Chemical Processes in Protoplanetary Disks
~ Water, Snowlines & Organic Molecules ~

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§1 Introduction
Gas & Dust Observations in PPDs

Observationally diagnosing physical & chemical structure of planet-forming regions
Obs. of Gas in Protoplanetary Disks

**UV**

$H_2$ Lyman-Werner band transitions

**Optical**

$[\text{OI}]$ 6300Å

**NIR**

$H_2$ v=1-0 S(1), S(0), CO $\Delta v=2$, $\Delta v=1$, etc.

**MIR**

$H_2$ v=0-0 S(1), S(2), S(4)

$H_2O$, OH, HCN, $C_2H_2$, CO$_2$

*(Spitzer Space Telescope)*

**FIR**

$[\text{OI}]$ 63μm, 145μm, CO, $H_2O$, $CH^+$, HD, etc.

*(Herschel Space Observatory)*

**(sub)mm**

$^{12}CO$, $^{13}CO$, $C^{18}O$, HCO$^+$, $H^{13}CO^+$, DCO$^+$, $C_2H$, c-$C_3H_2$, $H_2CO$, HCN, HNC, DCN, CN, $N_2H^+$, $HC_3N$, $CH_3CN$, CS, $C^{34}S$, etc.

→**ALMA**
Chemical Models of Protoplanetary Disks
Chemical reaction network + Physical model of PPDs
- Include physical processes:
  dust evolution & gas motion
- Include various chemical reactions:
  dueterated species, grain surface chemistry, etc.

Comparison between model & obs.
→ Physical structure of PPDs &
Origin of materials in our Solar System
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§2
Water & Snowlines in Protoplanetary Disks
H₂O Snow Line & Planet Formation

(e.g., Markwick+2002, Aikawa+ 2002, Bergin+ 2007, Dutrey+ 2014)

H₂O snow line divides rocky planet & gas giant forming regions

UV, X-rays

desorption of icy molecules

freeze-out of species

grain surface reactions

H₂O, CO₂, CH₄, CH₃OH,
H₂CO, NH₃, HCN, etc.

ESA

Halley

rocky planets

gas giants

ice giants

H₂O snow line
Obs. of water lines from PPDs

- **H$_2$O, OH, HCN, C$_2$H$_2$$^*$**
  - Spitzer/IRS
    - AA Tau
      - (Carr & Najita 2008)

- **[OI] H$_2$O, OH, H$_2$**
  - Herschel/PACS
    - AA Tau

- **H$_2$O**
  - TW Hya
    - Herschel/HIFI
      - (Riviere-Marichalar+ 2012)

- **CN, C$_2$H, HCN, H$_2$CO, H$_3^+$, H$_2$D**

- **UV, X-rays**

- **Spitzer** hot H$_2$O@10-35µm, TTSs: detect, HAEBEs: upper limits

- **Herschel** warm H$_2$O TTSs, HAEBEs: @55-180µm

- **Herschel** cold H$_2$O @267µm, 539µm, TW Hya, HD100546
H2O snow lines in PPDs

H2O line ratios + disk model → predict H2O snow lines

The results are model dependent...

H2O Snow line @ ~1AU (Meijerink+ 2009)
H2O Snow line @ ~4AU (Zhang+ 2013)
H$_2$O snow line will be detected using high-R (R~100,000) spectroscopic observations (ALMA, TMT, SPICA, ...)

H$_2$O Abundance

Kepler rotation

Inside snow line

Outside snow line

H$_2$O 17.8μm

(Notsu+ in prep.)
Fast Pebble Growth @ Snow Lines?

HL Tau (Brogan+ 2015)

ALMA 1.3mm

Grain growth @ snow lines?

Grain growth?

(Zhang et al. 2015)
**CO Snow Line**

**Freeze-out of molecules on grains changes elemental abundance in PPDs**

(Mathews et al. 2013)

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**HD163296**

**SMA**

- CO6-5@691GHz $^{13}$CO2-1@220GHz
- CO3-2@346GHz $^{18}$O2-1@220GHz
- CO2-1@231GHz $^{17}$O3-2@337GHz

**CO snow line @ R~155AU**

(Mathews et al. 2013)

- DCO$^+ 5-4$
- $[\text{DCO}^+] / [\text{HCO}^+] = 0.3$

T (K)

\[ Z(AU) \]

\[ \text{dust settling} \]

\[ \text{ALMA SV @ band7, DCO}^+ 5-4 \]

(ALMA cycle 0 (Qi et al. 2013c))

**CO snow line @ R~30AU**

Freeze-out of molecules on grains changes elemental abundance in PPDs

(Aikawa-san’s talk (Qi et al. 2013c))
Snow Lines & Planet Formation
(e.g., Markwick+2002, Aikawa+ 2002, Bergin+ 2007, Dutrey+ 2014)

**H$_2$O snow line** (Oberg et al. 2011)

- C-rich in Ice
- O-rich in Gas
- O-rich in Ice
- C-rich in Gas

Desorption of icy molecules
Freeze-out of species
Grain surface reactions

**Assembly**

- Rocky planets
- Gas giants
- Ice giants

**Graph**

- C/O ratio vs radius (A.U.)
- Gas: HCN, H$_2$CO
- Ice: H$_3^+$, H$_2$D$^+$

**Diagram**

- Gas particles
- Ice particles
Snow Lines & Planet Formation (e.g., Markwick+2002, Aikawa+ 2002, Bergin+ 2007, Dutrey+ 2014)

enhance C/O ratio

Comparison of C/O ratios in PPDs & exoplanetary atmospheres constrains planet formation theory

C-rich in Ice
O-rich in Gas
rocky planets

O-rich in Ice
C-rich in Gas
gas giants

H$_2$O snow line

C-rich

O-rich in Gas

ice giants
Obs. of Water & Organic Molecules

Spitzer/IRS (R=600)

- OH

S/N=250
AA Tau

HCN/H$_2$O $\Leftrightarrow$ M$_{\text{disk}}$?

Trap of H$_2$O in icy planetesimals?

HCN/H$_2$O

(Carr & Najita 2011, Najita+ 2013)

Infrared molecular lines could be tracer of C/O ratio distribution in PPDs

(e.g., Carr & Najita 2008; Salyk+ 2008, 2011; Pontoppiddan+ 2010)
Water & methane, etc. are found → C/O ratios → constrain planet formation theory?

(Lee+ 2013, Barman+ 2011)

(Marois et al. 2008, 2010)

(Konopacky+ 2013)

Transiting Short Period Jupiters, Neptunes & Super-Earths

Spitzer, GJ 436b

H₂O, CH₄, CO, CO₂

(Stevenson et al. 2010)
Deuterated Water

Obs. of Deuterated Species in PPDs
DCO$^+$: TW Hya, DM Tau, LkCa 15, HD163296  D/H~0.02-0.3  
DCN: TW Hya, LkCa 15 (Qi+ 2008, Oberg+ 2010, 2012)  ~0.02
HD: TW Hya  (Bergin+ 2013)  ~10$^{-5}$
HDO, H$_2$D$^+$: non-detection  (Guilloteau+ 2006, Chapillon+ 2011)
Deuterated Water in Disks

H$_2$O(ice) → O → H$_2$O(ice)

photodesorption ・ dissociation @ disk surface

D fractionation :
large adsorbed on grains
small

H$_2$O(ice)  →  O  →  H$_2$O(ice)

(Furuya+ 2013, Cleaves+ 2014)
Deuterated Water in Disks

Deuterium fractionation is consistent with:
- Earth @ ~1AU
- Comets @ ~10AU (2D mixing)

Obs. of HDO will test the models!
§3
Formation of Organic Molecules in Protoplanetary Disks
COMs Observations with ALMA

Iso-propyl cyanide around high mass star forming regions in Galactic center

Glycolaldehyde around low mass star forming regions

(Jorgensen et al. 2012)

(Belloche et al. 2014)
Complex Organic Molecules in Disks

$\text{HC}_3\text{N } J=16-15, 12-11, 10-9 @ 146, 109, 91\text{GHz}$
MWC480, LkCa15, GO Tau, IRAM 30m, PdBI

(Chapillon et al. 2012)

$c\text{-C}_3\text{H}_2 \ J=6-5 @ 218\text{GHz}$
HD163296, ALMA SV

(Qi et al. 2013b)

$\text{CH}_3\text{CN}$
$14_0-13_0, 14_1-13_1,$
@ 257GHz,
MWC480,
ALMA cycle 2

(Oberg et al. 2015)

→more complex mol. will be found by ALMA
### Observed Interstellar Molecules

<table>
<thead>
<tr>
<th>CH+</th>
<th>HCN</th>
<th>H2CO</th>
<th>HC3N</th>
<th>CH3OH</th>
<th>HC5N</th>
<th>HCOOCH3</th>
<th>HC7N</th>
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<tr>
<td>CS</td>
<td>HNC</td>
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<td>CO</td>
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<td>CN</td>
<td>OCS</td>
<td>HNCO</td>
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<td>CH3SH</td>
<td>CH3CHO</td>
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### Amino acids in comet @ STARDUST
(Elsila et al. 2009)

### Amino acids in meteorites ↔ relation with interstellar molecules ?

<table>
<thead>
<tr>
<th>C3N-</th>
<th>C4H-</th>
<th>HCNH+</th>
</tr>
</thead>
<tbody>
<tr>
<td>~10 species</td>
<td>~50 species</td>
<td>~100 species</td>
</tr>
<tr>
<td>1995</td>
<td>2015</td>
<td></td>
</tr>
<tr>
<td>~180 species</td>
<td></td>
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</tbody>
</table>
Complex Molecule Formation on Grain Surface

cold: < 20K

grain surface

C, O, N, S, CO, ...
desorption UV, CR, X-rays

UV, CR, X-rays

themal

Saturated mol.

CH₄, H₂O, NH₃, H₂S, CH₃OH, ...

migrate

Unsaturated mol.

NH₂, HCO, ... CH₃O

(e.g., Garrod+ 2006, 2008)

warm: 30–50K

UV

Complex molecules are formed on grains

More complex molecules on warm grains
Modeling Complex Molecules in PPD

Grain surface reactions

\[ \text{C, O, N, S, CO, ...} \rightarrow \text{H}_2\text{O, CH}_3\text{OH, ...} \]

Photodesorption

\[ \text{desorption} \quad \text{UV, CR, Xrays} \]

Grain surface reactions

\[ \text{C, O, N, S, CO, ...} \]

\[ \text{H}_2\text{O, CH}_3\text{OH, ...} \]

Observing complex mol. & grain surface reactions

Notes:
- Walsh, Millar, HN (2010)
- HCOOH
- CH\(_3\)OH
- z[AU], x[AU]
Prediction of CH$_3$OH line fluxes (ALMA)

H$_2$CO line spectra: consistent with observations
CH$_3$OH line fluxes: constrained by ALMA observations

→ Diagnosing grain surface reactions in PPDs

(Walsh, Millar, HN et al. 2014)
Complex Molecules on Warm Grains

OSU chemical network (Harada et al. 2010, Garrod et al. 2008)

Complex mol. are formed on warm grains at $T \sim 30-35$K ($\sim 50$AU) = cometary region

Walsh, Millar, HN et al. 2014

T$_{dust}$

30-50K

CH$_3$OH

CH$_3$COCH$_3$ aceton

$g$CH$_3$OH

C$_2$H$_5$OH

$g$C$_2$H$_5$OH

R [AU]

Z/R

R [AU]

Z/R

(Walsh, Millar, HN et al. 2014)
Comparison with Obs. tw. Comets

Mol. clouds (initial condition)  Model (ice) (R>20AU)  Obs. from Comet

Complex molecules are formed on grains in disk
Obs. toward comets are consistent with PPD model
Disks in a Young Star Cluster

Trapezium cluster in Orion Nebula

Effect of irradiation from nearby massive star on chemical structure in disks?

Most stars are formed in young star clusters
(e.g., Lada & Lada 2003)

Environmental effects in star clusters?

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COMs: irradiated vs. isolated

Irradiated: some COMs are not formed efficiently

\( G_{\text{FUV}} = 10^6 G_0 \)

Dependence on \( T_{\text{initial}} \)

30K 10K

\( Z/R \)

[Image -2x2 to 729x476]
Summary

Water, snow lines & organic molecules in protoplanetary disks

H₂O snow line in PPDs will be detected using high-R spectroscopic observations

Comparison of C/O ratios in PPDs & exoplanetary atmospheres constrains planet formation theory

Obs. of deuterated molecules constrain disk model

Obs. of complex molecules in PPDs & comets constrain formation process of COMs in PPDs
Carbon Fractionation in Disks

- Fractionation due to self-shielding surface: $^{12}\text{C}^{16}\text{O} \rightarrow ^{13}\text{CO} \rightarrow \text{C}^{18}\text{O} \rightarrow \text{C}^{17}\text{O} \rightarrow \ldots$ : midplane

- Fractionation due to chemistry

$$^{13}\text{C}^+ + ^{12}\text{CO} \rightleftharpoons ^{13}\text{CO} + ^{12}\text{C}^+ + \Delta E,$$

$$\text{H}^{12}\text{CO}^+ + ^{13}\text{CO} \rightleftharpoons \text{H}^{13}\text{CO}^+ + ^{12}\text{CO} + \Delta E,$$

$\Delta E=35\text{K}$

$\Delta E=9\text{K}$

Fractionation may depend on temperature