3$S        | 0.75–1.5          | (1, 2, 3, 4) | 0.15  | 0.09  | 0.06  |
| CS            | ~0.1              | (2)   | 0     | 0     | 0     |
| SO            | 0.2–0.8           | (1, 3, 4) | 0     | 0     | 0     |
| SO$_2$        | 0.1–0.2           | (1, 3, 4) | 0     | 0     | 0     |
| OCS           | 0.1–0.4           | (1, 3, 4) | 0     | 0     | 0     |
| H$_2$CS       | 0.02              | (3, 4) | 0.006 | 0     | 0     |
| S$_2$         | 0.005             | (4)   | 0     | 0     | 0     |

References. (1) Aikawa et al. 1999; (2) Biver et al. 1999; (3) Bockelé-Morvan et al. 2000; (4) Crovisier & Bockelé-Morvan 1999.

5.4. Observable Molecular Tracers of Dynamical Processes

In Table 16, we show the most promising tracers of transport processes in protoplanetary disks as found with our modeling. The quantity least biased by observational and modeling uncertainties is the ratio of the column density of an abundant steadfast species to that of a hypersensitive molecule. Among insensitive species (Table 5) the most promising are CO and water ice, since these terminal species incorporate substantial fractions of the elemental carbon and oxygen, and are easy to observe. Concentrations of C$^+$, light hydrocarbons, CN, HCN, and HNC are sensitive to the stellar X-ray and UV radiation rather than to mixing (e.g., Fogel et al. 2011; Aresu et al. 2011; Kamp et al. 2011). Other molecules and ices unresponsive to mixing have low abundances or are significantly model-dependent (e.g., S-bearing ices).

Among species sensitive and hypersensitive to turbulent transport (Tables 6 and 7) the most promising are gaseous and solid heavy hydrocarbons, C$_2$S, C$_3$S, SO, SO$_2$, CO$_2$, and complex organic molecules (e.g., HCOOH). Basically, any non-terminal, abundant molecule produced mostly via grain-surface reactions can be used as a tracer of dynamical transport in protoplanetary disks. The OH$^+$ and H$_2$O$^+$ ions are sensitive to the disk ionization structure and thus cannot be reliable tracers of turbulent mixing. Gas-phase molecules actually detected in disks are warm CO$_2$ at IR (e.g., Salyk et al. 2011) and SO at millimeter wavelengths (Fuente et al. 2010). Rotational lines of C$_2$S, C$_3$S and various hydrocarbons and hydrocarbon anions

Table 15

| Species        | Ref. | 10 AU | 20 AU | 30 AU |
|---------------|------|-------|-------|-------|
| CO            | 5–30 |       |       |       |
| CO$_2$        | 3–20 |       |       |       |
| H$_2$CO       | 0.04–1 |       |       |       |
| CH$_3$OH      | 2     |       |       |       |
| HCOOH         | 0.06–0.09 |       |       |       |
| HCOOCH$_3$    | 0.06–0.08 |       |       |       |
| CH$_4$        | 0.6–5 |       |       |       |
| C$_2$H$_2$    | 0.1–0.5 |       |       |       |
| C$_2$H$_6$    | 0.3–0.4 |       |       |       |
| NH$_3$        | 0.1–2 |       |       |       |
| HCN           | <0.25 |       |       |       |
| HNC           | 0.01–0.04 |       |       |       |
| HNCO          | 0.06–0.1 |       |       |       |
| N$_2$         | ~0.02 |       |       |       |
| CH$_3$CN      | 0.01–0.02 |       |       |       |
| H$_2$CN       | 0.02 |       |       |       |
| NH$_2$CHO     | 0.01–0.02 |       |       |       |
| H$_3$S        | 0.75–1.5 |       |       |       |
| CS            | ~0.1 |       |       |       |
| SO            | 0.2–0.8 |       |       |       |
| SO$_2$        | 0.1–0.2 |       |       |       |
| OCS           | 0.1–0.4 |       |       |       |
| H$_2$CS       | 0.02 |       |       |       |
| S$_2$         | 0.005 |       |       |       |

Table 16

| Steadfast | Hypersensitive |
|----------|---------------|
| H$_2$O ice | C$_2$S |
| CO        | C$_3$S |
| O$_2$     | SO |
| OCS       | SO$_2$ |
| OCS       | OCN |
| Complex organics (e.g., HCOOH) | |
have been detected in cold dense cores (e.g., Dickens et al. 2001; Kalenski et al. 2004; Sakai et al. 2010). The emission lines of SO, SO₂, and several organic molecules have been identified in submillimeter spectra of young stellar objects (e.g., Jørgensen et al. 2005). CO₂ ice feature at 15.2 μm has been detected in molecular clouds (e.g., Kim et al. 2011) and toward embedded young low-mass stars (e.g., Pontoppidan et al. 2008b). In addition, a plethora of other ices such as CH₄, SO₂, HCOOH, H₂CO, and CH₃OH have been observed in Class I/II objects (e.g., Zasowski et al. 2009). This gives hope that they can be observed in disks as well.

In the future forthcoming observational facilities such as ALMA, expanded VLA, and James Webb Space Telescope will allow us to observe many of the mixing tracers along with CO and water ice in nearby protoplanetary disks of various ages, masses, and sizes, and testify our predictions.

6. SUMMARY AND CONCLUSIONS

We study the influence of dynamical processes on the chemical evolution of protoplanetary disks. Our analysis is based on the 2D flared models of η-5 Myr DM Tau disk coupled to the large-scale gas–grain chemical code. To account for the production of complex molecules, the chemical network is supplied with a set of surface reactions (up to HCOOH, CH₃OH, CH₃OCH₃, etc.) and photoprocessing of ices. Our model disk covers a wide range of radii, 10–800 AU, and includes both warm planet-forming zone and cold outer region. Turbulent transport of gases and ices is modeled using the mixing-length approximation in full 2D (based on the α-prescription for viscosity). Since turbulent transport efficiency of molecules in disks is not well known, we consider two dynamical models with Schmidt numbers of 1 and 100. We come up with a simple analysis for laminar chemical models that allows to highlight the potential sensitivity of a molecule to turbulent transport. With our chemo-dynamical models, we find that turbulent transport influences abundances and column densities of many gas-phase species and especially ices. The results of the chemical model with reduced turbulent diffusion are much closer to those from the laminar model, but not completely. Mixing is important in disks since a chemical steady state is not reached for many species due to long timescales associated with surface chemical processes and slow evaporation of heavy molecules (t ≳ 10⁵ yr). When a grain with an icy mantle is transported from a cold disk midplane into a warm intermediate/inner region, raising the temperature makes heavy radicals mobile on the dust surface, enriching the mantle with complex ices, that can be released into the gas. In contrast, simple radicals and molecular ions, in which chemical evolution proceeds solely in the gas phase, are not much affected by the dynamics. We divide all molecules into three distinct groups with respect to the sensitivity of their column densities to the diffusive mixing. The molecules that are unresponsive to dynamical transport include such observed and potentially detectable molecules as C₂H, C³, CH₄, CN, CO, HCN, HNC, H₂CO, OH, as well as water and ammonia ices. Their column densities computed with the laminar and fast 2D mixing model do not differ by more than the factor of 2–5 (“steadfast” species). The molecules in which the vertical column densities in the laminar and dynamical models differ by no more than two orders of magnitude include, e.g., C₂S, C₂S, C₆H₆, CO₂, O₂, SiO, SO, SO₂, long carbon chain ices, CH₂CHO ice, HCOOH ice, O₂ ice, and OCN ice (“hypersensitive” species). The sulfur-bearing molecules, along with polyatomic (organic) molecules frozen onto dust grains, are among the species most sensitive to turbulent mixing. The chemical evolution of assorted molecules in the laminar and turbulent models is thoroughly analyzed and compared with previous studies. We find that observed column densities in the DM Tau disk are well reproduced both by the laminar and the mixing disk models. The observed abundances of reduced and oxidized cometary ices are also successfully reproduced in both the models. We propose several observable or potentially detectable tracers of dynamical processes in protoplanetary disks, e.g., ratios of the CO₂/O₂, SO/SO₂, C₂S/C₂S column densities to that of CO and the water ice. Some of these tracers have been observed in disks by current radio-interferometric and infrared facilities (e.g., PDBI, SMA, Spitzer, Keck, VLT) and some will be targeted by the Herschel telescope. The detection of complex species (e.g., dimethyl ether, formic acid, methyl formate, etc.) in protoplanetary disks with ALMA and JWST will be a strong indication that chemical evolution of these objects is influenced by transport processes.

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