

Chemical Evolution of a Protoplanetary Disk

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Abstract. In this paper we review recent progress in our understanding of the chemical evolution of protoplanetary disks. Current observational constraints and theoretical modeling on the chemical composition of gas and dust in these systems are presented. Strong variations of temperature, density, high-energy radiation intensities in these disks, both radially and vertically, result in a peculiar disk chemical structure, where a variety of processes are active. In hot, dilute and heavily irradiated atmosphere only the most photostable simple radicals and atoms and atomic ions exist, formed by gas-phase processes. Beneath the atmosphere a partly UV-shielded, warm molecular layer is located, where high-energy radiation drives rich ion-molecule and radical-radical chemistry, both in the gas phase and on dust surfaces. In a cold, dense, dark disk midplane many molecules are frozen out, forming thick icy mantles where surface chemistry is active and where complex polyatomic (organic) species are synthesized. Dynamical processes affect disk chemical composition by enriching it in abundances of complex species produced via slow surface processes, which will become detectable with ALMA.

Keywords. accretion disks, astrochemistry, diffusion, line: formation, molecular processes, protoplanetary disks, submillimeter, techniques: interferometric, turbulence

1. Introduction

Protoplanetary disks (PPDs) are ubiquitous around young stars (e.g., Lin & Papaloizou 1980; Lissauer 1987). Their chemical composition and physical properties regulate the efficiency and timescale of planet formation. Molecules and dust serve as heating and cooling agents of the gas, while dust grains also dominate the disk opacities. Molecular lines observed at infrared and (sub-)millimeter wavelengths are useful probes of physical conditions (temperature, density, kinematics, turbulence) in PPDs.

Over the past decade significant progress has been achieved in our understanding of disk chemical composition, both theoretically and observationally. Since molecular hydrogen is not observable when it is cold, we have to rely on other trace species to infer disk physics and chemistry (Table 1). Multi-molecule, multi-transition interferometric observations, coupled to line radiative transfer and chemical modeling, allowed to constrain disk sizes, kinematics, distribution of temperature, surface density, and molecular column densities (see reviews by Bergin *et al.* (2007) and Dutrey *et al.* (2007a)).

Observations of thermal dust emission are employed to constrain dust properties, infer disk masses, whereas IR spectroscopy is used to study mineralogical composition of dust in PPDs. Recently, with space-borne (*Spitzer*) and ground-based (Keck, VLT, Subaru) infrared telescopes, molecules have been detected in very inner zones of planet-forming systems, at $r \lesssim 1 - 10$ AU.

The conditions of planets formation in the early Solar system have been revealed by a detailed analysis of chemical and mineralogical composition of meteoritic samples and cometary dust particles (e.g., Bradley 2005). The recent *Stardust* and *Genesis* space missions have returned first samples of pristine materials, likely of cometary origin, showing a complex structure of high-temperature crystalline silicates embedded in low-temperature

Table 1. Molecular species commonly utilized to study disks

Tracer	Quantity	Midplane	Molecular layer	Atmosphere	Inner zone
^{12}CO , ^{13}CO	Temperature	mm*	mm	mm	IR
H_2	—	0	0	0	IR
NH_3	—	cm	cm	0	0
CS , H_2CO	Density	0	mm	0	IR
CCH , HCN , CN	Photochemistry	0	mm	0	IR
HCO^+	Ionization	0	mm	0	0
N_2H^+	—	mm	0	0	0
C^+	—	0	0	IR	IR
complex organics	Surface processes	IR**	IR-cm	0	IR,mm
DCO^+ , DCN , H_2D^+	Deuterium fractionation	mm	mm	0	0

* – “mm/cm” and “IR” mean radio-interferometric and infrared observations, respectively.

** – Complex molecules frozen onto dust surfaces could be detected through absorption lines in infrared, while the gas-phase counterparts emit at (sub-) millimeter frequencies.

condensates (Brownlee *et al.* 2004; Flynn *et al.* 2006; Brownlee *et al.* 2008). The presence of crystalline silicates in 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 Myr of evolution (e.g., Boss 2004; Ciesla 2009).

These intriguing findings are partly understood in modern astrochemical models of protoplanetary disks (Aikawa & Herbst 1999; Markwick *et al.* 2002; van Zadelhoff *et al.* 2003; Tscharnuter & Gail 2007; Agúndez *et al.* 2008; Woods & Willacy 2009; Visser *et al.* 2009b; Walsh *et al.* 2010; Semenov & Wiebe 2011). The major result of the chemical modeling is that disks have a layered chemical structure due to heavy freeze-out of gas-phase molecules in the cold midplane and their photodissociation in the atmosphere. Observed column densities of CO , HCO^+ , N_2H^+ , CN , HCN , HNC , CS , etc. are qualitatively agree with the chemical models.

In this paper we briefly review the major observational findings and modeling predictions for the chemical composition and evolution of protoplanetary disks.

2. Observational constrains on composition of gas and ices

Apart from CO and its isotopologues, and occasionally HCO^+ , DCO^+ , CN , HCN , DCN , CCH , H_2CO , and CS , the molecular content of protoplanetary disks remains largely unknown (e.g., Dutrey *et al.* 1997; Kastner *et al.* 1997; Aikawa *et al.* 2003; Thi *et al.* 2004; Piétu *et al.* 2007; Qi *et al.* 2008; Henning *et al.* 2010). Molecular line data are limited in sensitivity and resolution. Thus the spatial distribution of molecular abundances is still poorly determined (e.g., Piétu *et al.* 2005; Dutrey *et al.* 2007b; Panić *et al.* 2009). Observational facilities such as the Plateau de Bure interferometer (France) and Submillimeter Array (USA) have permitted measurements of several brightest nearby disks (DM Tau, LkCa 15, AB Aur, and TW Hya). Soon, with the Atacama Large Millimeter Array entering its full power in 2013, we will make substantial progress in our knowledge of molecular disk structure.

Typically, studies of disk physics begin with observations of bright CO lines. These lines are thermally excited at densities $\sim 10^3 - 10^4 \text{ cm}^{-3}$. The ^{12}CO lines are optically thick and

their intensities measure kinetic temperature in the upper disk layer (e.g., Dutrey *et al.* 1997). The lines of less abundant ^{13}CO and C^{18}O are typically optically thin or partially optically thick and are sensitive to both temperature and corresponding column densities throughout the entire disk. Strong CO lines are most suitable for accurate determination of disk kinematics as well as orientation and geometry. Their measured widths indicate that turbulence in disks is subsonic, with typical velocities of about $0.05 - 0.2 \text{ km s}^{-1}$ (Dutrey *et al.* 2007a; Semenov *et al.* 2010a; Hughes *et al.* 2011).

It has been found that disks appear progressively larger from observations of dust continuum, onwards to C^{18}O , ^{13}CO , and ^{12}CO , respectively, with typical values of $300 - 1000 \text{ AU}$. This is a manifestation of selective isotopic photodissociation. Most disks exhibit a vertical temperature gradient, ranging from $\sim 10 \text{ K}$ at the midplane to $\sim 50 - 100 \text{ K}$ in the atmosphere region, as determined by physical models (e.g., Dartois *et al.* 2003; Qi *et al.* 2006; Piétu *et al.* 2007; Isella *et al.* 2010), though several disks with large inner cavities do not show evidence for such a gradient (e.g., GM Aur and LkCa 15; Dutrey *et al.* 2008; Hughes *et al.* 2009).

By comparing intensities of 6-5 to 2-1 CO transitions it was found by Qi *et al.* (2006) that the TW Hya disk has a surface region that is superheated, so that an additional heating mechanism is required, possibly stellar X-ray radiation (Glassgold *et al.* 1997). A significant reservoir of very cold CO, HCO^+ , CN and HCN gases has been found in the disk of DM Tau at temperatures $\lesssim 6\text{-}17 \text{ K}$, 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).

The second most readily observed molecular species in disks is HCO^+ . The low-lying transitions of this ion are thermalized at densities of about 10^5 cm^{-3} . This is one of the most abundant charged molecule in disks, the other being C^+ (not observable at millimeter wavelengths) and H_3^+ (lacking dipole moment). The ionization degree measured from HCO^+ is $\sim 10^{-10} - 10^{-9}$ inside warm molecular disk layer (Qi *et al.* 2003; Dutrey *et al.* 2007b).

Less strong lines of C_2H , CN, and HCN are sensitive to the intensity and shape of the incident UV spectrum and are excellent tracers of photochemistry (e.g., Bergin *et al.* 2003a). Recently detected DCO^+ and DCN have abundances that are about $1 - 10\%$ of the HCO^+ and HCN densities (Qi *et al.* 2008). It remains to be verified whether such a large degree of deuteration is a heritage of cloud chemistry or produced *in situ*.

A key observational result is that molecular abundances are depleted by factors 5-100 compared to the values in the Taurus Molecular Cloud (Dutrey *et al.* 2007a). Since disks have higher densities up to $10^7 - 10^{10} \text{ cm}^{-3}$ and enshrouded in stronger ionizing radiation fields, this depletion can be attributed to a combined effect of photodissociation and freeze-out.

The results from the Infrared Space Observatory and Spitzer telescope have proven the existence of a significant amount of frozen material and various types of silicates and polycyclic aromatic hydrocarbons (PAH) in disks (van den Ancker *et al.* 2000; van Dishoeck 2004; Bouwman *et al.* 2008). The PAH features at $\sim 3\text{-}12\mu\text{m}$ probe the incident radiation field and density distribution of the upper disk (e.g., Habart *et al.* 2004). Recently, with space-borne (*Spitzer*) and ground-based (Keck, VLT, Subaru) infrared telescopes, molecules have been detected in very inner zones of planet-forming systems, at $r \lesssim 1 - 10 \text{ AU}$. Rotational-vibrational emission lines from CO, CO_2 , C_2H_2 , HCN, OH, H_2O 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; Pontoppidan *et al.* 2008; Pascucci *et al.* 2009; van der Plas *et al.* 2009; Salyk *et al.* 2011). Through *ISO* and *Spitzer* infrared spectroscopy abundant ices in cold disk regions

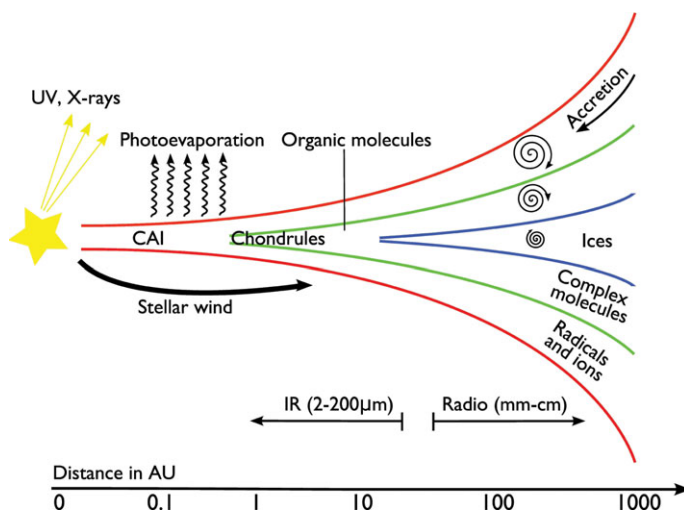


Figure 1. Physical and chemical structure of a protoplanetary disk. Timescales are rough estimates and given for a radius of about 100 AU.

consisting of water ice and substantial amounts ($\sim 1 - 30\%$) of volatile materials like CO, CO₂, NH₃, CH₄, H₂CO, and HCOOH have been detected (e.g., Pontoppidan *et al.* 2005; Terada *et al.* 2007; Zasowski *et al.* 2009).

In Table 1 the various molecules used to study protoplanetary disks are summarized.

3. Global evolutionary picture of disk chemical structure

The current scheme of the disk chemical structure is presented in Fig. 1. The disk can be divided into 4 distinct chemical regions, primarily determined by temperature. The warm “inner zone” corresponds to radii < 20 AU that are accessible with the IR instruments, while the other 3 regions dubbed “midplane”, “molecular layer”, and “atmosphere” represent the outer disk regions ($r > 20 - 50$ AU) that are observed with radio-interferometers.

Dense midplane is opaque to the UV and X-ray radiation and remains cold and essentially neutral (10 – 20 K). Chemical complexity in this region is initially reached by fast ion-molecular reactions in the gas, followed by slow accretion onto grains and surface reactions (mostly hydrogenation). Once formed, a molecule is seldom re-emitted into the gas phase. Typical chemical timescales for this region are determined by freeze-out and surface reactions, and are $> 10^5 - 10^6$ years in the outer disk. In the very inner part, the midplane is hot due to viscous accretion heating ($T \gtrsim 50$ K) and gas-grain interactions are not important, so the chemical timescale is due to gas-phase neutral-neutral reactions (~ 100 years). The planet-forming zone is in general in a chemical steady-state, which allows the application of simple condensation/evaporation thermodynamical chemical models.

Adjacent to the midplane lies a less dense, warmer layer ($T \sim 30 - 70$ K) that is partly shielded from stellar and interstellar UV/X-ray radiation. Young stars emit intense non-thermal UV and thermal and variable X-ray radiation fields that strongly mediate disk chemistry at intermediate heights (e.g., Bergin *et al.* 2007). UV excess in T Tauri stars is related to their chromospheric activity (e.g., Bouvier *et al.* 2007). Soft X-ray radiation

Table 2. Chemical reactions active in disks

Process	Formula	Midplane	Molecular layer	Atmosphere	Inner zone
Bond formation					
Radiative association	$A + B \rightarrow AB + h\nu$	X	X	X	X
Surface formation	$A + B _{gr} \rightarrow AB + gr$	X	X	0	0
Three-body	$A + B + M \rightarrow AB + M$	0	0	0	X
Bond destruction					
Photodissociation	$AB + h\nu \rightarrow A + B$	0	X	X	X
Dissociation by CRP	$AB + CRP \rightarrow A + B$	X	X	0	0
Dissociation by X-rays	—	0	X	X	X
Dissociative recombination	$AB^+ + e^- \rightarrow A + B$	X	X	X	X
Bond restructuring					
Neutral-neutral	$A + BC \rightarrow AB + C$	X	X	0	X
Ion-molecule	$A^+ + BC \rightarrow AB^+ + C$	X	X	X	X
Charge transfer	$A^+ + BC \rightarrow A + BC^+$	X	X	X	X
Unchanged bond					
Photoionization	$AB + h\nu \rightarrow AB^+ + e^-$	0	X	X	X
Ionization by CRP	$AB + CRP \rightarrow AB^+ + e^-$	X	X	0	0
Ionization by X-rays	—	0	X	X	X

has likely the same origin, while harder X-rays are produced in magnetic reconnection loops or due to jets (e.g., Güdel & Nazé 2009).

These energetic photons dissociate and ionize gas and photodesorb surface species, thus enriching the gas composition and initiating a rich chemistry. Abundances of most molecules attain high concentrations in this zone, and numerous molecular lines are excited and observable emission produced. Chemistry does not reach a steady state in this region and a typical timescale, as determined by surface chemistry and gas-grain interactions, exceeds 10^5 years.

Above the intermediate layer a hot, dilute, and heavily irradiated disk atmosphere exists ($T \gtrsim 100$ K). This is a molecularly-poor region, where only simple light hydrocarbons, their ions, and other radicals such as CCH and CN are able to survive. Chemical timescales are short (~ 100 years) and defined by photochemical processes and dissociate recombination.

4. Gas-phase chemistry

Models of chemical evolution employ a set of chemical reactions of relevance to conditions in disks. Modern astrochemical databases include up to 600 species involved in 4-7000 reactions (Smith *et al.* 2004; Le Petit *et al.* 2006; Woodall *et al.* 2007; Wakelam 2009). Only 10 – 20% of reaction rates have been studied in the laboratory or calculated theoretically and thus models are prone to inherent uncertainties (see, e.g., Wakelam *et al.* 2010). All reactions can be divided into 4 distinct groups that are dominant in different disk regions, see Table 2 (after van Dishoeck & Black 1988).

Apart from the very dense inner zone, all reactions in disks are two-body processes. Three-body reactions become competitive only at $\lesssim 10$ AU, where $n \gtrsim 10^{10}$ cm $^{-3}$ (Aikawa *et al.* 1999). The main processes leading to formation of molecular bonds are slow radiative association and surface reactions. Upon collision, a collisional complex

in an excited state may form, which is stabilized with a low probability by emission of a photon (e.g., Bates 1951; Williams 1972; Herbst & Klemperer 1973). For example, formation of light hydrocarbons starts with radiative association of C^+ and H_2 , leading to excited CH_2^+ (Herbst 1985).

Ionized by FUV, X-ray photons or CRPs, ions and molecule drive rapid ion-neutral chemistry, which constitutes the largest fraction of astrochemical models. These reactions are exothermic, with high rate coefficients $\sim 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$, which often increase toward low temperatures ($\beta < 0$) (e.g., Dalgarno & Black 1976). Ion-neutral reactions result in bond restructuring of the reactants. Some of the most important reactions of this category are protonation reactions.

Molecular ions are destroyed by dissociative recombination with electrons and negatively charged grains. These processes are especially fast at low temperatures, with typical rates of about $10^{-7} \text{ cm}^{-3} \text{ s}^{-1}$ at 10 K (Woodall *et al.* 2007). For nearly all observed species, dissociative recombination is an important formation pathway (e.g., water and hydrocarbons). Often, at later evolutionary times, $\gtrsim 10^5$ years, dissociative recombination is balanced by protonation reactions, e.g. $CO + H_3^+ \rightarrow HCO^+ + H_2$ followed by $HCO^+ + e^- \rightarrow CO + H$. Products and branching ratios for polyatomic ions are not easily obtainable (e.g., Bates & Herbst 1988; Spanel & Smith 1994).

A number of neutral-neutral reactions involving open-shell radicals can also be active in both cold outer and warm inner disk regions (van Dishoeck 1998). The typical rate coefficient for these reactions is $\sim 10^{-11}$ – $10^{-10} \text{ cm}^{-3} \text{ s}^{-1}$, i.e., only about an order of magnitude lower than for the ion-molecule processes (e.g., Clary *et al.* 1994; Smith *et al.* 2004). One of the most interesting reactions of this type is formation of HCO^+ upon collision between O and CH ($\alpha_0 = 2.0 \cdot 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$; Woodall *et al.* 2007).

5. Photochemistry

The photochemical reactions are overviewed in this book in the paper by van Dishoeck & Visser and only briefly discussed here.

Young T Tau stars ($T_{\text{eff}} \simeq 4000 \text{ K}$) emit intense non-thermal UV radiation that has a spectra different from the interstellar UV field (Bergin *et al.* 2003a), with a prominent Lyman- α line, while hot ($T_{\text{eff}} \gtrsim 10000 \text{ K}$) Herbig Ae/Be stars produce a lot of thermal UV emission. The overall intensity of the stellar UV radiation at 100 AU from the star can be as high as 500 and 10^5 for a T Tau and a Herbig Ae star, respectively, in units of the interstellar UV field (Habing 1968).

Many molecules, such as CO, H_2 , and CN, are dissociated by radiation at short wavelengths ($\lambda \lesssim 1100 \text{ \AA}$), while photodissociation of other species, such as HCN, occurs at longer wavelengths (van Dishoeck & Black 1988; van Dishoeck *et al.* 2006). Some molecules (e.g., H_2 and CO) dissociate via absorption of UV photons at discrete lines to the excited (Rydberg) states, whereas other molecules are dissociated either by the continuum (e.g., CH_4) or by the continuum and lines (e.g., C_2) (van Dishoeck 1988; van Dishoeck *et al.* 2006). The high ratio of CN to HCN abundances, observed in disks (Dutrey *et al.* 1997), can be explained by more intense photodissociation of HCN if part of the UV flux comes as Ly- α photons (1216 Å; Bergin *et al.* 2003a).

Since the dissociation of the abundant H_2 and CO molecules result from photoabsorption at discrete wavelengths, isotopically selective photodissociation based on self-shielding is possible (e.g., Visser *et al.* 2009a). Two conditions for that are required: 1) dissociation via line absorption for each isotopically substituted molecule, and 2) differential photolysis that depends upon the isotopic abundances. Self-shielding occurs when the spectral lines leading to dissociation of the major isotopic species optically saturate,

while the other residual lines relevant for dissociation of the minor isotopes remain transparent. Under conditions of protoplanetary disks, isotopic-selective chemistry may occur for abundant CO molecules (e.g., Dalgarno & Stephens 1970; Thieme & Heidenreich 1983; van Dishoeck & Black 1988; Lee *et al.* 1996; Visser *et al.* 2009a).

6. Gas-grain interactions

In cold disk regions grains serve as a passive sink for heavy molecules and electrons, while providing free electrons to dissociate positive ions. In the darkest midplane zone dust grains become the dominant charged species (Semenov *et al.* 2004). At low temperatures of $\lesssim 20 - 50$ K, many molecules adhere to a grain with a nearly 100% sticking probability since their kinetic energy is much smaller than the binding energy (see, e.g., d'Hendecourt *et al.* 1985; Buch & Zhang 1991). This sticking probability also depends on surface properties, such as porosity and distribution of surface chemi- and physisorption sites. Chemisorption requires formation of a chemical bond between a surface species and a grain, and such a species does not evaporate easily (e.g., Cazaux *et al.* 2005).

The most effective desorption processes for disk chemistry are thermal evaporation, cosmic ray induced desorption, and photodesorption. Thermal evaporation occurs if a molecule has energy that exceeds its binding energy. Typical binding energies of physisorbed species are about 1000 K for light molecules like CO and N₂ (Bisschop *et al.* 2006), and much larger for heavier cyanopolyynes and carbon chains. Chemisorbed species do not desorb until very high temperatures of 100 – 1000 K are reached.

In disk midplane CRPs provide energy that allows dust mantles (partly) thermally evaporate. A relativistic iron nucleus may eventually collide with a grain and impulsively heat it, releasing a portion of the volatile component (e.g., Watson & Salpeter 1972; Leger *et al.* 1985; Hartquist & Williams 1990). In less opaque disk regions, penetrating UV photons lead to photoevaporation of surface species. The probability of evaporation per one UV photon has been measured in the laboratory for some simple molecules, such as CO, H₂O, CH₄, and NH₃, and is about $10^{-6} - 10^{-2}$ (e.g., Öberg *et al.* 2007, 2009b,a). The dilute UV radiation field produced by cosmic rays in the disk midplane (Prasad & Tarafdar 1983) can also be important for high values of the photodesorption rates. Another mechanism is the X-ray induced desorption which is efficient only for tiny grains, $\lesssim 0.05 \mu\text{m}$ (Najita *et al.* 2001).

7. Surface formation of complex species

The surfaces of dust grains serve as a catalyst for reactions that do not proceed efficiently in the gas phase. The most notable example is formation of molecular hydrogen, which occurs almost entirely on dust surfaces (e.g., Hollenbach & Salpeter 1971; Watson & Salpeter 1972). Tielens & Hagen (1982) have studied the chemical evolution of surface species on large grains and considered the effect of various migration rates for light atoms and heavy molecules. A typical $0.1 \mu\text{m}$ amorphous silicate grain accommodates $\sim 10^6$ surface sites available for accretion. An atom or light radical, if it is not chemisorbed, may migrate over the surface from site to site by thermal hopping, when its energy exceeds the barriers for particle motions and react with other species.

There is an increasing body of evidence from laboratory measurements that complex molecules like methanol cannot be produced in the gas phase via radiative association forming a large protonated precursor followed by its dissociative recombination (Geppert *et al.* 2005). Thus, surface reactions due to thermal hopping remain the only viable

formation pathway for production of complex (organic) molecules in protoplanetary disks, found also in meteoritic samples in Solar system.

8. Importance of dynamical processes for disk chemistry

While most of the chemical studies are still based on laminar disk models, evidences for mixing call for a more sophisticated treatment. 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). Ilgner *et al.* (2004) for the first time 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 1D vertical mixing modifies chemical composition of the outer disk region and that the mixing results better agree to observations. Semenov *et al.* (2006, Paper I) and Aikawa (2007) have found that turbulent transport allows explaining the presence of a large amount of cold ($\lesssim 15$ 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. 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). Hersant *et al.* (2009) have studied various mechanisms to retain gas-phase CO in very cold disk regions. They concluded that efficient photodesorption in moderately obscured disk regions ($A_V < 5^m$) greatly enhances gas-phase CO concentrations, while the role of vertical mixing is less important. Finally, Heinzeller *et al.* (2011) have investigated the disk chemical evolution with radial advection, vertical mixing, and vertical wind transport processes. They have found that the disk wind has a negligible effect on disk chemistry, whereas the radial accretion alters the molecular abundances in the cold midplane, and the vertical turbulent mixing affects the chemistry in the warm molecular layer.

We study the influence of turbulence mixing on the chemical evolution of protoplanetary disks in Semenov & Wiebe (2011). Mixing is important in disks since a chemical steady-state is not reached due to long timescales associated with surface chemical processes and slow evaporation of heavy molecules. Our analysis was based on the α -model of a ~ 5 Myr DM Tau disk coupled to the large-scale gas-grain chemical code “AL-CHEMIC” (Semenov *et al.* 2010b). To account for production of complex molecules, our chemical network was supplied with a set of surface reactions and photoprocessing of ices.

The adopted flaring disk structure is based on a 1+1D steady-state α -model similar to D’Alessio *et al.* (1999) model. The non-thermal FUV radiation field from DM Tau is represented by the scaled ISRF of Draine (1978), with the un-attenuated intensity at 100 AU of $\chi_*(100) = 410$ (e.g., Bergin *et al.* 2003b). For the X-ray luminosity of the star we adopt a value of 10^{30} ergs $^{-1}$, which is constrained by recent measurements with Chandra and XMM in the range of 0.3-10 keV.

The turbulence in disks is likely driven by the magnetorotational instability (MRI), which is operative even in a weakly ionized medium (e.g., Balbus & Hawley 1991). This turbulence causes anomalous viscosity that enables efficient redistribution of the angular momentum. We have followed the parametrization of Shakura & Sunyaev (1973), where

Table 3. Detectable tracers of turbulent mixing.

Steadfast	Hypersensitive
CO	Heavy hydrocarbons (e.g., C ₆ H ₆)
H ₂ O ice	C ₂ S
	C ₃ S
	CO ₂
	O ₂
	SO
	SO ₂
	OCN
	Complex organics (e.g., HCOOH)

turbulent viscosity ν is related to local disk properties such as the vertical spatial scale $H(r)$, the sound speed $c_s(r, z)$, and the dimensionless parameter α :

$$\nu(r, z) = \alpha c_s(r, z) H(r). \quad (8.1)$$

From observational constraints α is $\sim 0.001 - 0.1$ (Andrews & Williams 2007; Guilloteau *et al.* 2011), so we adopt the constant value of 0.01. Consequently, the diffusion coefficient is calculated as

$$D_{\text{turb}}(r, z) = \nu(r, z)/Sc, \quad (8.2)$$

where Sc is the Schmidt number describing efficiency of turbulent diffusivity (see e.g. Shakura & Sunyaev 1973; Schr apler & Henning 2004). We assume that gas-phase species and dust grains are well mixed, and transported with the same diffusion coefficient.

We show that the higher the ratio of the characteristic chemical timescale to the turbulent transport timescale for a given molecule, the higher the probability that its column density will be affected by dynamical processes. Thus, turbulent transport influences abundances of many gas-phase species and especially ices. 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. The radial temperature gradient is weaker, and thus is only relevant for the evolution of polyatomic ices formed via surface reactions of heavy radicals, whereas steep vertical gradients of temperature and high-energy radiation intensity cause much sharper transition from the ice-dominated chemistry in the disk midplane to the rich gas-phase chemistry in the molecular layer.

The simple molecules that are unresponsive to dynamical transport include C₂H, C⁺, CH₄, CN, CO, HCN, HNC, H₂CO, OH, as well as water and ammonia ices. The sensitive species to dynamics are carbon chains and other heavy species, in particular sulfur-bearing and complex organic molecules frozen onto the dust grains. Mixing steadily transports ice-coated grains in warmer regions, allowing more efficient surface processing due to enhanced hopping rates of heavy radicals. In warm intermediate layer these organically-rich ices 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 in the outer region. Still, mixing does not completely erase the layered chemical structure of protoplanetary disks.

Several promising detectable tracers of dynamical processes in protoplanetary disks are the column density ratios of the CO₂, O₂, SO, SO₂, C₂S, C₃S to that of CO and the water ice (see Table 3). 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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Discussion

PAUL M. WOODS: There were some dynamical models recently that show that the accretion flow proceeds inwards along the disc surface and outwards along the disc midplane. Are those models credible, and how would that affect the disc chemistry?

D. SEMENOV: Turbulence is a 3D phenomenon and its magnitude varies greatly across a disk. Global 3D MHD models show that viscous transport occurs in all directions in any given disk location, albeit with different efficiencies, and that there is no a specific direction for it. According to observations, advective transport seems to be an effective mechanism that regulates overall lifetime of disks, $\sim 1 - 10$ Myr, in which most of disk matter accretes onto the central star and photoevaporates. Consequently, disk structure changes with time, as well as the FUV and X-ray penetration, and grain properties. This strongly affects chemical evolution of protoplanetary disks, and favors the use of evolutionary disk models (see R. Vissier's presentation and proceeding paper).

JAMES R. LYONS: What turbulent viscosity parameter α -values were used for slow vs. fast mixing?

D. SEMENOV: We considered Fickian diffusion, in which the diffusion coefficient $D_{\text{turb}}(r, z)$ is attributed to the α -parameterized viscosity, $\alpha = 0.01$: $D_{\text{turb}}(r, z) = \nu(r, z)/Sc = \alpha c_s(r, z) H(r)/Sc$, where the characteristic spatial scale is $H(r)$ and the sound speed is

$c_s(r, z)$. The Sc the Schmidt number describing efficiency of turbulent diffusivity. The “fast” mixing model has $Sc = 1$ and the “slow” model has “ $Sc=100$ ”.

JAMES R. LYONS: Have you included isotopes in vertical mixing calculations?

D. SEMENOV: No.

JAMES R. LYONS: What did you mean by “isotopic homogeneity of the Solar nebula”? It is not homogeneous in oxygen isotopes.

D. SEMENOV: I’ve meant that the inner, 1-20 AU region of the Solar nebula has been isotopically homogenized at bulk level, though oxygen anomalies at percentage level still persist.