Astrochemical models for the formation of COMs in star-forming regions

Vianney Taquet
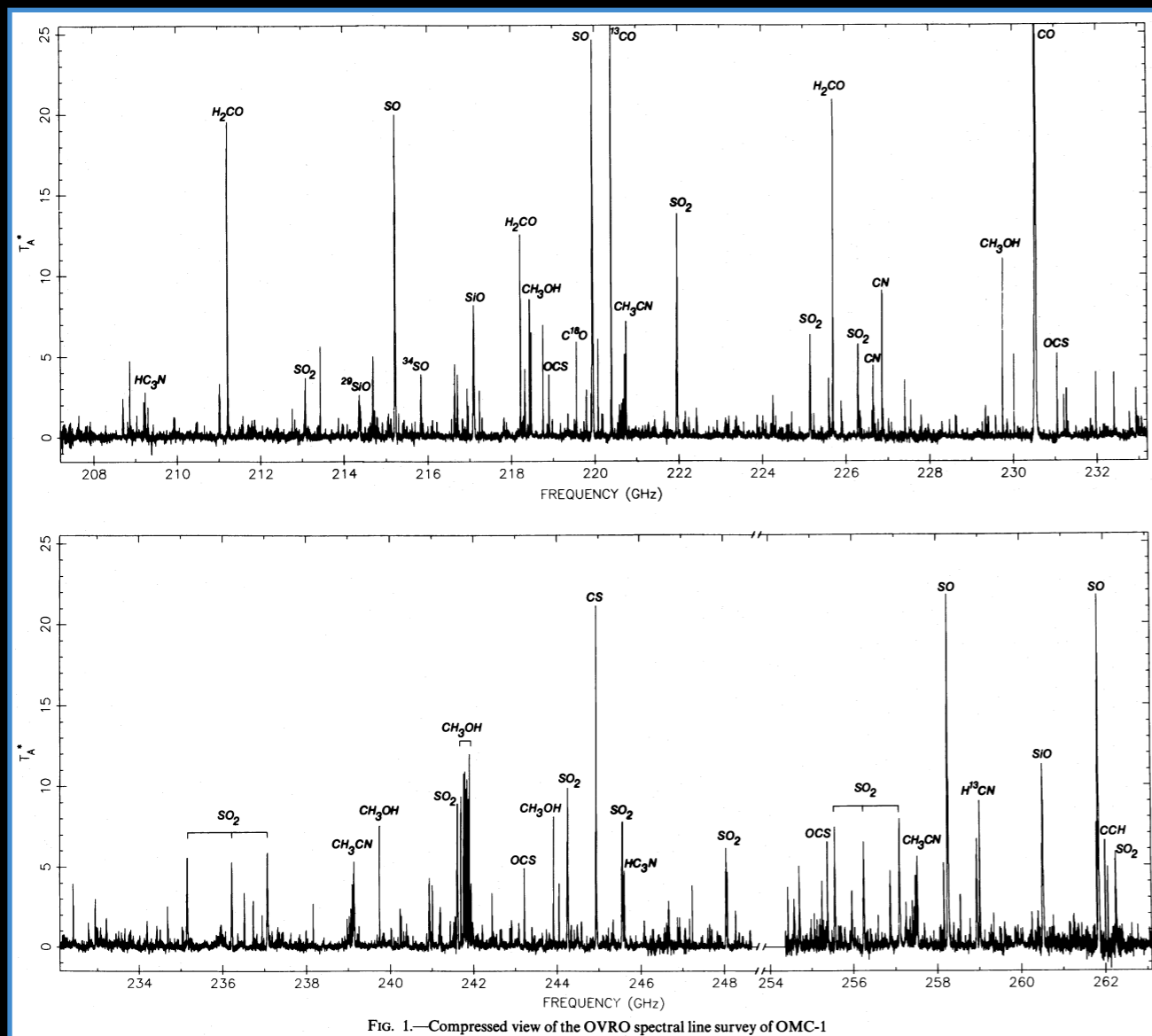Osservatorio Astrofisico di Arcetri - INAF
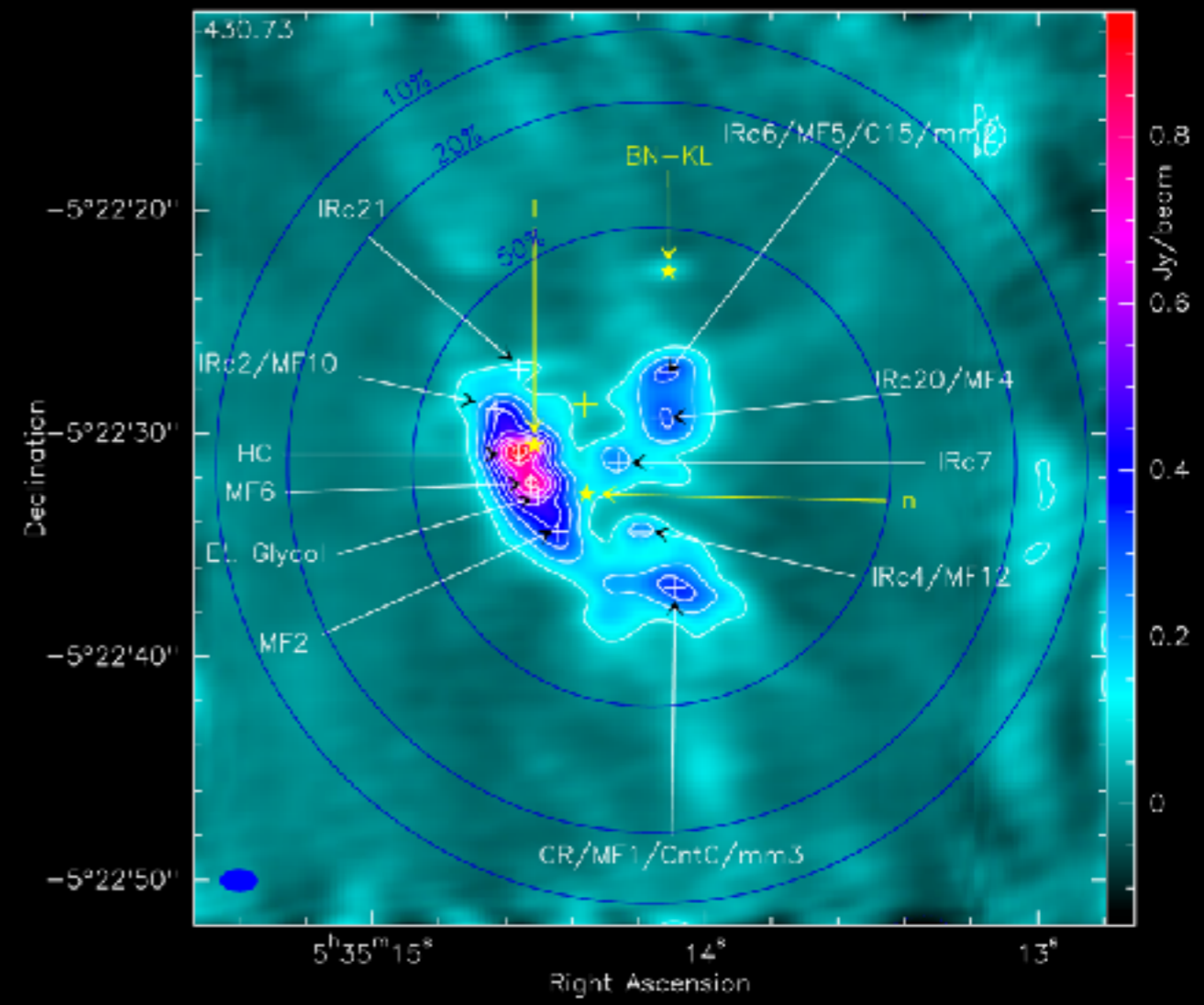Marie Skłodowska-Curie AstroFIt 2 Fellow

Outline

Complex Organic Molecules in Orion KL

Blake et al. 1987
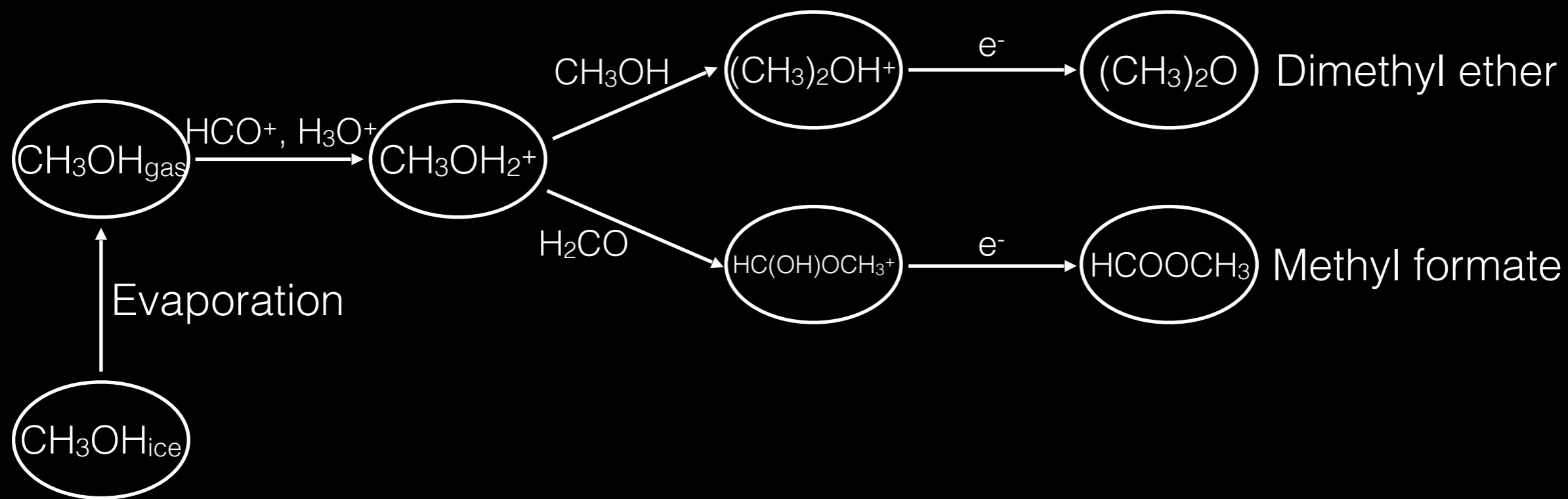(see also **Sutton** et al. 1985, **Irvine** et al. 1987)

Pagani et al. (2017)

Hot-Core gas phase chemistry

Astrochemical models developed in the 90s to explain the chemical differences between the Orion Hot Core and the Compact Ridge observed in the 80s:

- **pseudo time-dependent** (physical conditions of Hot-Cores are fixed)

- **evaporation of ice mantles** with free chemical composition

- Hot-Core **ion-neutral gas phase chemistry** for COMs

CH_3OH_{gas} —HCO^+, H_3O^+→ $CH_3OH_2^+$

$CH_3OH_2^+$ —CH_3OH→ $(CH_3)_2OH^+$ —e^-→ $(CH_3)_2O$ Dimethyl ether

$CH_3OH_2^+$ —H_2CO→ $HC(OH)OCH_3^+$ —e^-→ $HCOOCH_3$ Methyl formate

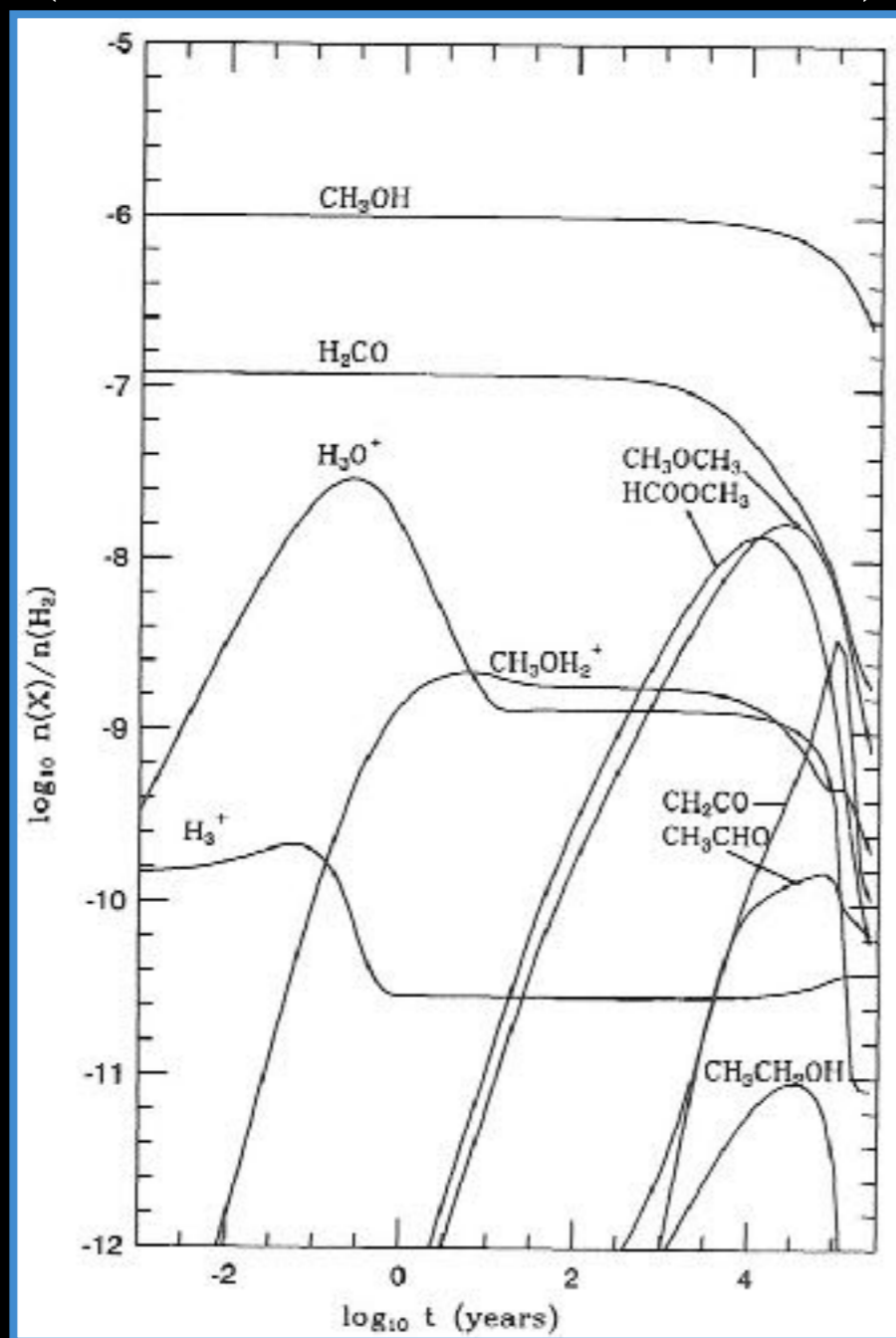CH_3OH_{ice} —Evaporation→ CH_3OH_{gas}

(**Millar** et al. 1991, **Charnley** et al. 1992, 1995, see also **Caselli** et al. 1993)
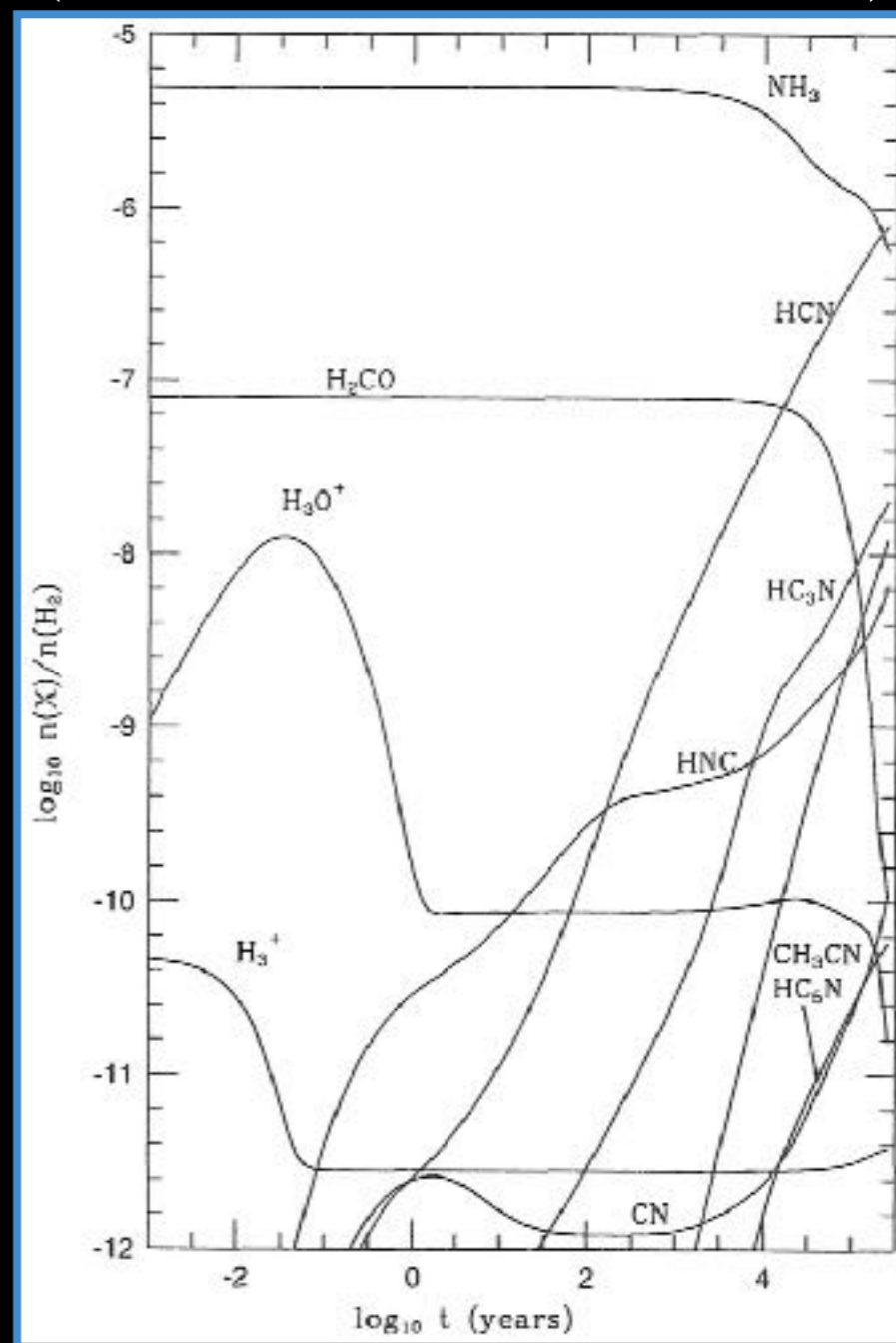
Hot-Core gas phase chemistry

Astrochemical models developed in the 90s to explain the chemical differences observed between the Orion Hot Core and the Compact Ridge in the 80s:

Compact Ridge
($n_H = 2 \times 10^6$ cm^{-3}; T = 100 K)

Hot Core
($n_H = 2 \times 10^7$ cm^{-3}; T = 200 K)

(**Millar** et al. 1991, **Charnley** et al. 1992, 1995, see also **Caselli** et al. 1993)

Hot-Core gas phase chemistry seems inefficient
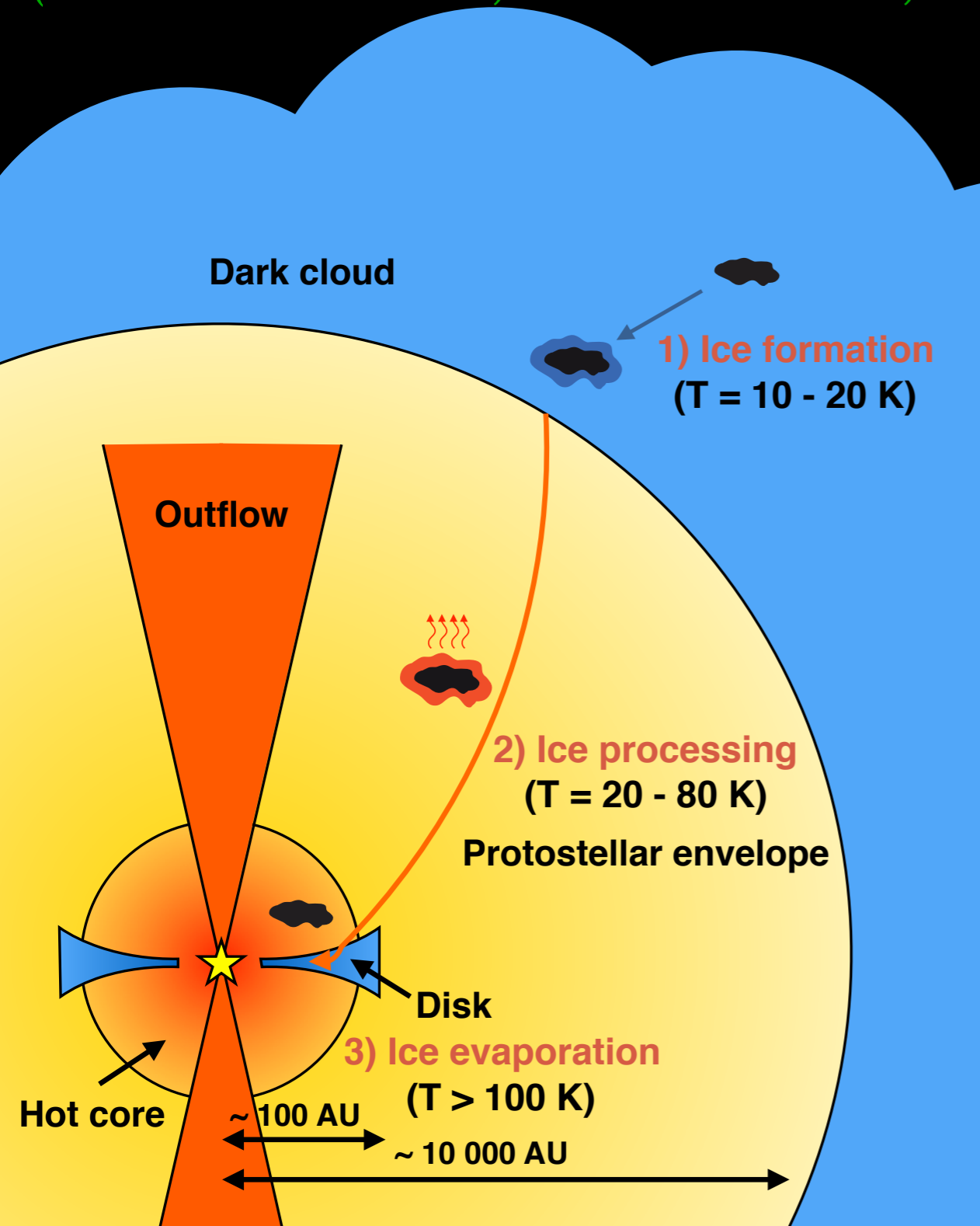
Subsequent experiments and calculations carried out in the early 2000s limited the efficiency of this Hot-Core gas phase chemical network:

- Reaction between **$CH_3OH_2^+$ and H_2CO inefficient** in the ISM **(Horn** et al. 2004)

- **Electronic recombination** is mostly **dissociative** ($\approx$ 80 - 90 %)
  (Geppert et al. 2006, **Vigren** et al. 2010, **Hamberg** et al. 2010)
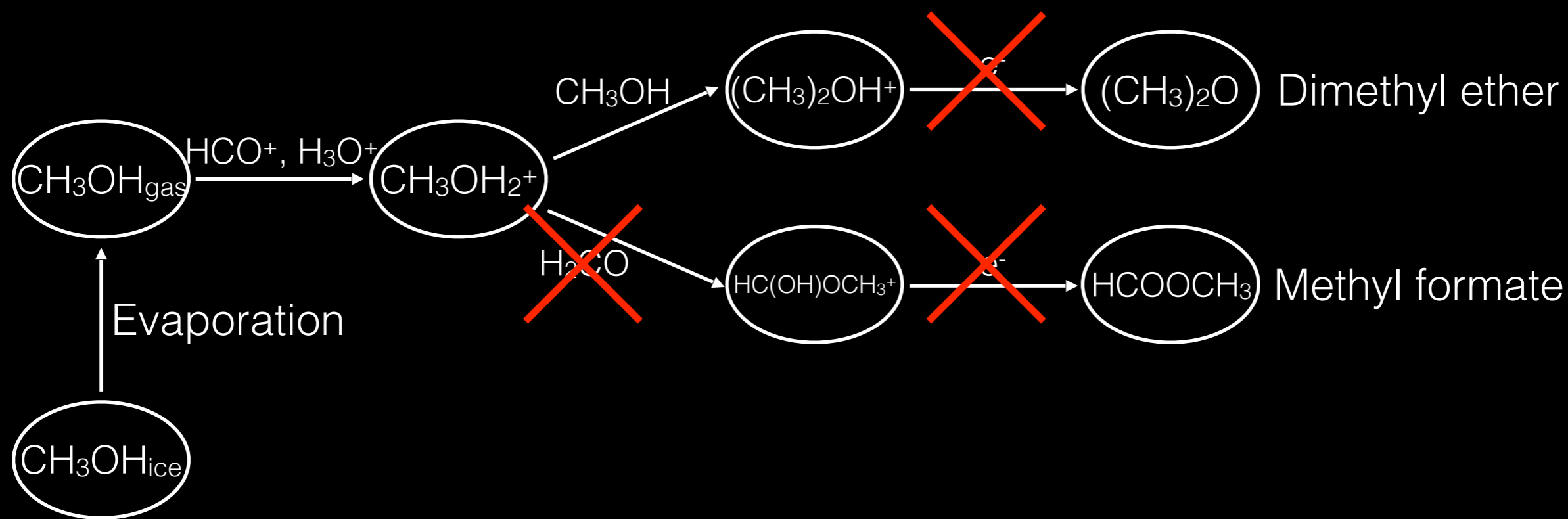
UV-induced formation of COMs in ices

A new paradigm based on the recombination of radicals produced UV photolysis **was then suggested as also supported by lab. experiments**
(**Gerakines** et al. 1996, **Garrod** et al. 2006, 2008, Ob**erg** et al. 2009)

Dark cloud

1) Ice formation
(T = 10 - 20 K)

Outflow

2) Ice processing
(T = 20 - 80 K)

Protostellar envelope

Disk

3) Ice evaporation
(T > 100 K)

Hot core   **~ 100 AU**

~ 10 000 AU

1) Ice formation (T = 10 - 20 K)
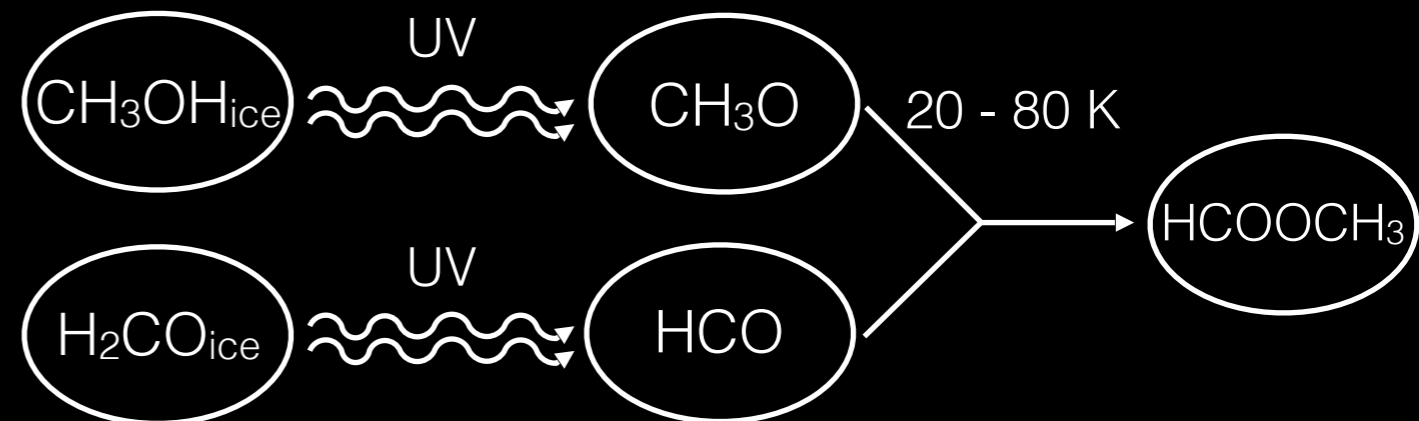Example for methanol:

CO_{ice} → H_2CO_{ice} → CH_3OH_{ice}

2) Ice reprocessing (T = 20 - 80 K)
- Photodissociation of main ice species
- Diffusion of solid radicals produced by UV photolysis

Example for methyl formate:

CH_3OH_{ice} ～～～ UV ～➤ CH_3O 20 - 80 K

H_2CO_{ice} ～～～ UV ～➤ HCO

$HCOOCH_3$

Outline

Methods for grain surface modelling

Microchemical Accuracy

Off-Lattice Monte Carlo
(Garrod 2013)

**On-Lattice Monte Carlo
(a.k.a CTRW, kMC)**
(Chang et al. 2005, 2014; Cuppen et al. 2007, 2009)

Master equation
(Biham et al. 2001, Green et al. 2001)

Macroscopic Monte-Carlo models
(Tielens & Hagen 1982, Charnley 2001, Vasyunin et al. 2009)

Modified Rate equations
(Caselli et al. 1998, Garrod 2008)

Rate equations
(Pickes & Williams 1977, Hasegawa et al. 1992, 1993)

Chemical Complexity

Processes included in astrochemical models

Processes:

Accretion:
- $S.v.\sigma.n_{gas}$

Diffusion:
- thermal hopping
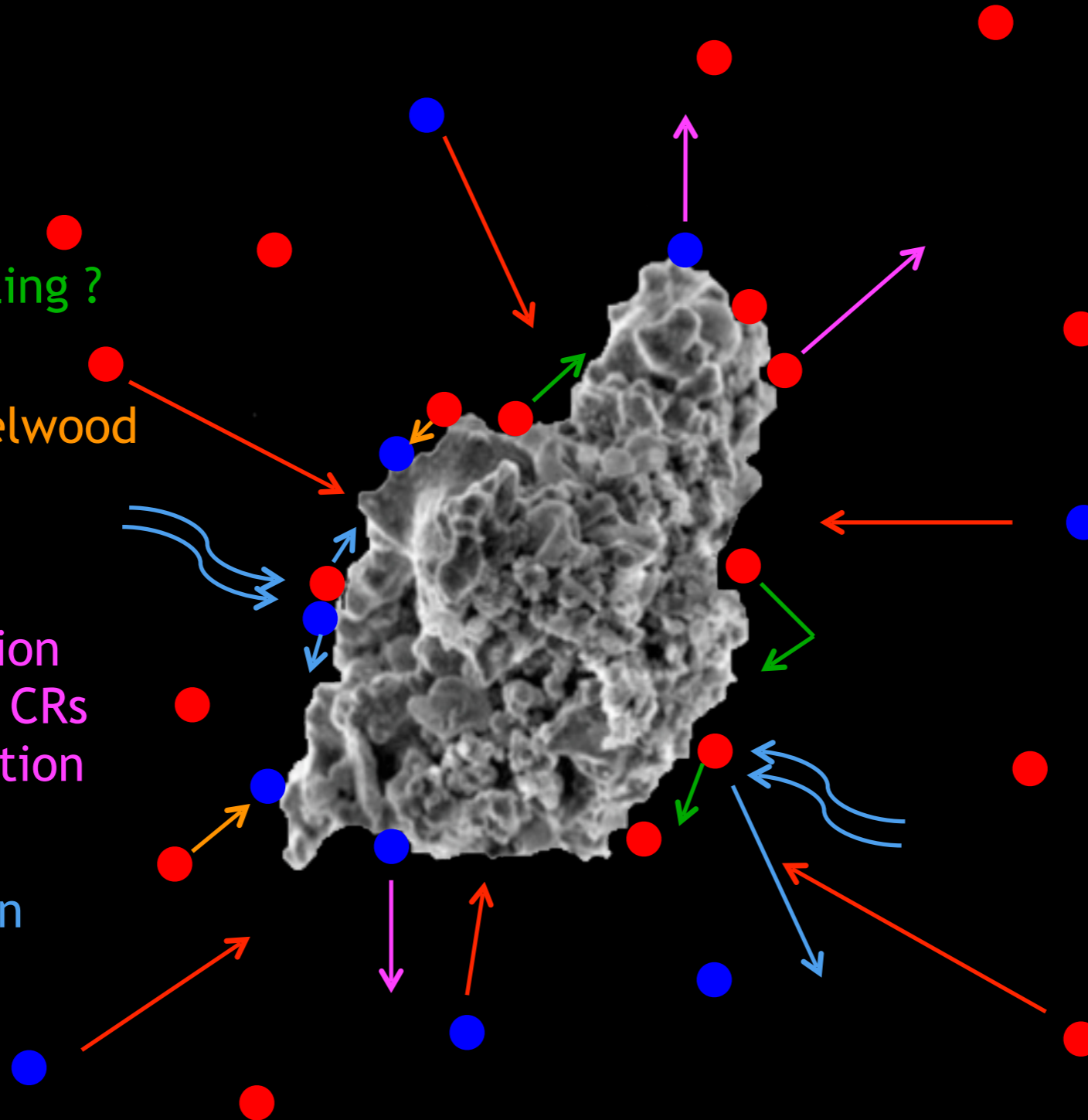- quantum tunnelling ?

Reaction:
- Langmuir-Hinshelwood
- Eley-Rideal

Desorption:
- thermal desorption
- grain heating by CRs
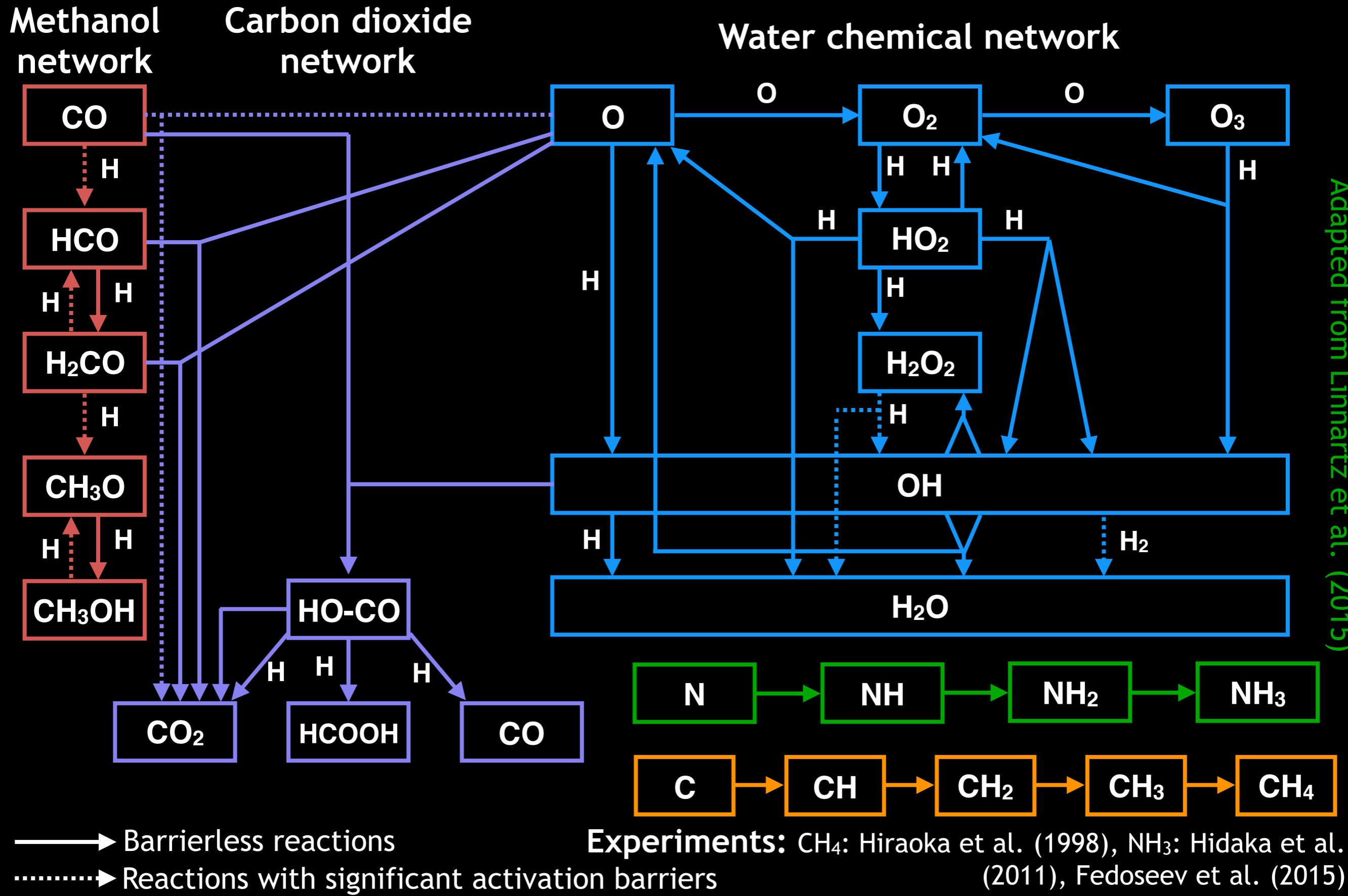- chemical desorption

Photolysis:
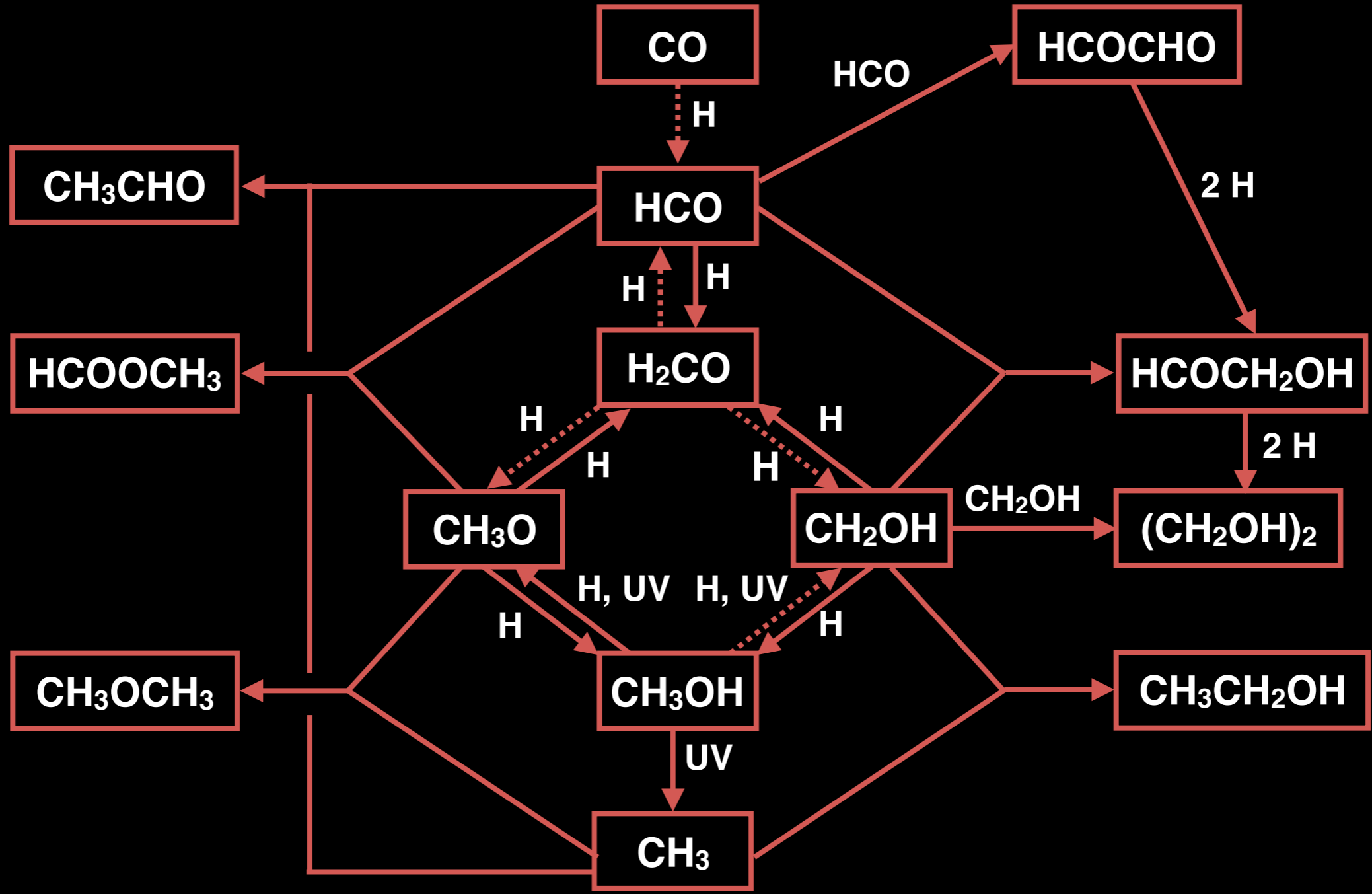- photodissociation
- photodesorption

Input parameters:

- grain size
- sticking coefficient

- diffusion energy E_d/E_b
- site size

- surface reactions
- transmission probas

- binding energy E_b
- chemical desorption probability

- UV absorption by ice
- photo. probas/BRs

Surface networks included in chemical models

Methanol network

Carbon dioxide network

Water chemical network

Adapted from Linnartz et al. (2015)

CO →H→ HCO →H, H→ H₂CO →H→ CH₃O →H, H→ CH₃OH

O →O→ O₂ →O→ O₃

HO-CO →H, H, H→ CO₂, HCOOH, CO

O₂ →H, H→ HO₂ →H→ H₂O₂ →H→

OH

H₂O

N → NH → NH₂ → NH₃

C → CH → CH₂ → CH₃ → CH₄

→ Barrierless reactions

┈┈> Reactions with significant activation barriers

Experiments: CH₄: Hiraoka et al. (1998), NH₃: Hidaka et al. (2011), Fedoseev et al. (2015)

Surface networks included in chemical models

Complex Organic Molecules

Barrierless reactions
Reactions with significant activation barriers

Diffusion of light particles into the bulk

Laboratory experiments studying the impact of ice thickness on formation of stable species show that:
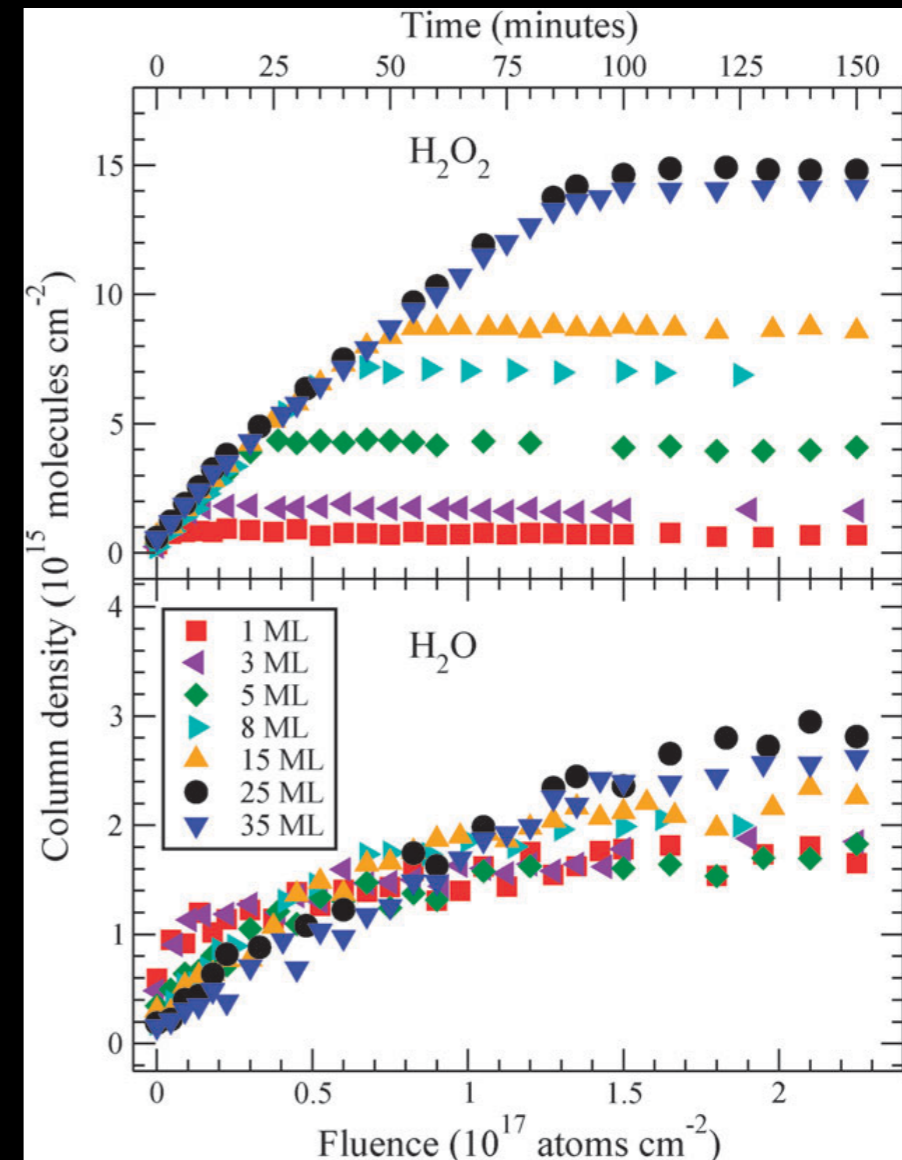
- saturation value of consumption quickly drops with ice thickness → **chemical processes mostly occur in the few outermost layers**
- ice penetration depends on ice morphology, temperature, composition

Hydrogenation of O$_2$ ice

Hydrogenation of CO ice
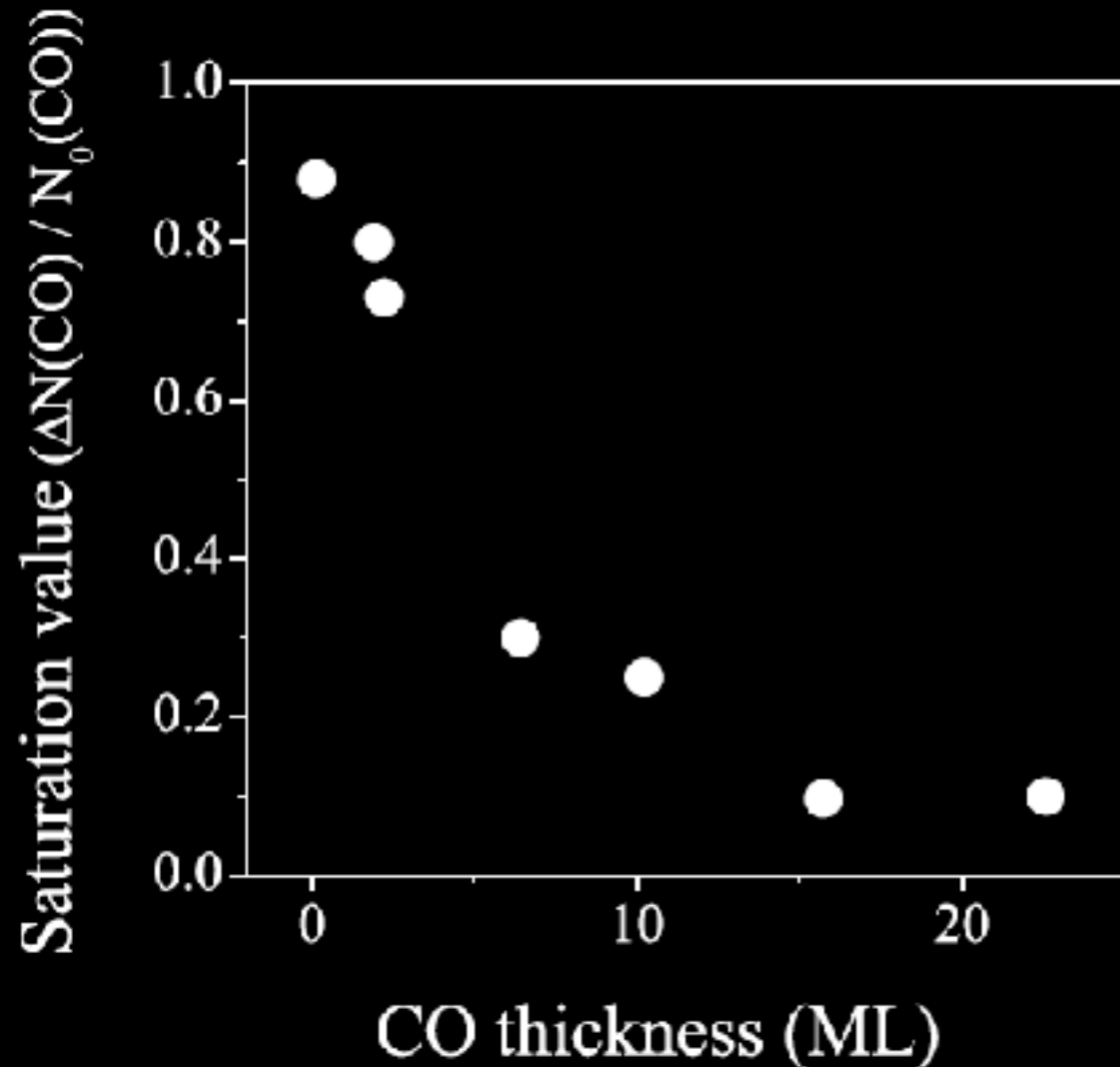
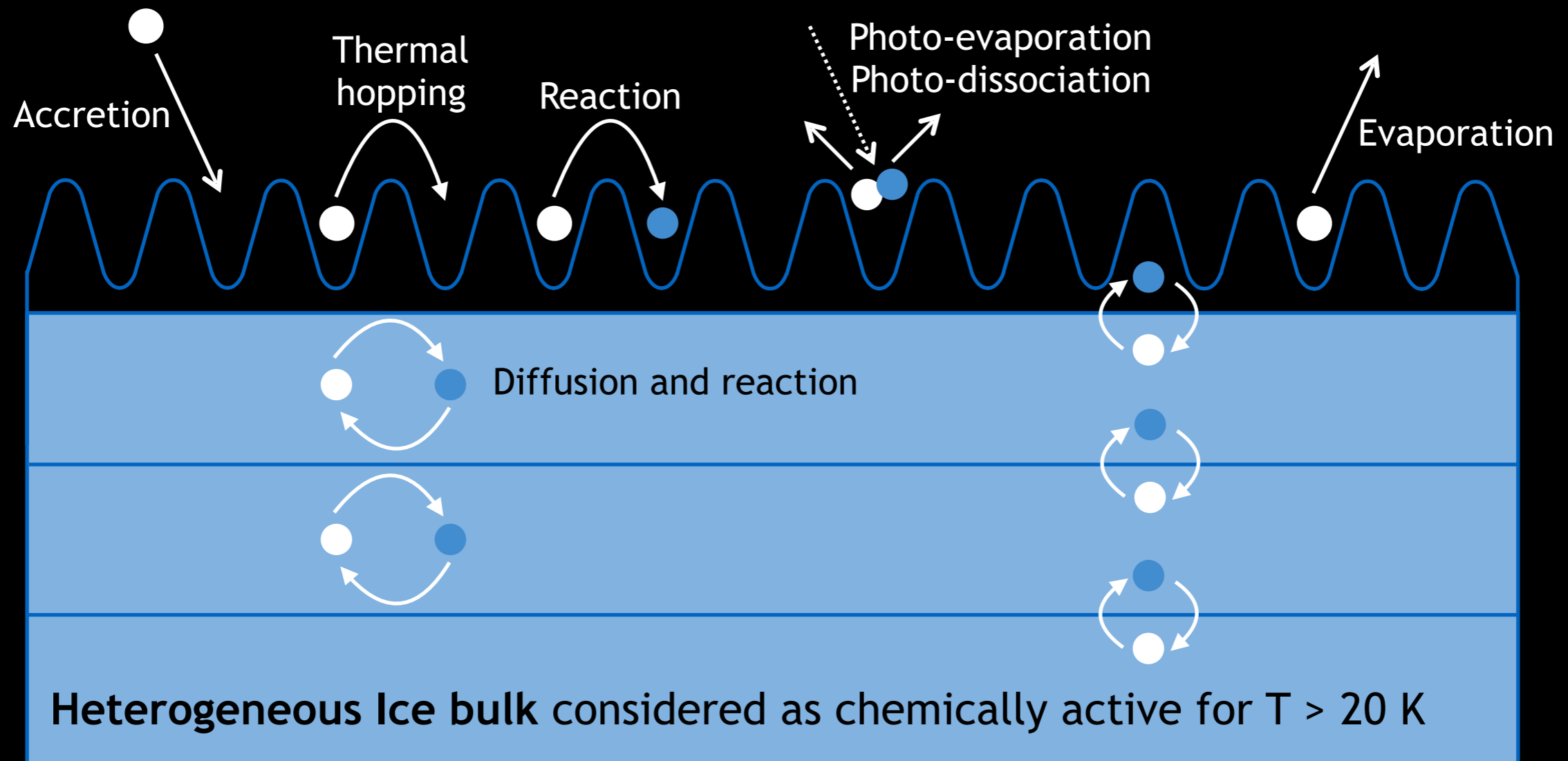Watanabe et al. (2004)

Ioppolo et al. (2010)

Multiphase models

3-phase or multiphase models distinguish chemically active ice layers and more inert ice bulks
(**Hasegawa** & **Herbst** 1993, **Garrod** & **Pauly** 2011, **Taquet** et al. 2012, **Garrod** 2013, **Vasyunin** & **Herbst** 2013, **Taquet** et al. 2014, **Furuya** et al. 2017)

Gas phase chemistry

Ice surface

Accretion

Thermal hopping

Reaction

Photo-evaporation
Photo-dissociation

Evaporation

Diffusion and reaction

Heterogeneous Ice bulk considered as chemically active for T > 20 K
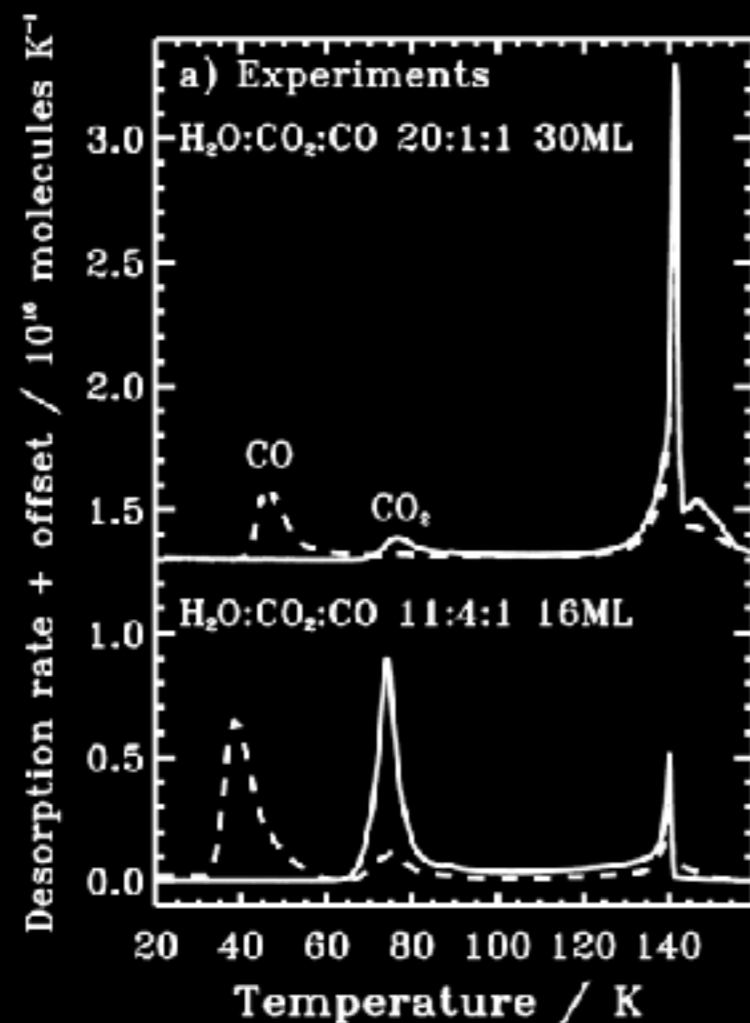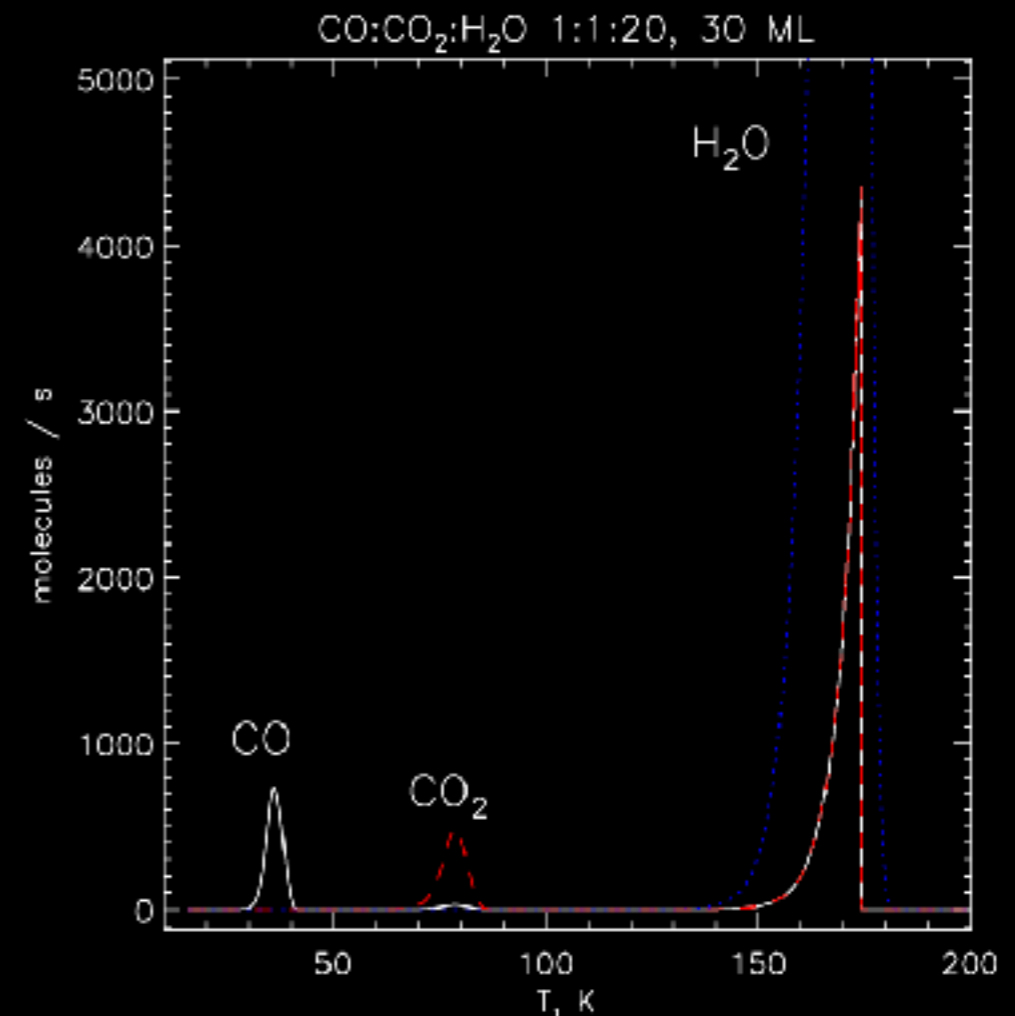
Constraining the models with experiments: desorption

TPD experiments of ice mixtures show different kinds of evaporation features:

- **surface, volcano, and co- desorptions**, depending on the species properties

- multiphase models are able to reproduce the desorption rates with **4 active MLs**


Experiments
Fayolle et al. (2011)

Model
Vasyunin et al. (2013)

Constraining the models with experiments: chemistry

Time evolution of abundances induced by irradiation of ice analogs can be reproduced by chemical models
→ validation of the formalism and constraints on surface/chemical parameters ?

Example for CO hydrogenation (Watanabe et al. 2004 and Fuchs et al. 2009):
$E_d/E_b = 0.3 \pm 0.05$; $E_a(CO+H) = 1300 \pm 300$ K; $E_a(H_2CO+H) = 1300 \pm 300$ K
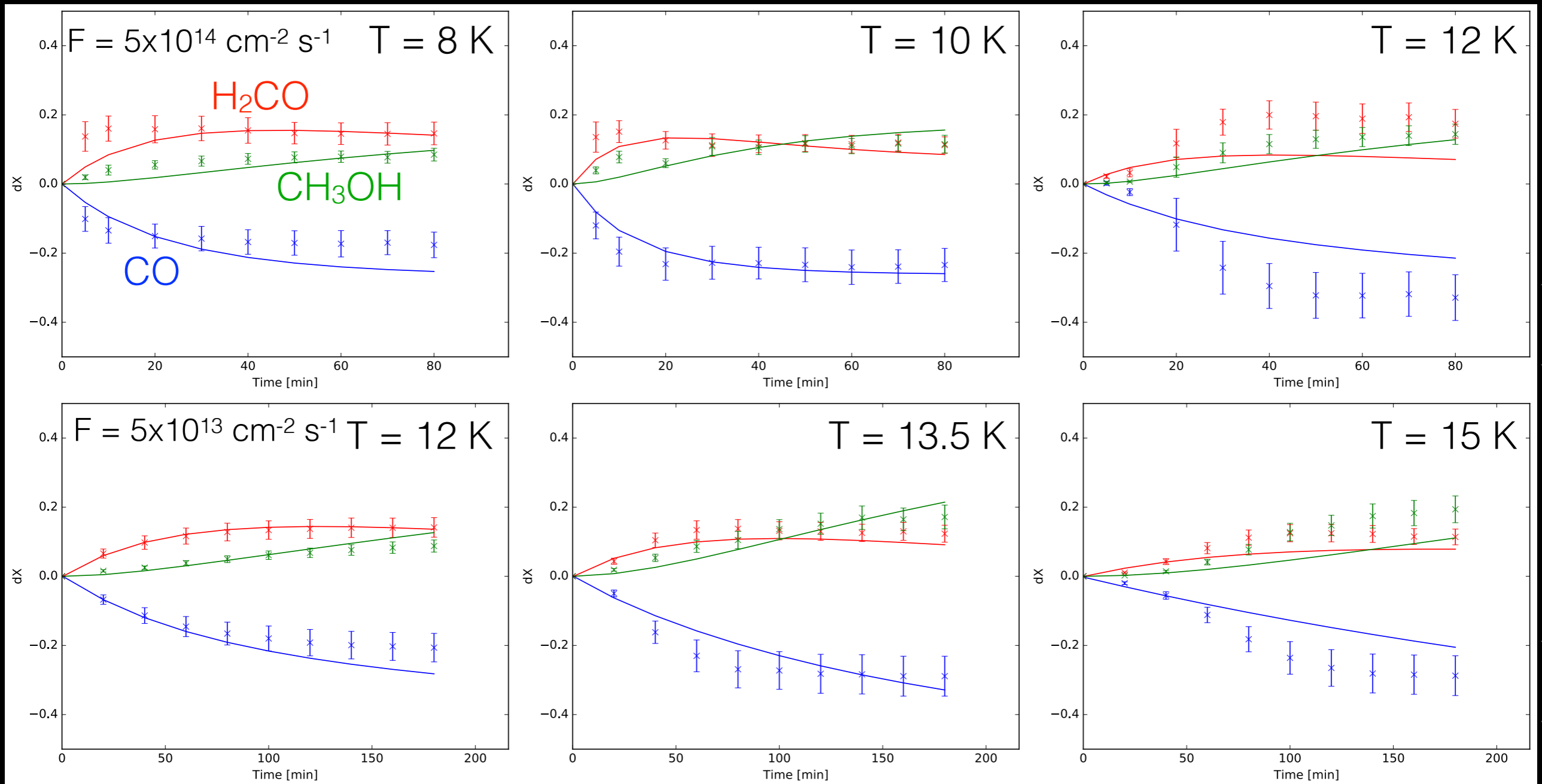
UV-induced ice chemistry

UV photolysis of methanol ice predominantly produces molecules that show lower abundances in dark clouds and around protostars

◇ 70 K
✳ 20 K
20 MLs ice

HCOOH
HCOOCH$_3$ and HCOCH$_2$OH
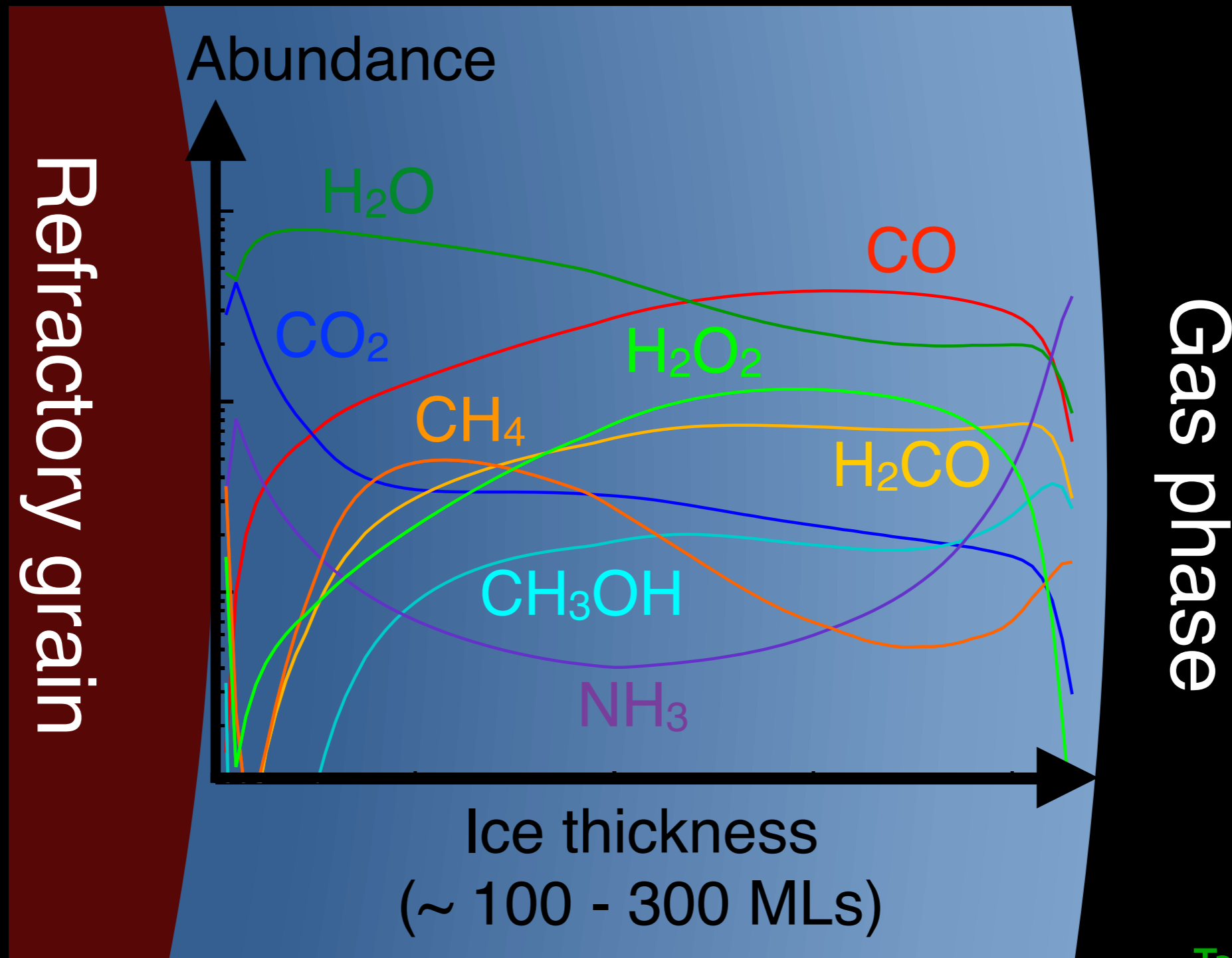CH$_3$COOH

Oberg et al. (2009)
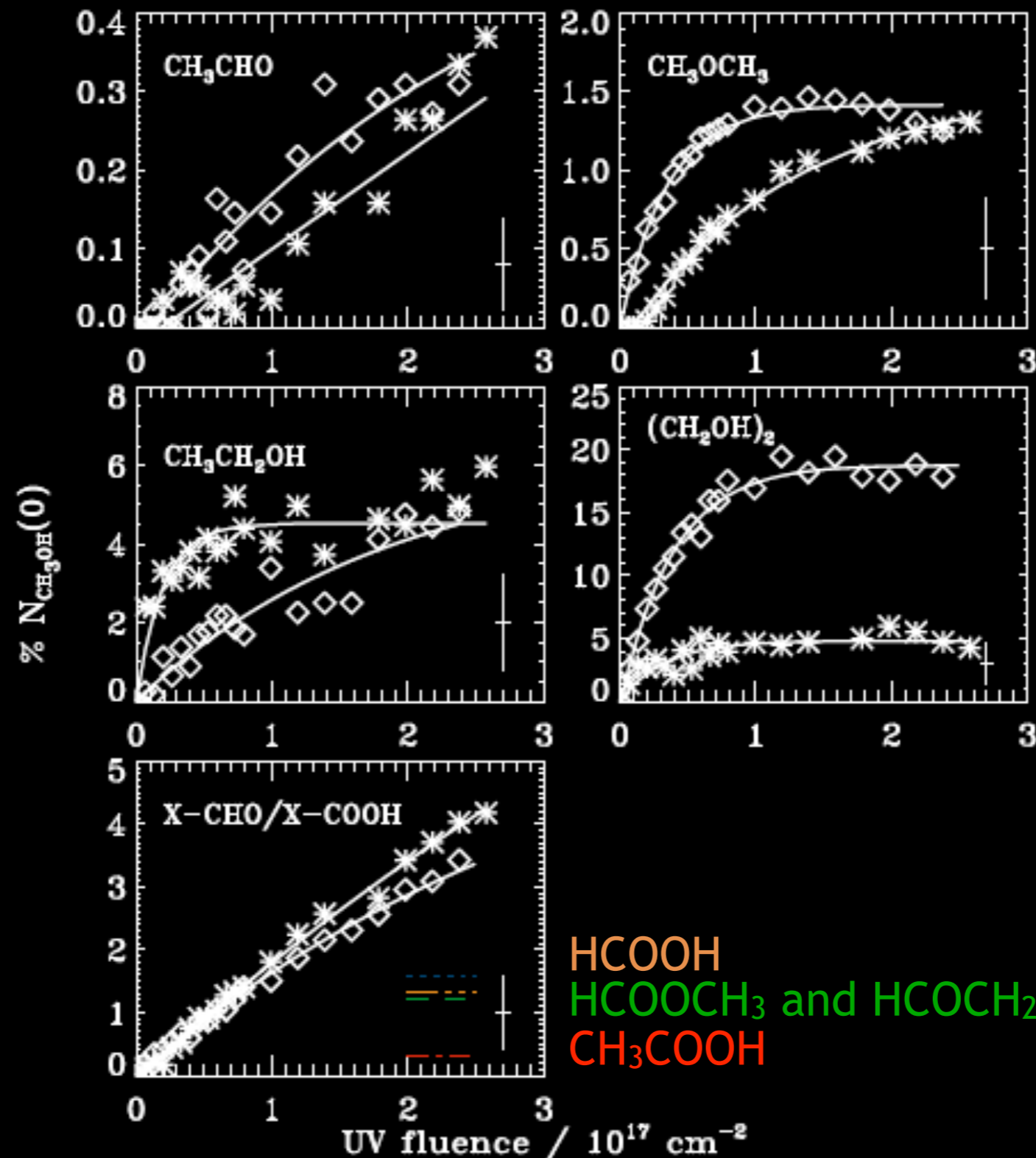
Outline

1. Historical review

2. Grain surface chemical models

3. **Recent results**

4. Limits and Perspectives

Ice structure predicted by multiphase models

Macroscopic multiphase models also predict the **chemical heterogeneity of ices** induced by the gas phase abundance and physical evolutions in dark clouds

Formation of COMs in cold ices

Two main scenarios for the formation of *Gaseous* COMs detected in dense cores:

1) **Gas phase formation**: See JC's talk

2) **Grain surface formation**: chain-reaction followed by chemical desorption (Chuang et al. 2015, Chang & Herbst 2016)
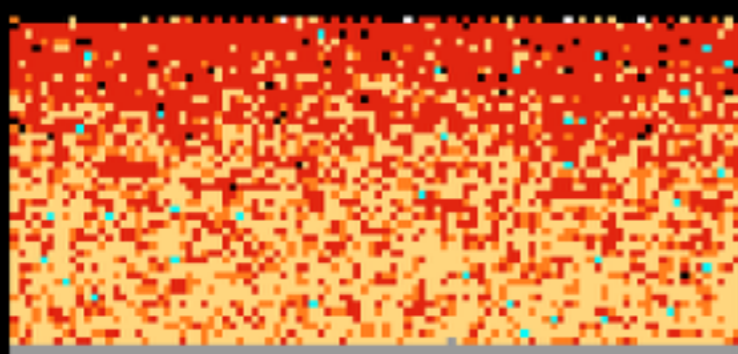
Methanol formation with CTRW model

T = 12 K

n_H = 2x10^5 cm^{-3}
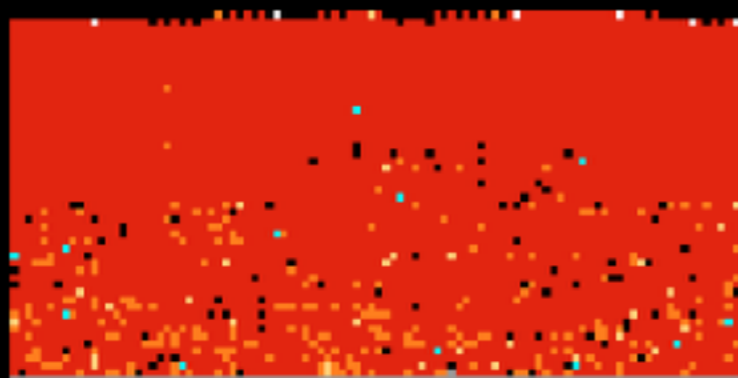
T = 13.5 K

T = 15 K

CH$_3$OH
H$_2$CO
CO
Radicals

Cuppen et al. (2009)
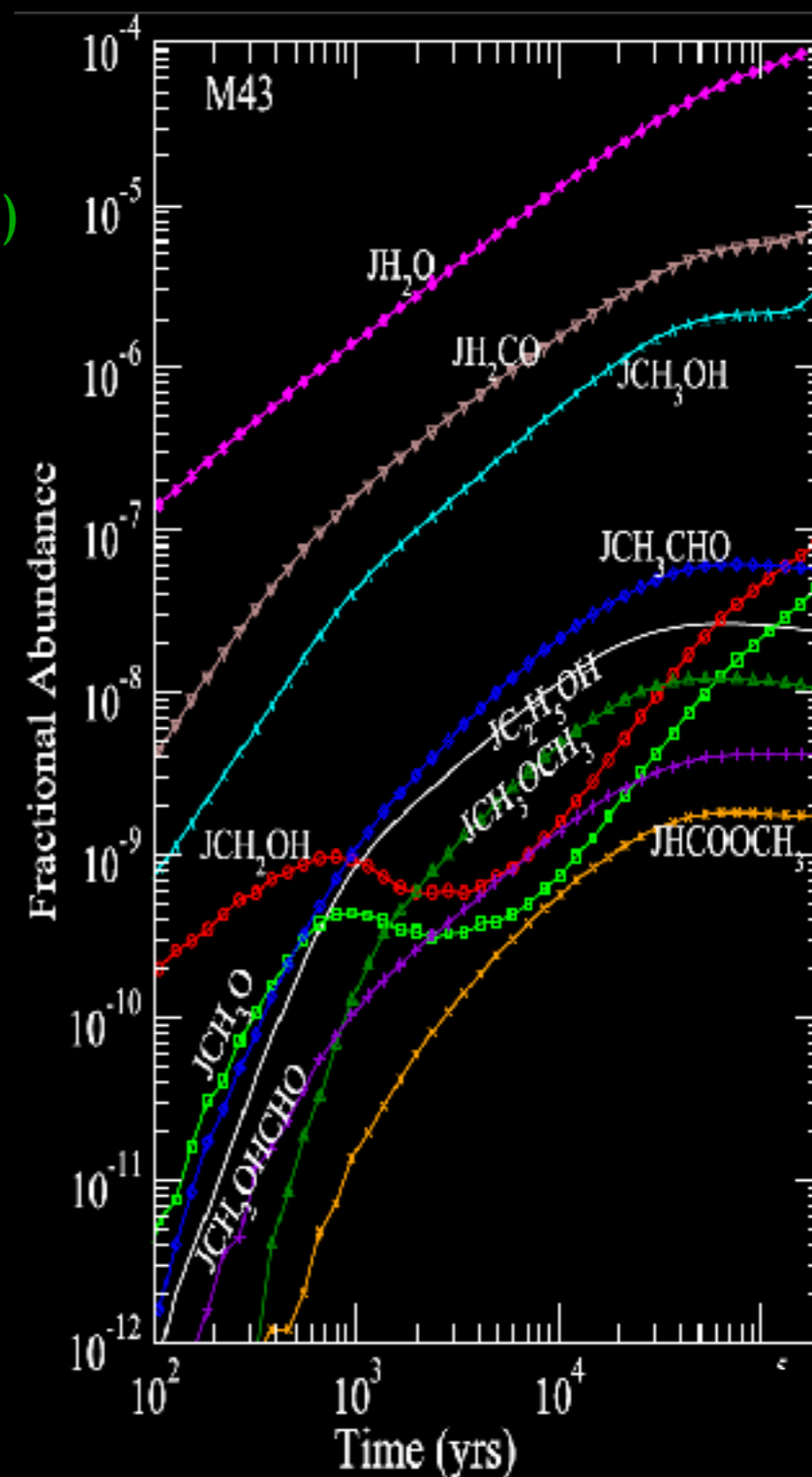
Chang & Herbst (2016)

n_H = 10^5 cm^{-3}; T = 10 K

Abundance profiles of "icy" species around protostars

Multiphase models predict double abundance jump profiles around protostars, due to the complex evaporation features in mixed ices
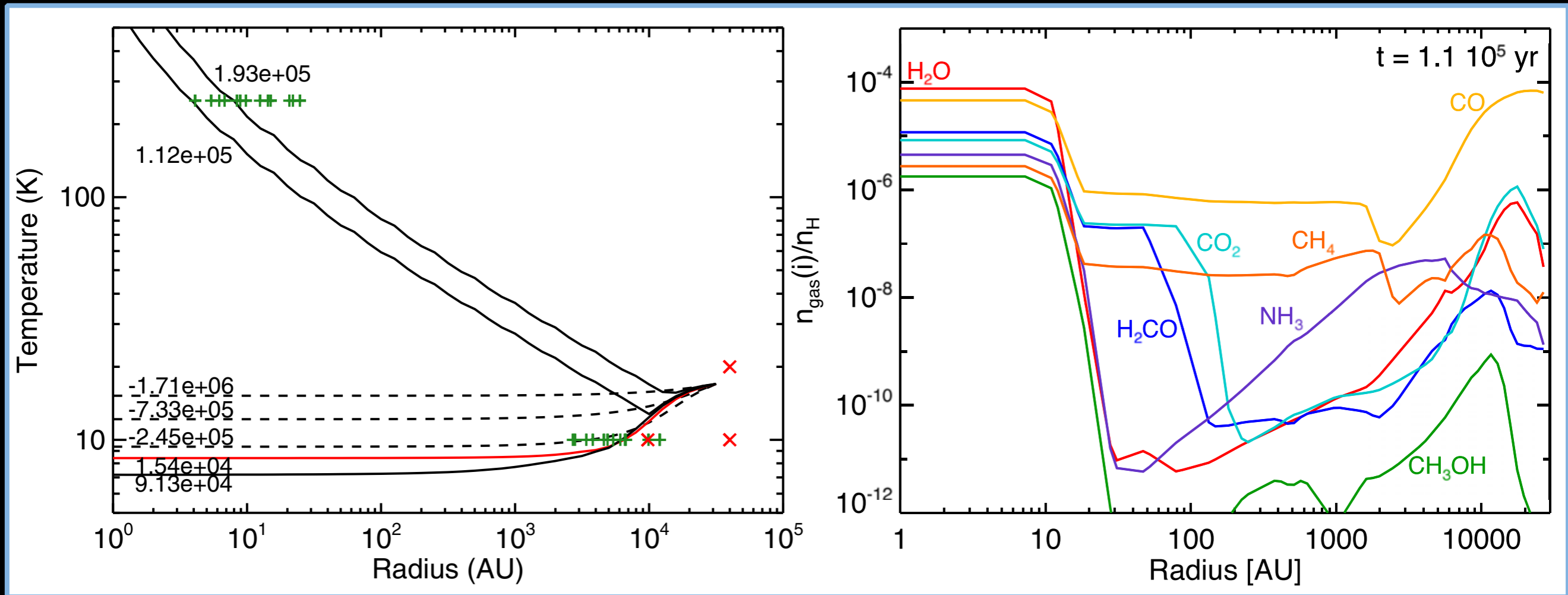
Taquet et al. (2014)

→ in good agreement with H₂CO observations by Ceccarelli et al. (2001) who needed two abundance jumps at 50 K and 100 K to reproduce their data

see also Aikawa et al. (2008, 2012), Furuya et al. (2012), Hincelin et al. (2013), Vasyunin et al. (2013), Drozdovskaya et al. (2016) and many others

Formation of COMs during warm-up around protostars

UV-induced chemistry triggers an efficient formation of complex organics during the warm-up phase in protostellar envelopes
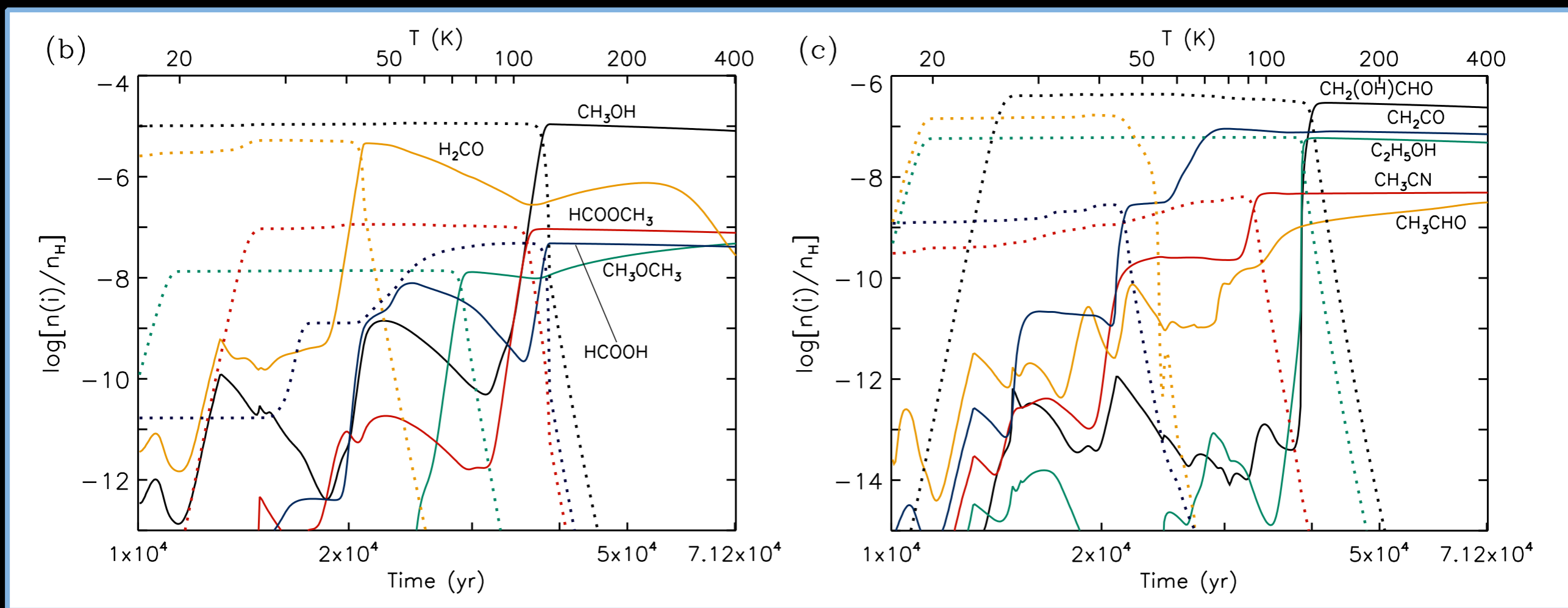
Garrod (2013)

Hard to deduce a general trend about efficiency of complex organics formation in ice mantle and surface

Underprediction of abundances

Abundance ratios of HCOOCH₃, CH₃OCH₃, or CH₃CN are still underpredicted by grain surface models

Garrod (2013)

Data compiled in Taquet et al. (2015)

Impact of proton-transfer reactions

Proton-transfer reactions involving NH_3 increase gas-phase abundances of COMs by one-to-two orders of magnitude

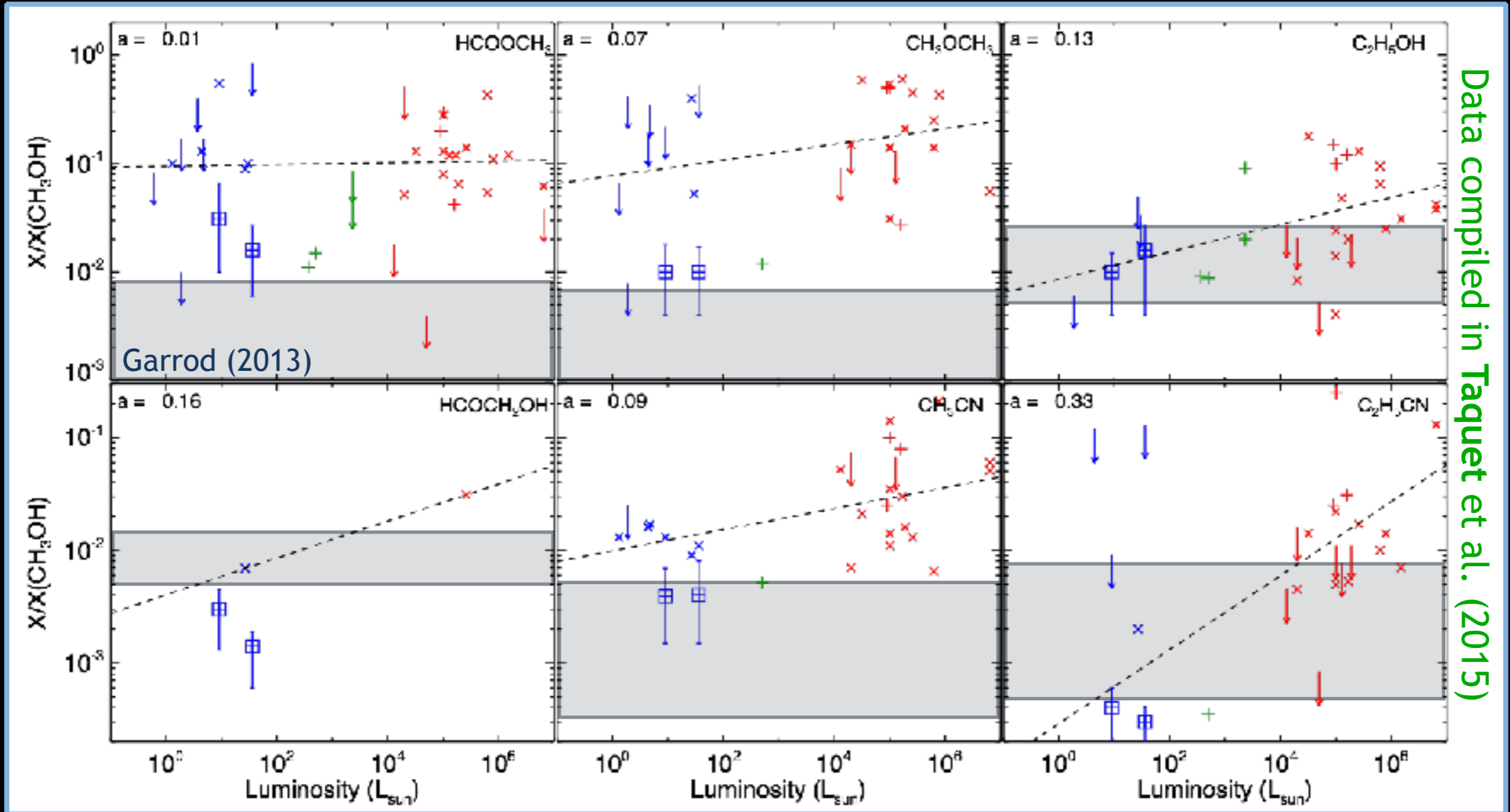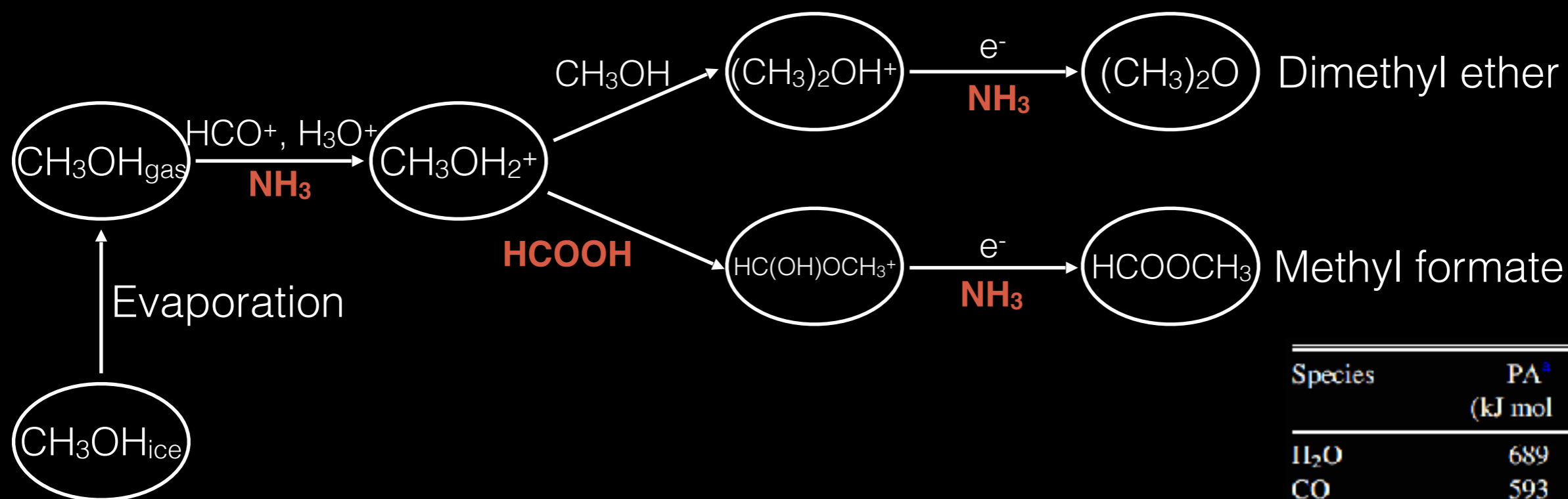CH_3OH_{gas} —HCO^+, H_3O^+ / NH_3→ $CH_3OH_2^+$

$CH_3OH_2^+$ —CH_3OH→ $(CH_3)_2OH^+$ —e^- / NH_3→ $(CH_3)_2O$ Dimethyl ether

$CH_3OH_2^+$ —$HCOOH$→ $HC(OH)OCH_3^+$ —e^- / NH_3→ $HCOOCH_3$ Methyl formate

Evaporation

CH_3OH_{ice}

- Highly exothermic proton transfer reaction between protonated COMs and NH_3 due to higher proton affinity of NH_3

$XH^+ + NH_3 \longrightarrow X + NH_4^+$

($k \approx 2\times10^{-9}$ $cm^3 \cdot s^{-1}$ for all studied reactions; see Hemsworth et al. 1974)

Species	PA[a] (kJ mol^{-1})
H_2O	689
CO	593
N_2	494
CO_2	539
CH_4	544
NH_3	854
H_2CO	713
CH_3OH	754
HCOOH	743
C_2H_5OH	776
CH_3OCH_3	792
CH_3OCHO	782
C_2H_5OCHO	799
$CH_3OC_2H_5$	809
$C_2H_5OC_2H_5$	828
CH_3CN	781

Taquet, Wirstrom, & Charnley (2016)

Impact of proton-transfer reactions

Proton-transfer reactions involving NH₃ increase gas-phase abundances of COMs by one-to-two orders of magnitude

Without proton-transfer reactions   With proton-transfer reactions

$n_H = 10^7$ cm^{-3}, T = 150 K, $\zeta = 3 \times 10^{-17}$ s^{-1}

Taquet, Wirstrom, & Charnley (2016)
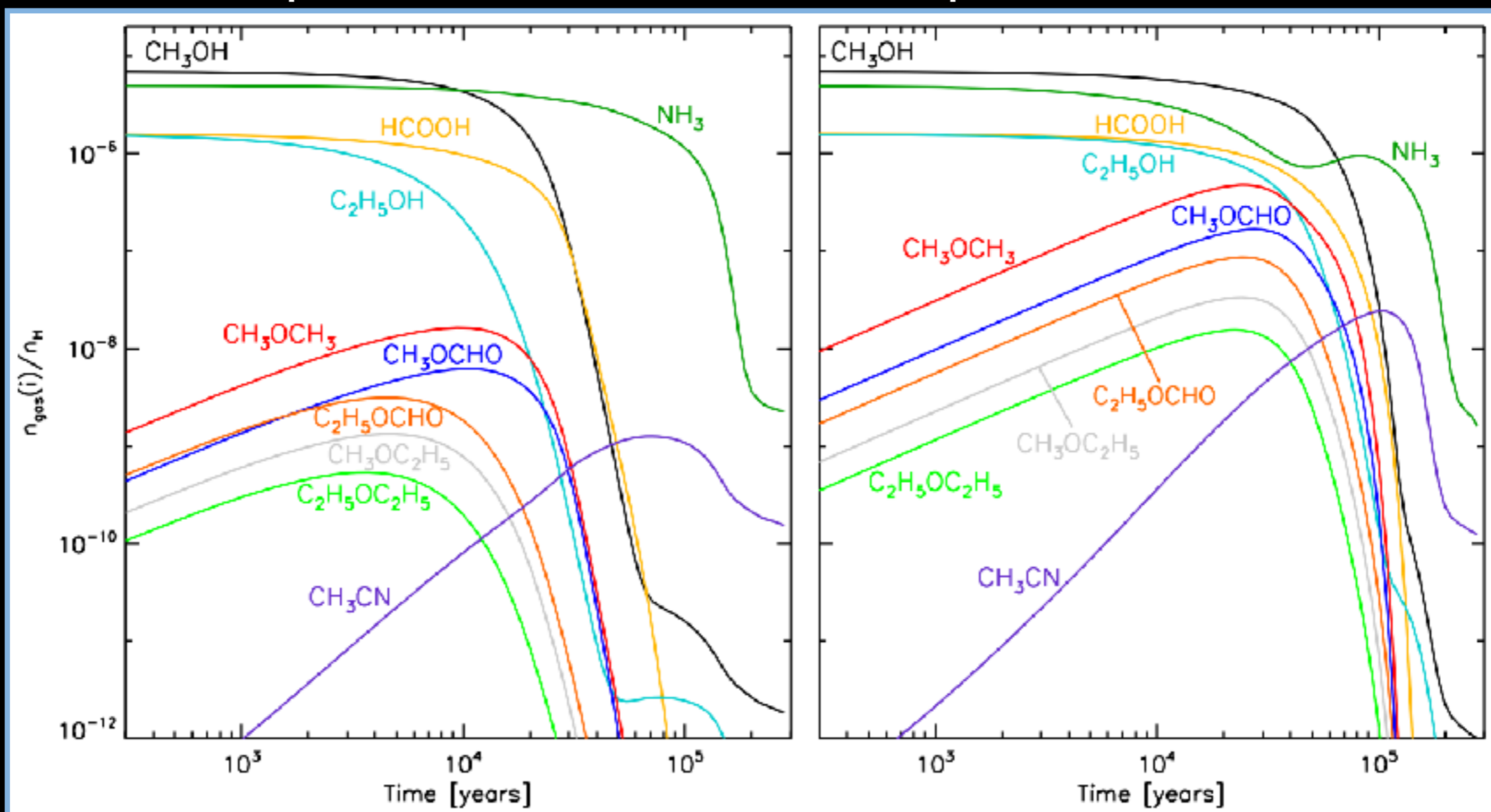
Formation pathways

Species	Observed abundances / CH_3OH	Ices	Gas phase
CH_3OH	100	CO hydrogenation	/
CH_3CHO	High-mass: ~ 1 % Low-mass: ~ 0.5 %	$CH_3 + HCO$ $HCCO + 2H$	$C_2H_5 + O$ $CH_4 + H_2CO^+$ (+PT)
$HCOOCH_3$	High-mass: ~ 14 % Low-mass: ~ 4 %	$HCO + CH_3O$	$CH_3OH_2^+ + HCOOH$ (+PT) $CH_3OCH_2 + O$
CH_3OCH_3	High-mass: 30 % Low-mass: ~ 4 %	$CH_3 + CH_3O$	$CH_3OH_2^+ + CH_3OH$ (+PT) $CH_3 + CH_3O$
C_2H_5OH	High-mass: ~ 6 % Low-mass: ~ 1 %	$CH_3 + CH_2OH$ $CH_3CHO + 2H$	/
$HCOCH_2OH$	High-mass: 3 % Low-mass: ~ 0.4 %	$HCO + CH_2OH$	/
$(CH_2OH)_2$	Low-mass: ~ 1 %	$CH_2OH + CH_2OH$	/
CH_3CN	High-mass: ~ 5 % Low-mass: ~ 1 %	$CH_3 + CN$ C_2N hydrogenation	$CH_3^+ + HCN$ (+PT)
C_2H_5CN	High-mass: ~ 4 % Low-mass: ~ 0.1 %	$CH_3 + CH_2CN$ HC_3N hydrogenation	/
NH_2CHO	Low-mass: ~ 0.1 %	$NH_2 + HCO$ OCN hydrogenation	$NH_2 + H_2CO$

Outline

Ion formation in ices

Can **Acid-base chemistry** explain the observational features attributed to $HCOO^-$, OCN^-, NH_4^+ in infrared absorption spectra ?

Species	$X_{H_2O}{}^a$ [%]				$X_H{}^b$ [10^{-6}]		
	MYSOs	LYSOs	BG Stars[c]	Comets	MYSOs	LYSOs	BG Stars[c]
OCN^-	$0.6^{0.7}_{0.3}$	$0.6^{0.8}_{0.4}$ (0.4)	nd	nd	$0.4^{0.5}_{0.2}$	$0.4^{0.4}_{0.2}$ (0.06)	nd
	0.1–1.9	(<0.1)–1.1	<0.5	nd	0.2–0.6	(<0.04)–0.4	<0.16
$HCOO^{-i}$	$0.5^{0.7}_{0.5}$ (0.5)	nd	nd	nd	$0.18^{0.28}_{0.12}$ (0.14)	nd	nd
	0.3–1.0	~0.4	<0.1	nd	(<0.10)–0.42	~0.2	<0.8
NH_4^+	11^{13}_9	11^{15}_7	8^{11}_6	nd	$4.1^{5.4}_{1.8}$	$4.6^{5.8}_{3.2}$	$3.8^{4.9}_{2.9}$
	9–34	4–25	4–13	nd	1.4–6.0	0.8–12	1.9–9.6

from Boogert et al. (2015)

Reactants			Products h	v_0, E_a, [T interval, K]	References
Acid-base reactions					
Generation 0	Generation 0	Generation 1			
H_2O	+ HNCO	→	$H_3O^+OCN^-$	$(3 \times 10^8, 26)$ [110–130]	Raunier et al. (2004) and Theule et al. (2011a)
NH_3	+ HCOOH	→	$NH_4^+HCOO^-$		Schutte et al. (1999)
NH_3	+ HNCO	→	$NH_4^+OCN^-$	$(4 \times 10^{-3},$ 0.4) [8–40]	Demyk et al. (1998), Raunier et al. (2003), van Broekhuizen et al. (2004) and Mispelaer et al. (2012)
NH_3	+ HCN	→	$NH_4^+CN^-$	$(1.6 \times 10^{-2},$ 2.7) [60–105]	Clutter and Thompson (1969) and Noble et al. (2013)

from Theulé et al. (2013)

Bulk chemistry between abundant species

Increase of temperature can trigger the reactivity in the bulk: reactions between abundant and stable species through reactions with activation barriers

Nucleophilic additions
    ex: $NH_3 + H_2CO \rightleftarrows NH_2CH_2OH$ (Bossa et al. 2009)

Acid-base reactions
    ex: $H_2O + HNCO \rightleftarrows H_3O^+OCN^-$ (Theulé et al. 2011)

H/D exchange reactions
    ex: $CD_3OD + H_2O \rightleftarrows CD_3OH + HDO$ (Ratajczak et al. 2009, Faure et al. 2015)

- Rates derived for isothermal experiments with ice mixtures of "pure" reactions
- Evolution of rate with temperature then fitted with Arrhenius law to derive pre-factor v and activation barrier E_{act}

→ v can be much lower than v computed by models
→ Reactions are not always limited by diffusion

$HNCO + NH_3 \rightleftarrows NH_4^+OCN^-$
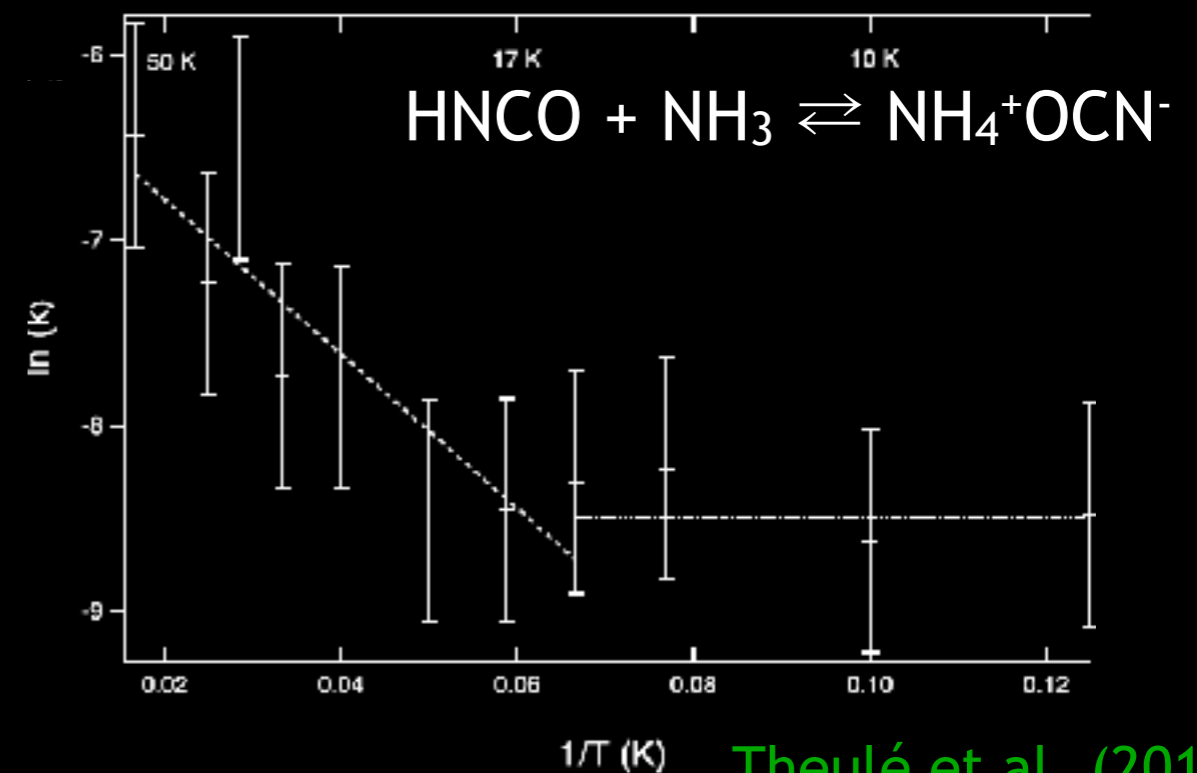
Theulé et al. (2013)

Bulk chemistry between abundant species

Rate-equations models are based on second-order rate constants and are diffusion-limited:

But reactions with abundant species do not only depend on diffusion and can be interpreted as first-order kinetics

Ex: $NH_3 + H_2CO \rightleftarrows NH_2CH_2OH$ (Bossa et al. 2009, Theulé et al. 2013)

Measured rate constant: $K = v \exp(-E_{reac}/T)$
with $E_{reac} = 4.5$ kJ/mol and $v = 0.05$ s^{-1}

K_{reac} scaled by probability that two reactants occupy two neighbouring sites
(~ abundance of most abundant reactant)