Fractionation in Young Stellar Objects:
Can the fractionation be used as chemical tracer of observed molecules ?

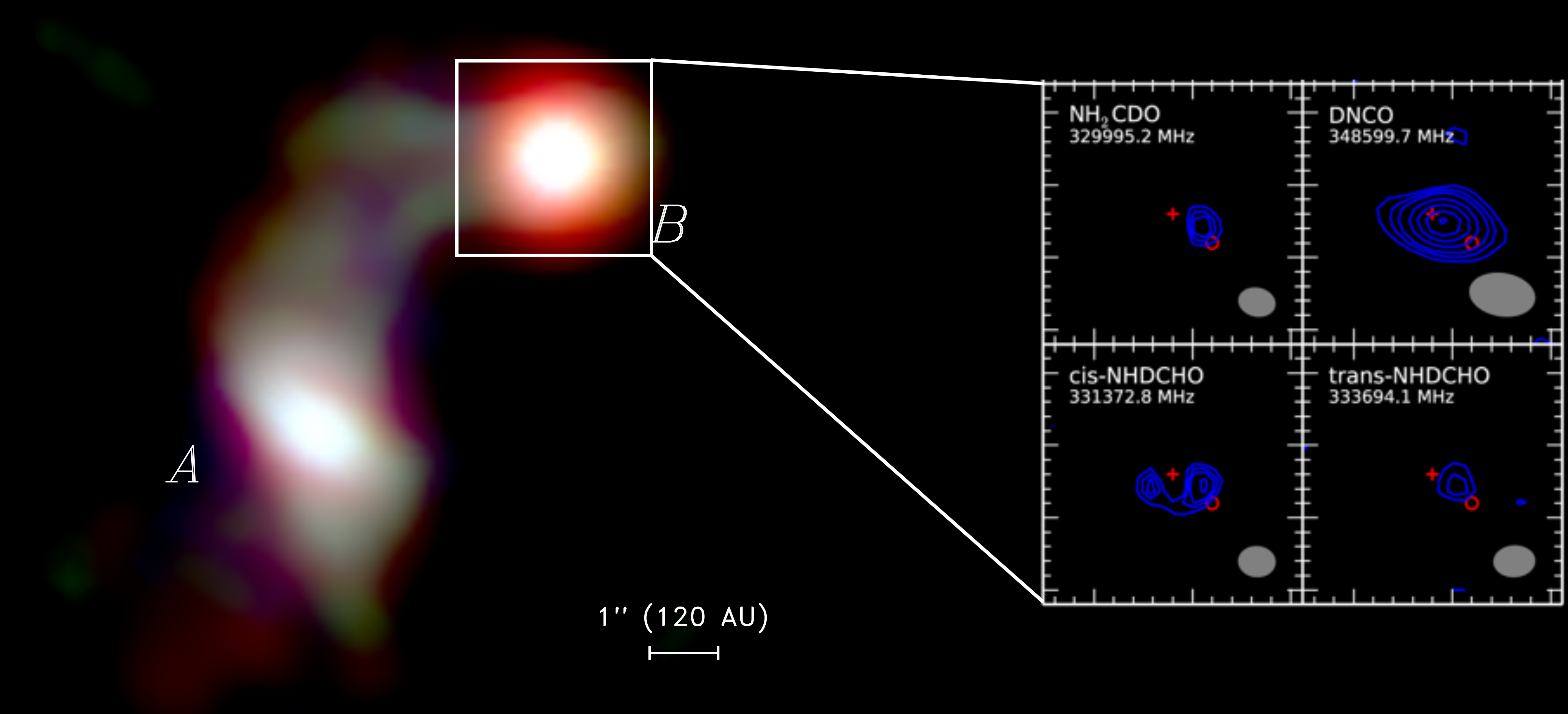


Image credit: Jørgensen et al. (2016), Coutens et al. (2016)

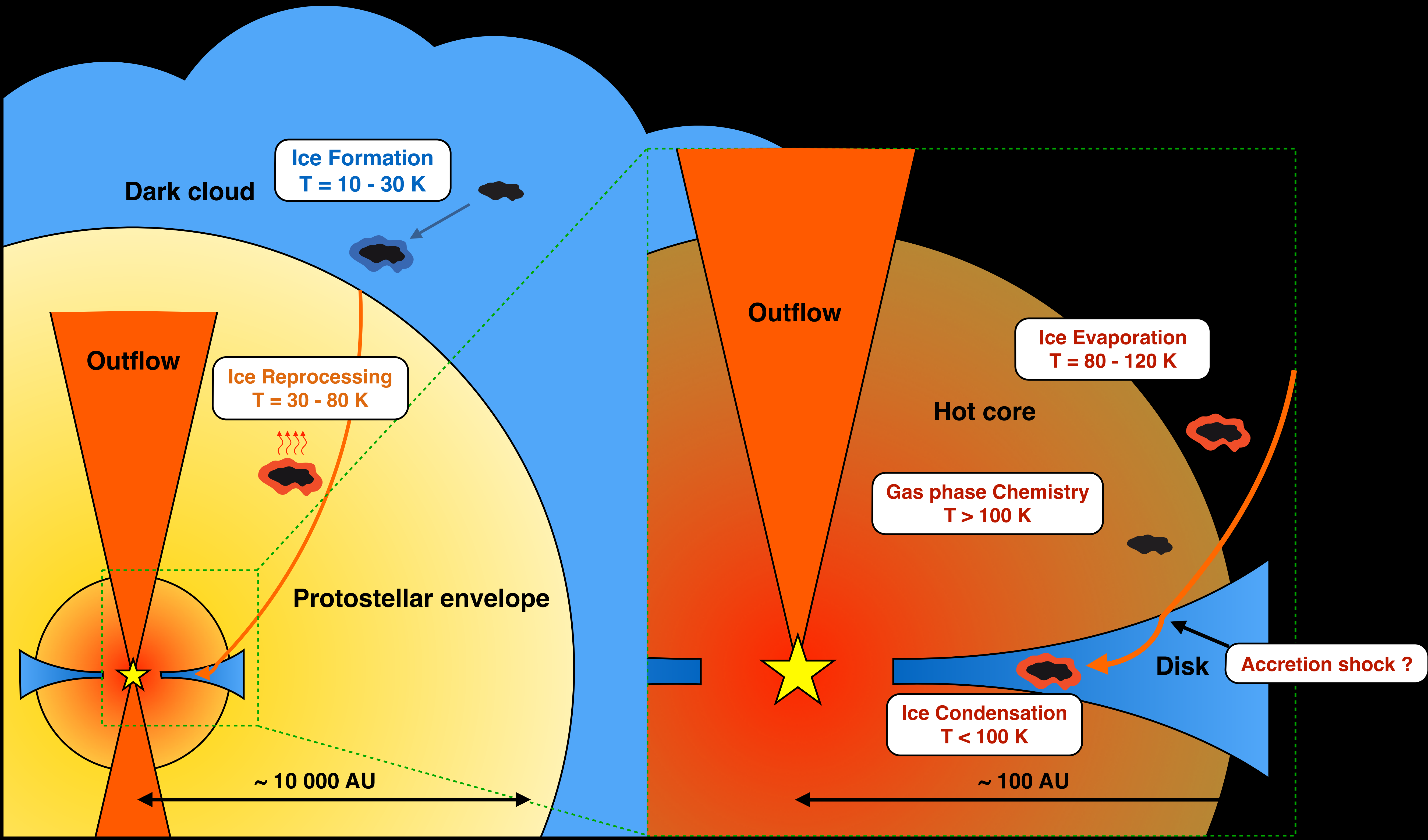
Vianney Taquet, Leiden Observatory

"Fractionation in Space", Arcetri, 11/10/2016

Sterrewacht Leiden
Universiteit Leiden

Chemical evolution in protostars

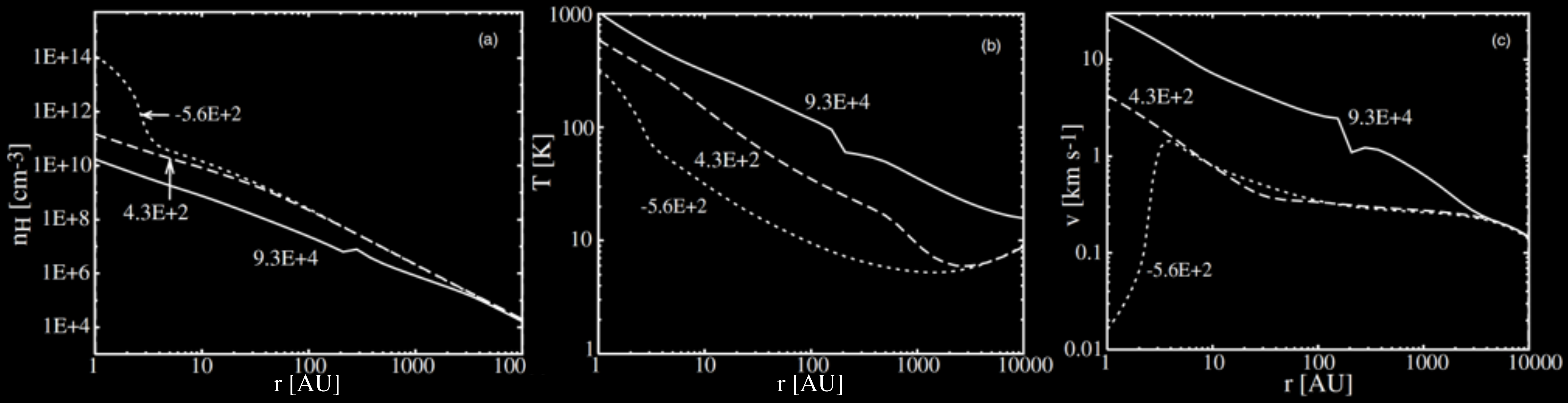
Fractionation of molecules observed around protostars (mostly) traces chemistry during prior stages → need to follow the chemistry from dark clouds



Physical and astrochemical models

Astrochemical models are usually coupled with 1D/2D physical models to follow the chemical evolution from dark clouds to hot cores:

- **0D free-fall collapse**: Cazaux et al. (2011), Awad et al. (2014)
- **1D parametric collapse model + Radiative Transfer**: Taquet et al. (2014)
- **Hydrodynamic simulations**: Aikawa et al. (2012), Wakelam et al. (2014), Furuya et al. (2016)



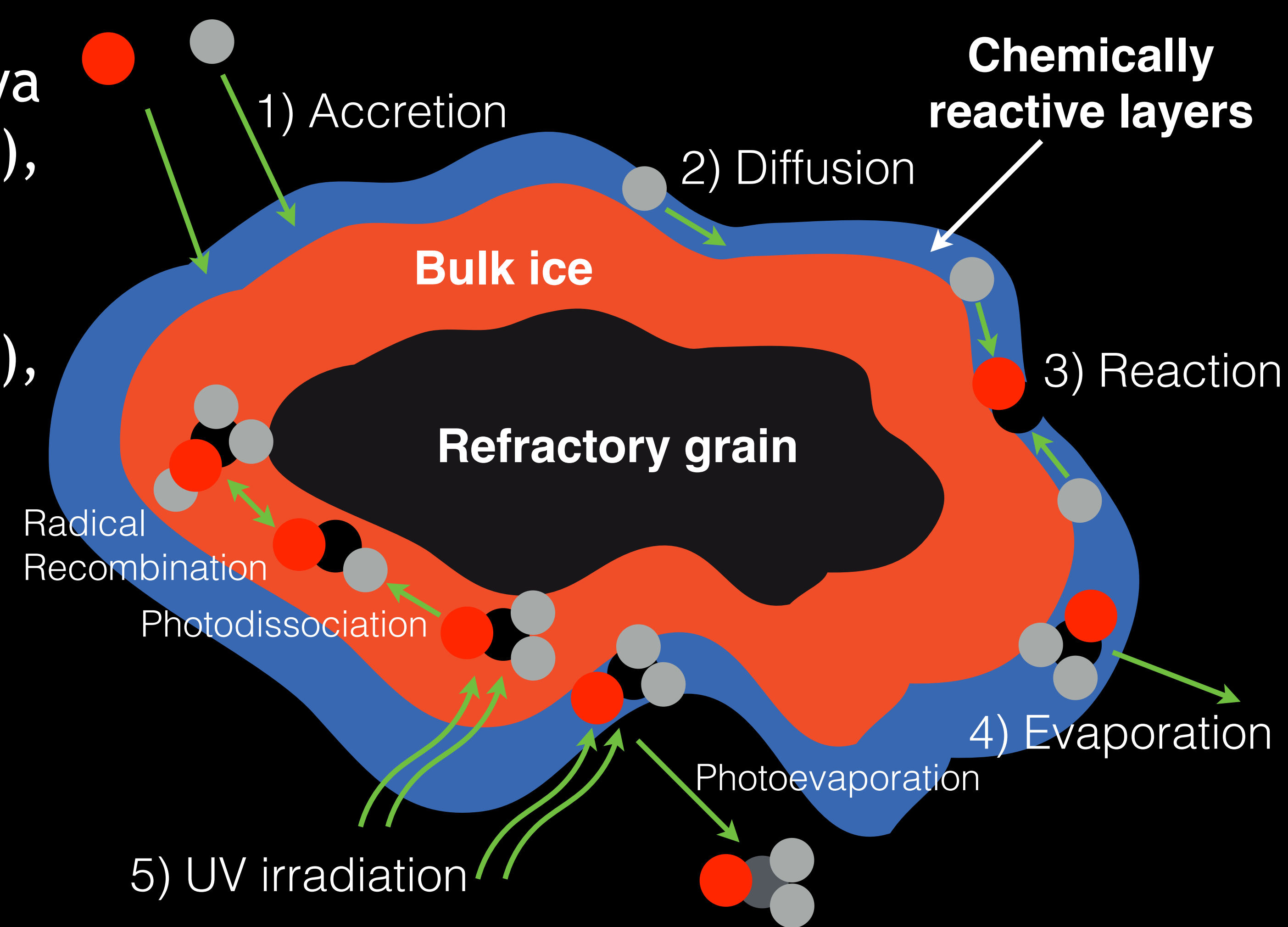
Hydrodynamical simulations used in Aikawa et al. (2012)

Physical and astrochemical models

- **Gas phase chemical networks are usually based on KIDA/OSU/UMIST networks and extended**
  - to include **spin states of various species** (H_2, H_3^+, etc), **deuterium exchange reactions** (H_3^+ - H_2 system: Ugo et al. 2009; CH_3^+ - H_2: Roberts et al. 2000, 2004; etc)
  - **deuterated counterparts of reactions** involving hydrogenated species (scrambling assumption + exceptions, see Aikawa et al. 2012, Sipila et al. 2013, Albertsson et al. 2013)

→ > 50 000 reactions, 2 000 species !

- **Gas-grain chemical processes:**
  - **2 phase**: Cazaux et al. (2011), Aikawa et al. (2012), Wakelam et al. (2014), Awad et al. (2014)
  - **3 phase**: Taquet et al. (2012, 2014), Furuya et al. (2015, 2016)



Outline

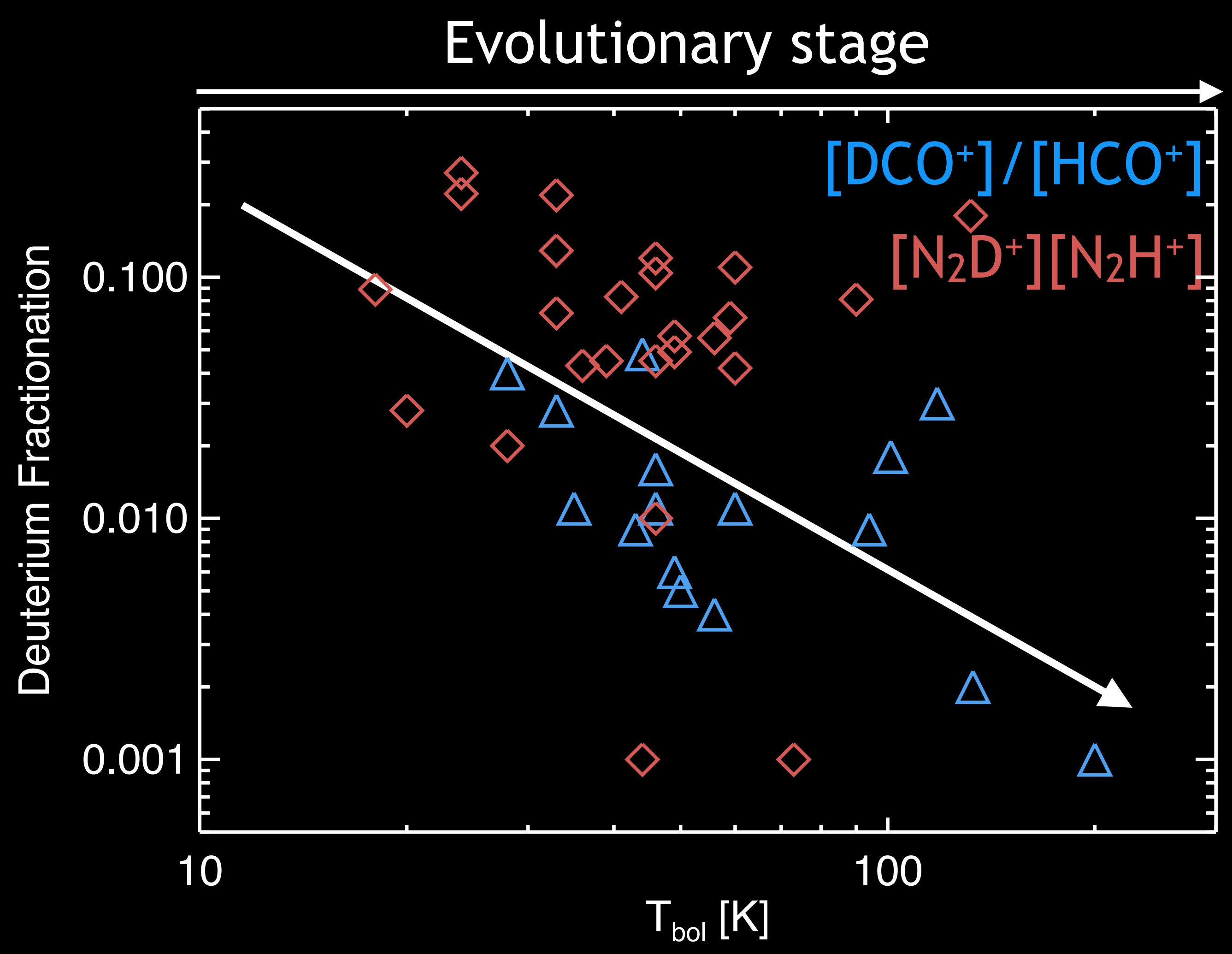
- Introduction
- Deuteration of ions in low-mass YSOs
- Deuteration of water and icy species in low-mass YSOs
- Deuteration of complex organic in low-mass YSOs
- Deuteration in massive YSOs

Ion deuteration around low-mass protostars

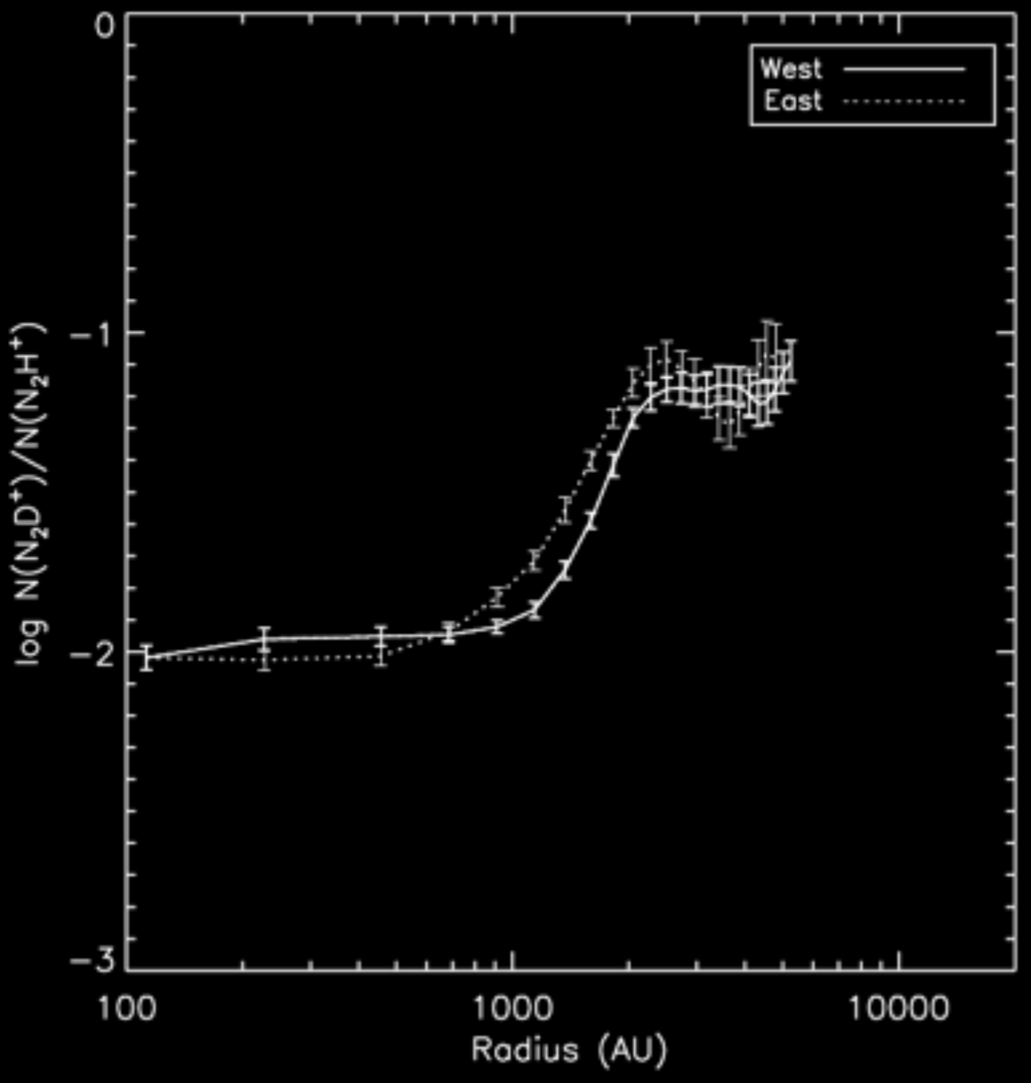
Observations show:

1) Decrease of HCO^+ and N_2H^+ deuterations with the evolutionary stage
2) Increase of deuteration with the distance from the protostar

Deuteration evolution with the evolutionary stage



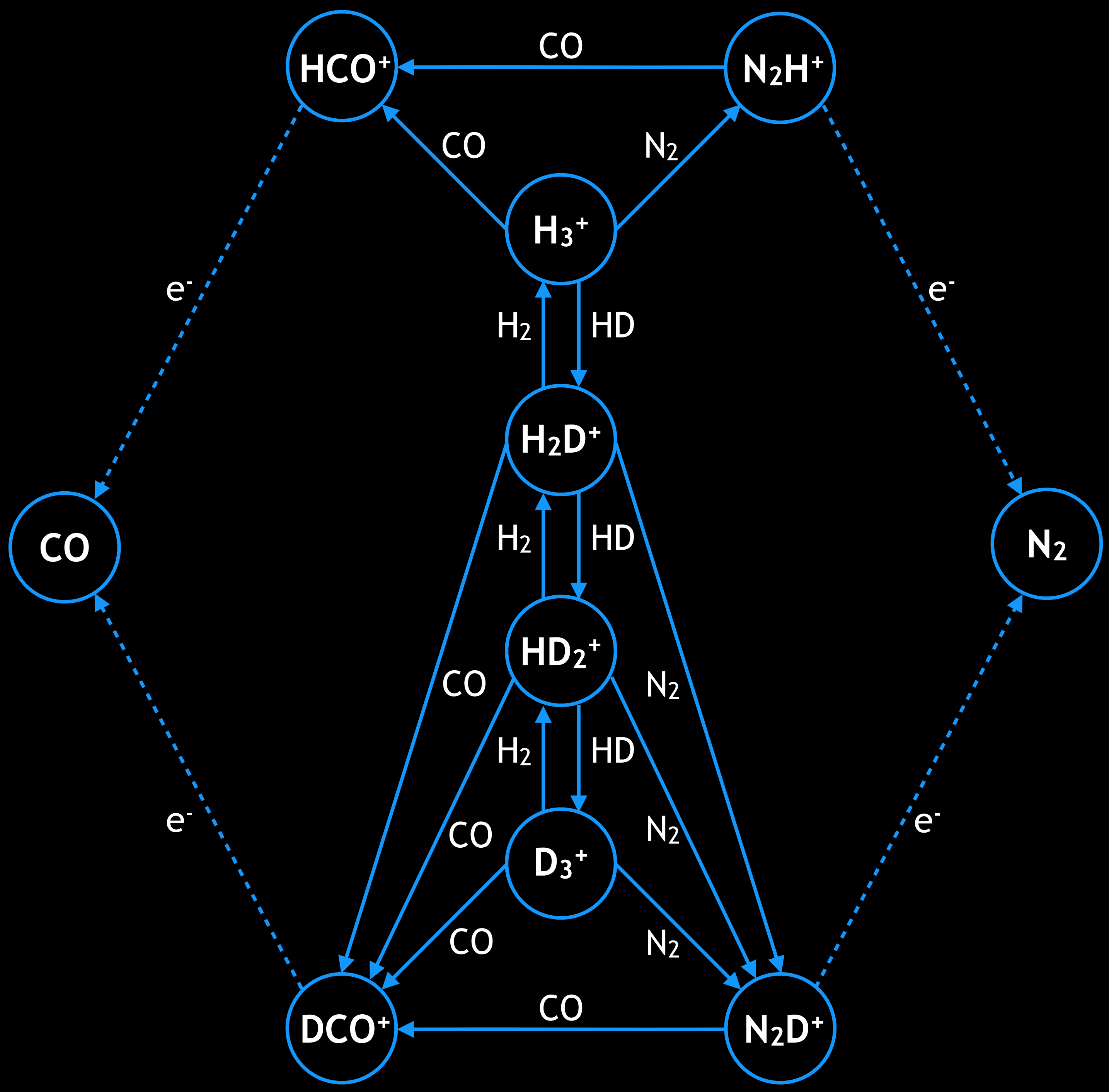
Observed deuteration around L1157

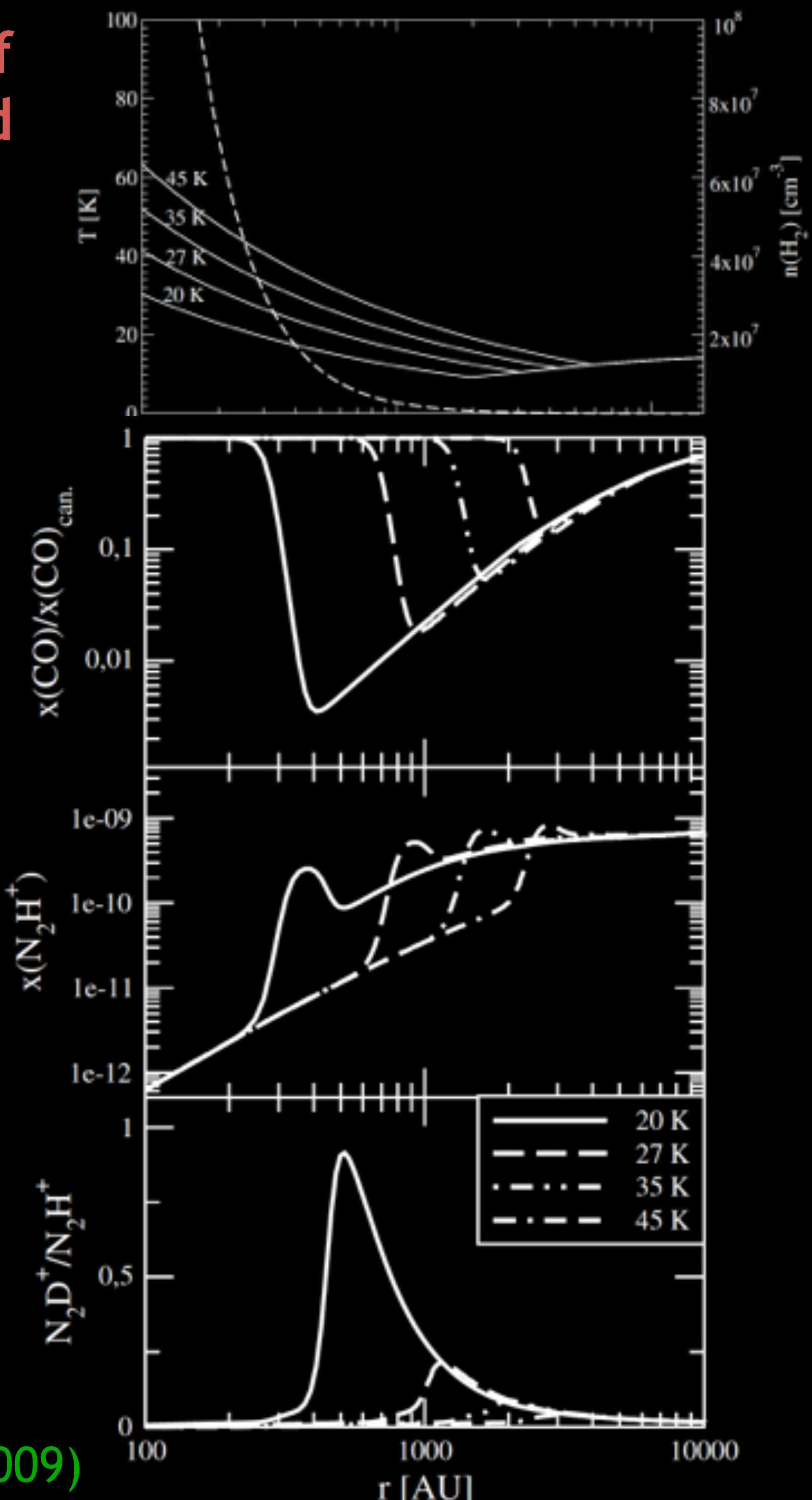


Data from Jørgensen et al. (2004), Emprechtinger et al. (2009), Tobin et al. (2011)

Deuteration of ions around protostars

Observational trend mainly due to increase of temperature with evolutionary stage and decreased distance from protostar





Emprechtinger et al. (2009)

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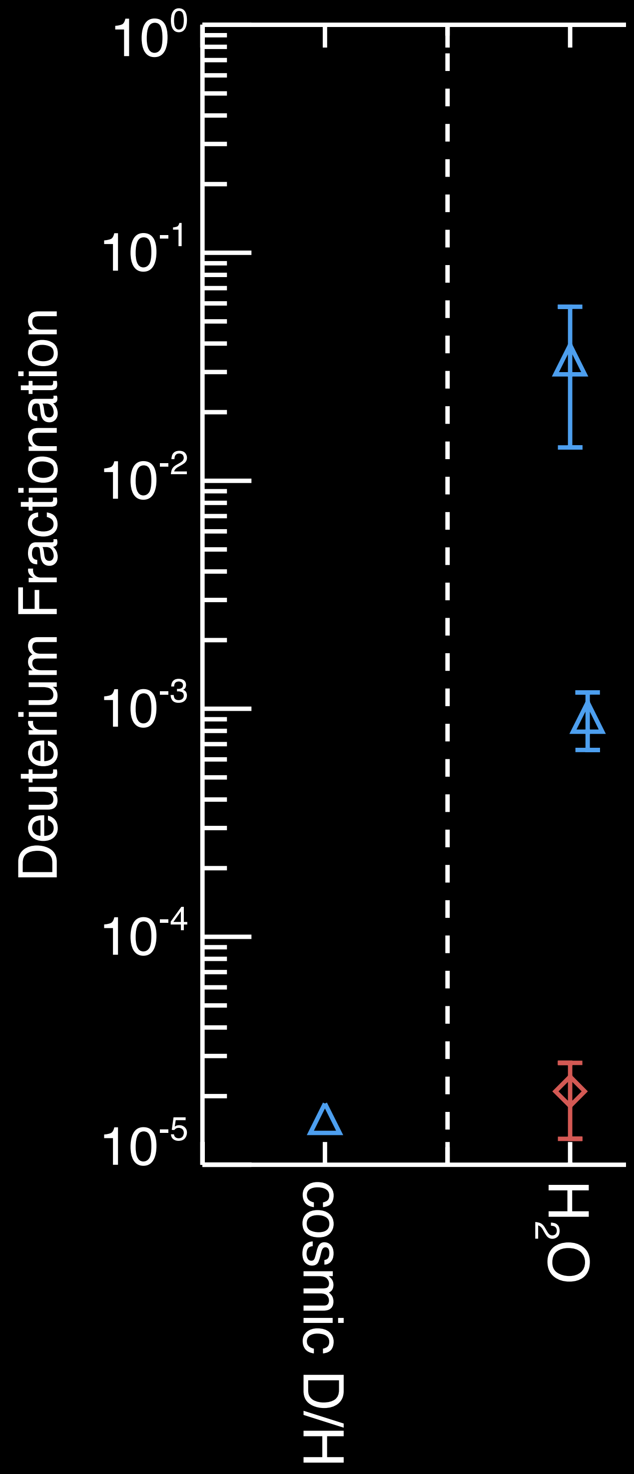
Deuteration in low-mass YSOs

Deuteration observed towards IRAS 16293-2422

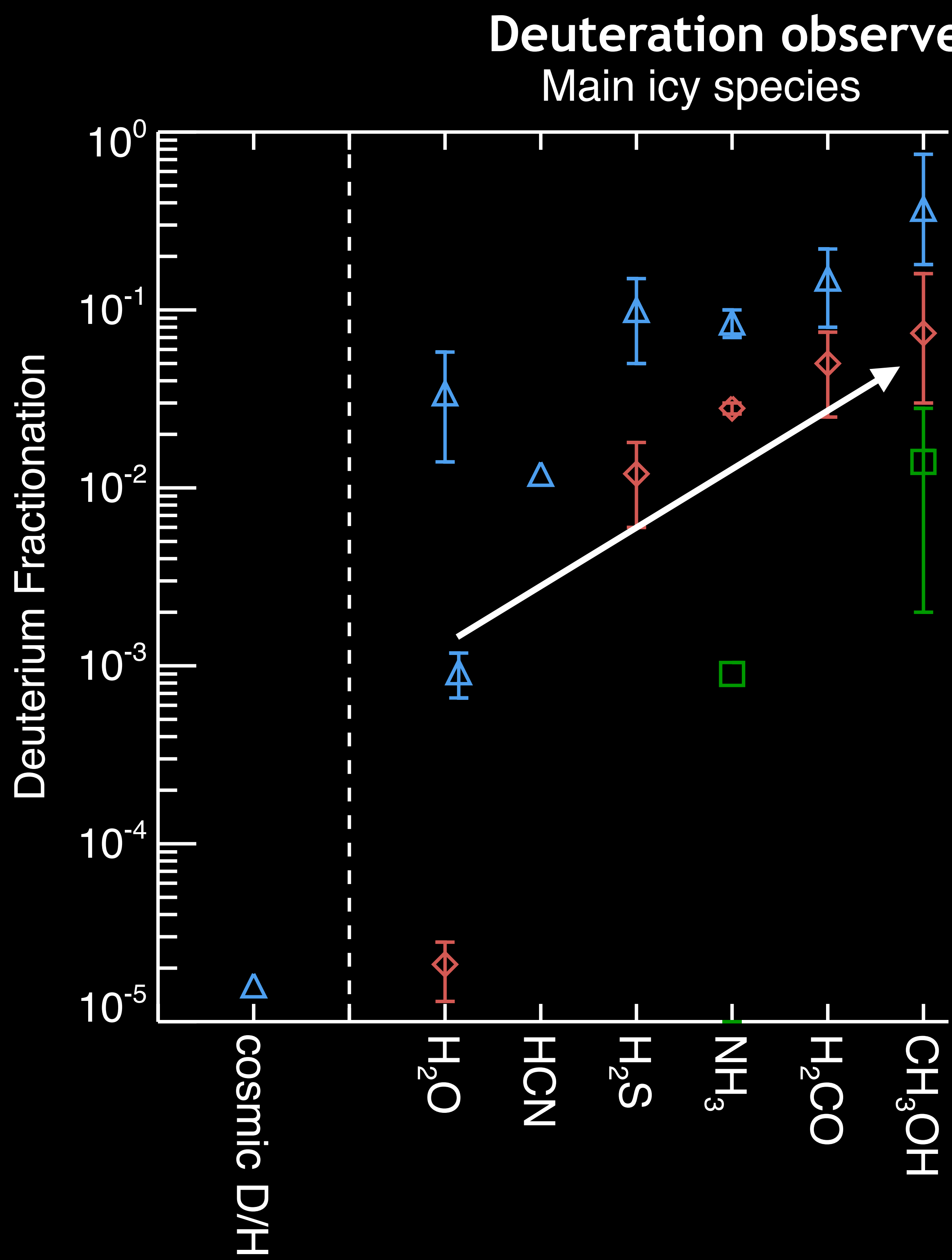


Herschel observations by Coutens et al. (2012)

ALMA/SMA observations by Persson et al. (2012)

PdBi observations by Coutens et al. (2014)
$[D_2O]/[HDO] \sim 7\ [HDO]/[H_2O]$

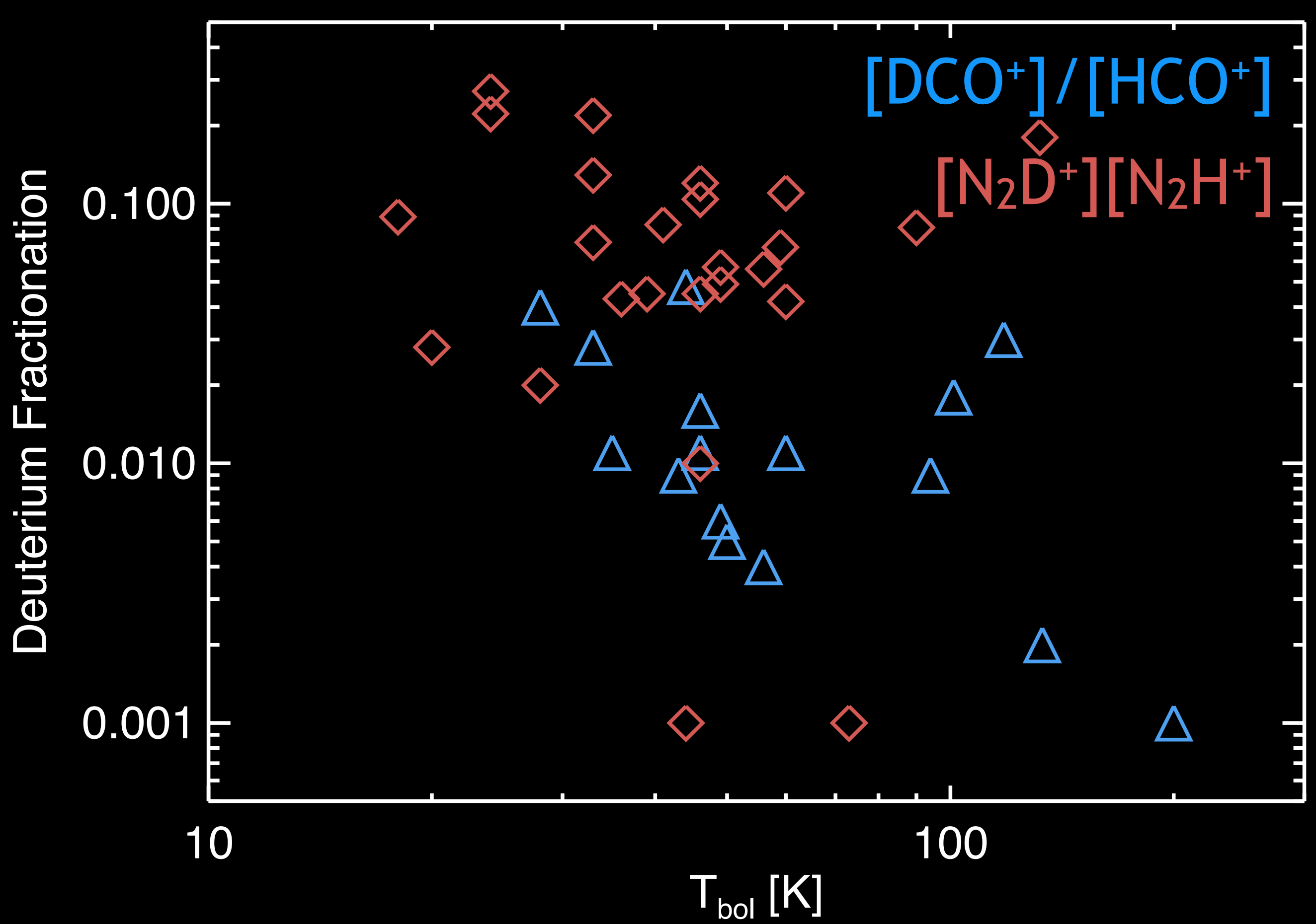
Deuteration in low-mass YSOs

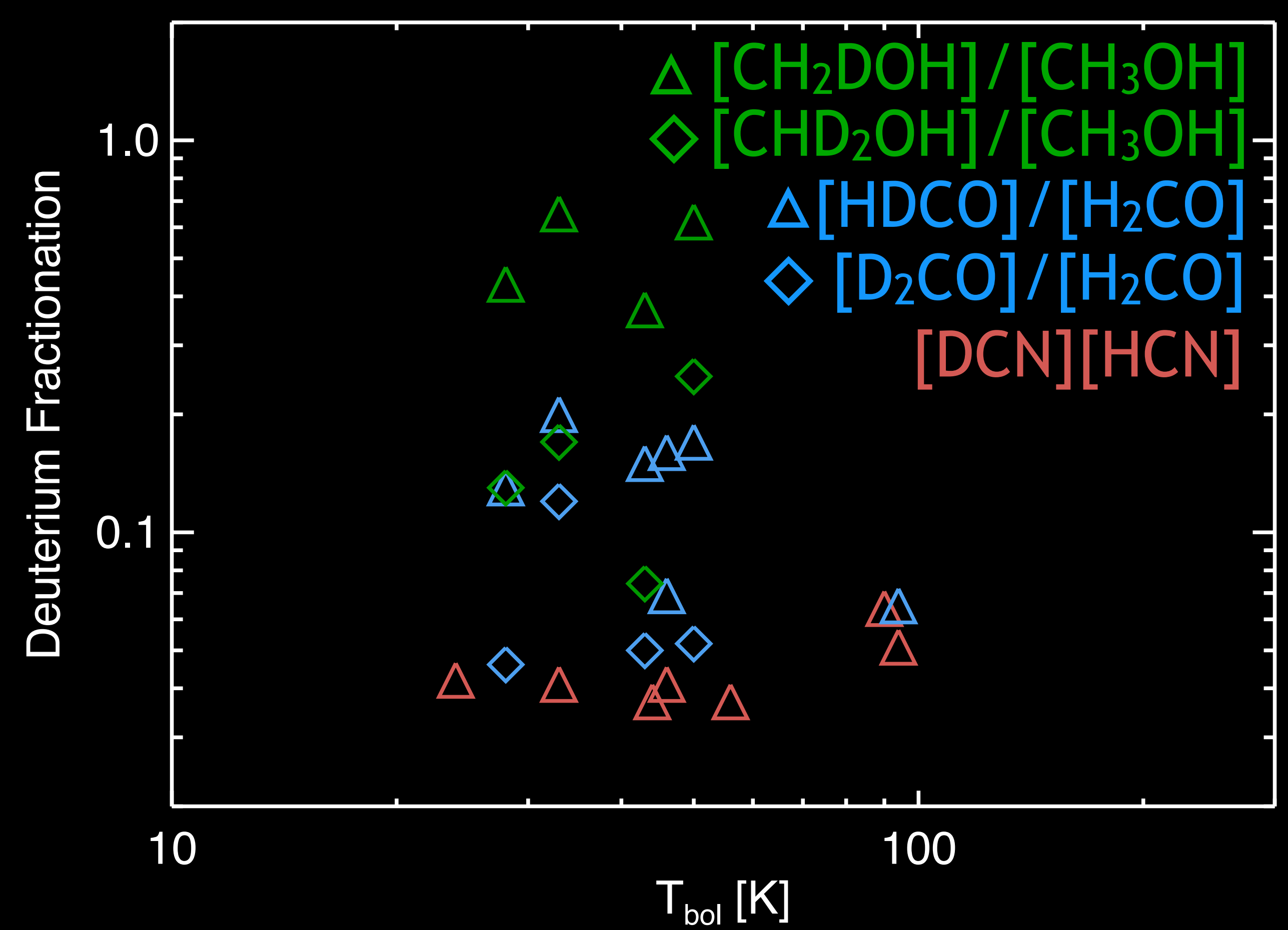


HCN: van Dishoeck et al. (1995); **H_2S:** van Dishoeck et al. (1995), Vastel et al. (2003); **NH_3:** van Dishoeck et al. (1995), Loinard et al. (2001), van der Tak et al. (2002); **H_2CO:** Ceccarelli et al. (1998, 2001); **CH_3OH:** Parise et al. (2004, 2006)

Deuteration evolution in low-mass YSOs

Unlike ions, neutral species do not show any trend with evolutionary stage (some exceptions, see E. Bianchi's talk)

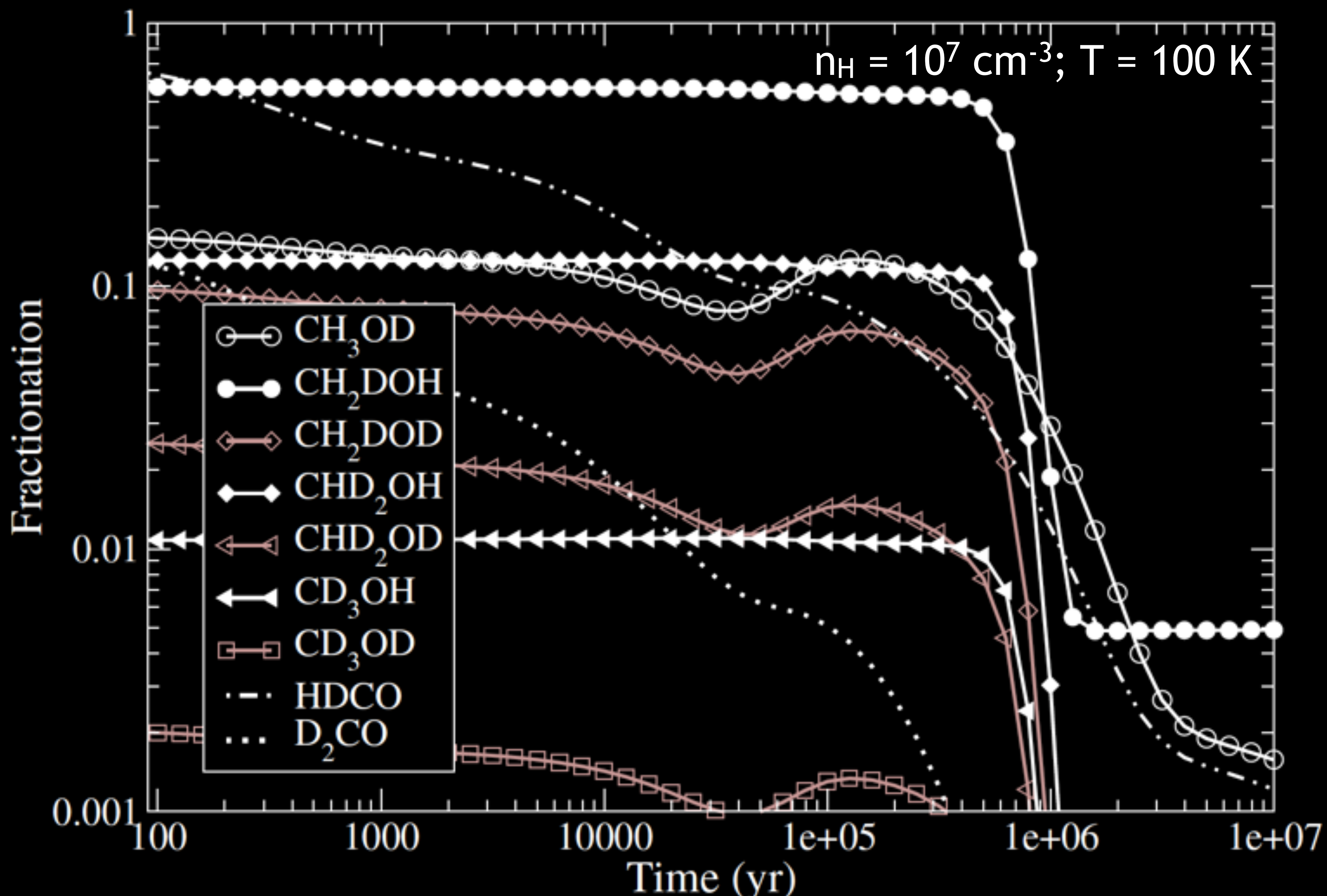




HCO^+: Jørgensen et al. (2004); **N_2H^+**: Emprechtinger et al. (2009), Tobin et al. (2011); **HCN**: Roberts et al. (2007); **H_2CO**: Parise et al. (2006), Roberts et al. (2007); **CH_3OH**: Parise et al. (2006)

Evolution of gas phase deuteration in hot cores

Gas phase chemistry after ice evaporation is likely too slow to significantly alter the deuteration of most neutral species in protostellar envelopes

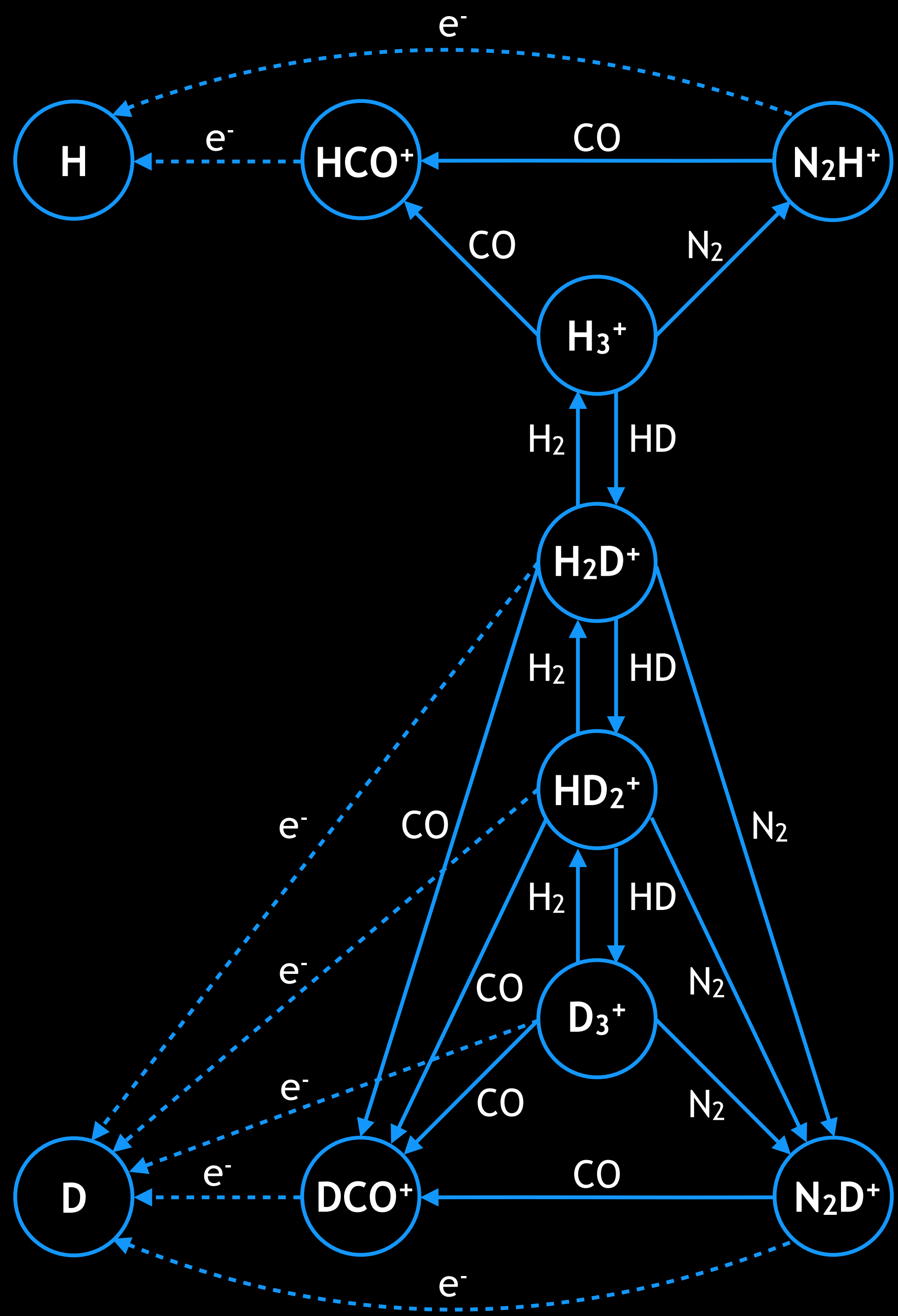


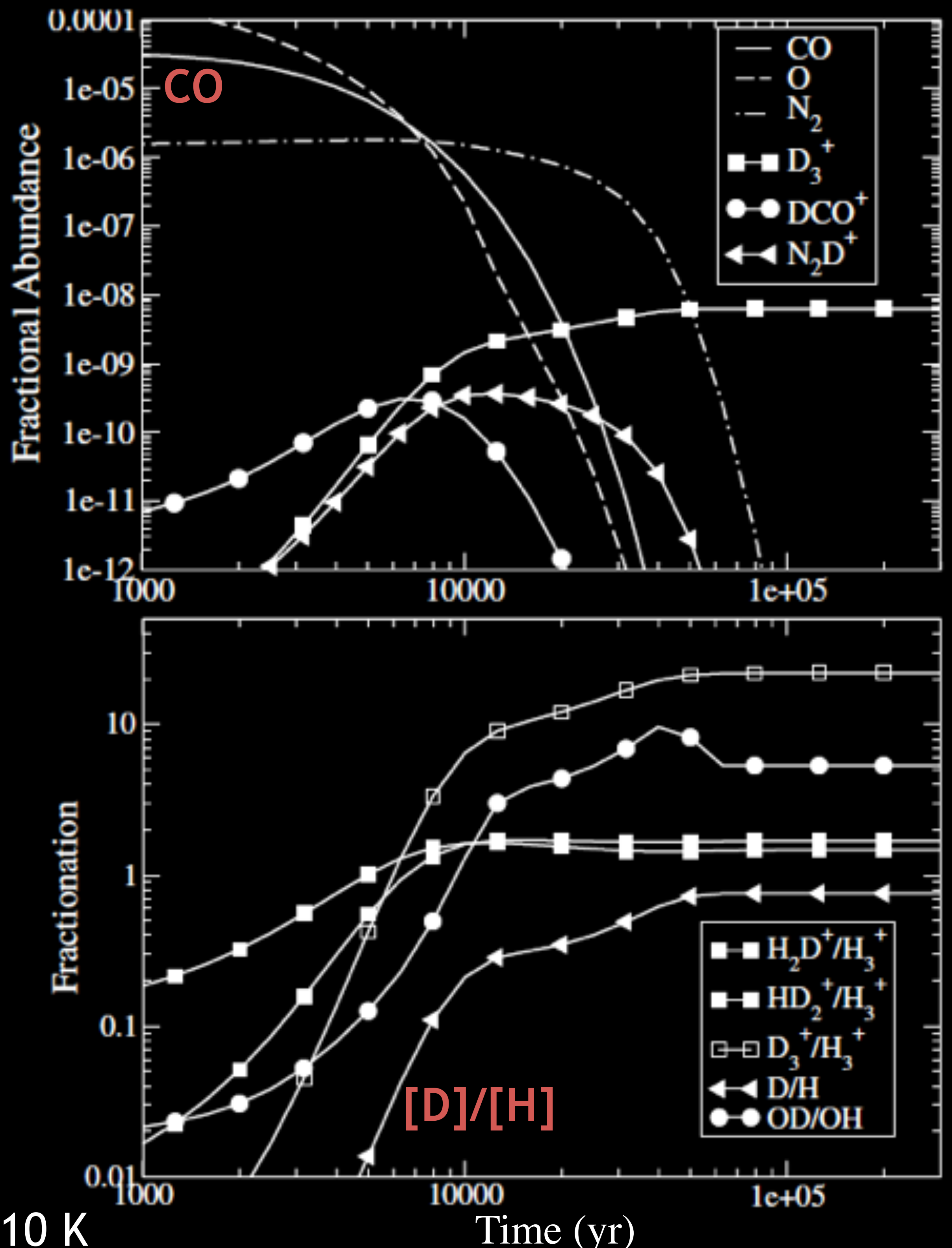
Osamura et al. (2004)
see also Charnley et al. (1997)

→ deuteration of most neutral species observed in Class 0/Class I should be due to their formation at prior stage

Gas phase [D]/[H] in dark clouds

Main icy species are formed from sequential hydrogenation of O, N, C, CO on interstellar grains → their deuteration depends on gas [D]/[H] at the prestellar stage



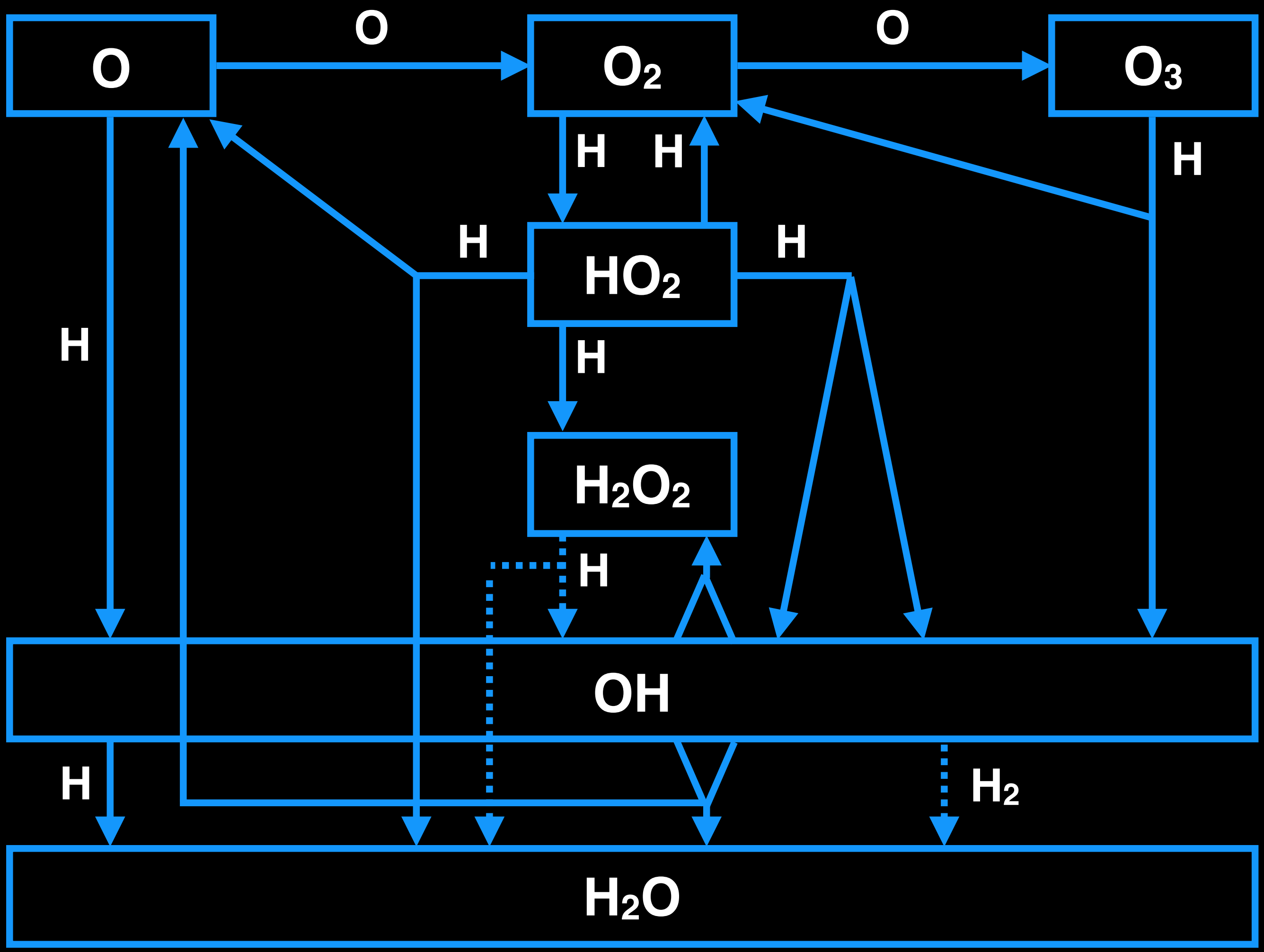


Roberts et al. (2003, 2004)

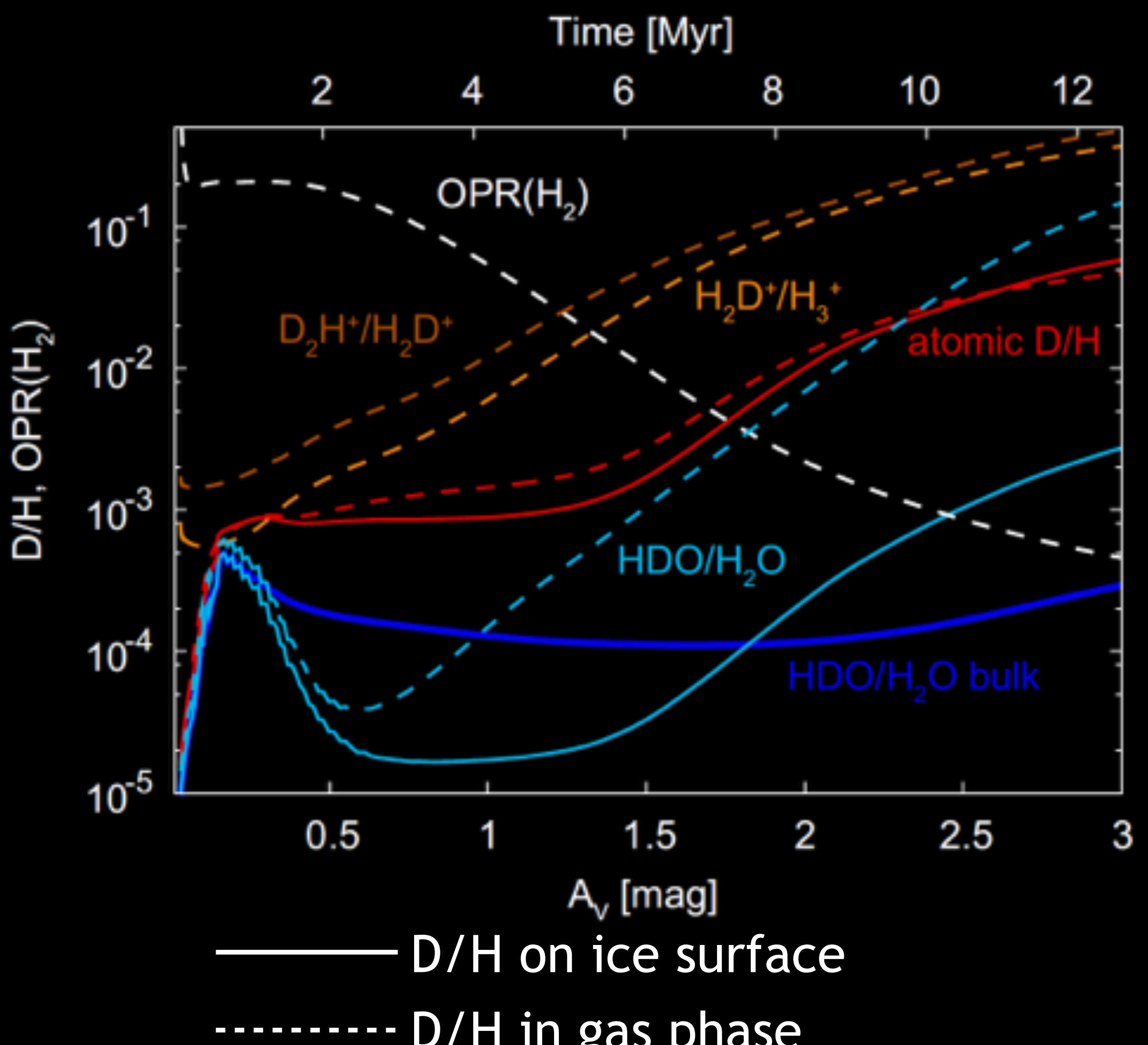
$n_H = 10^6$ cm^{-3}, T = 10 K

Water chemical network

Water and its deuterated isotopologues are formed through addition reactions from O, O_2, and O_3 on ices



Adapted from Linnartz et al. (2015)

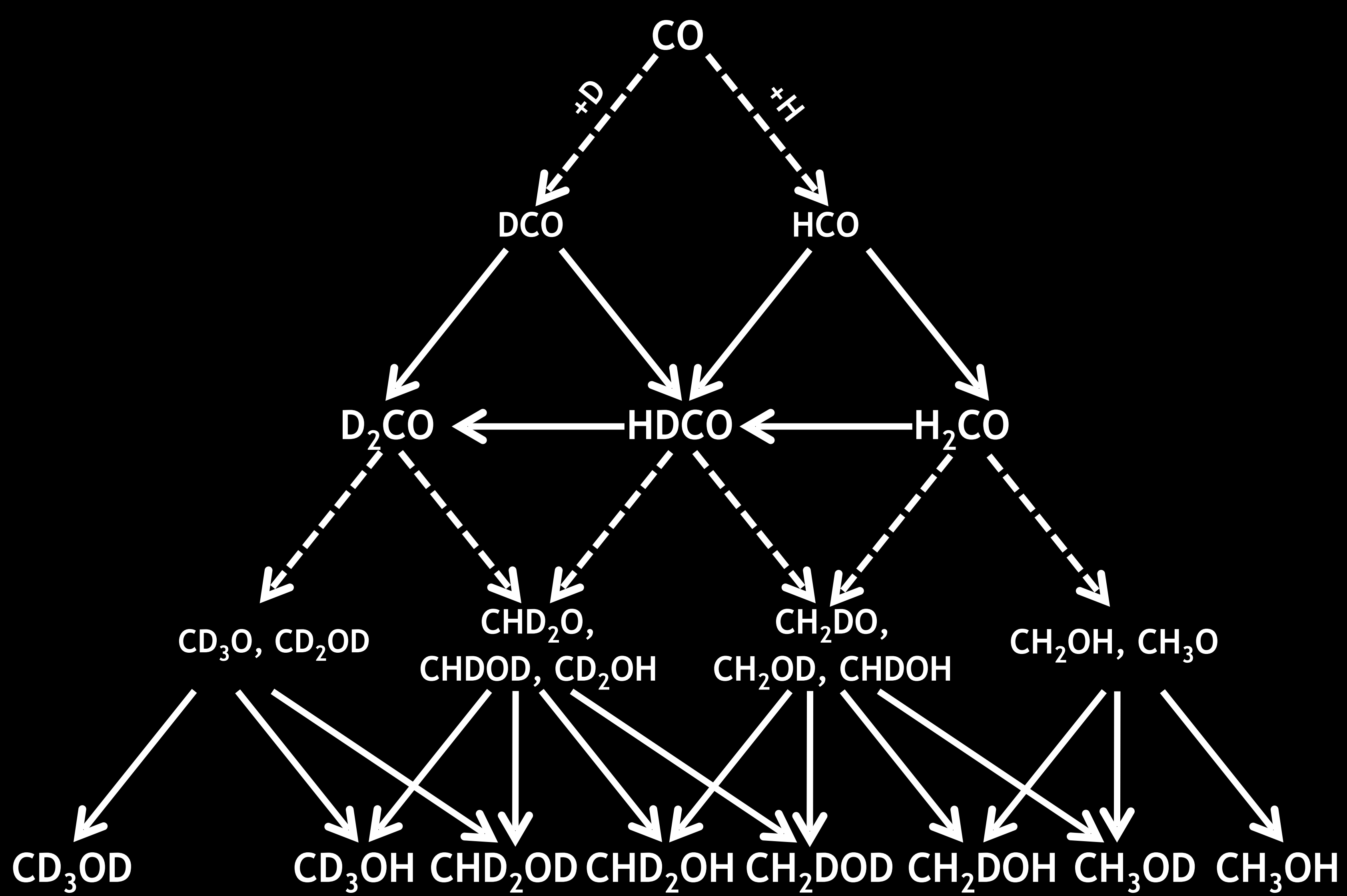


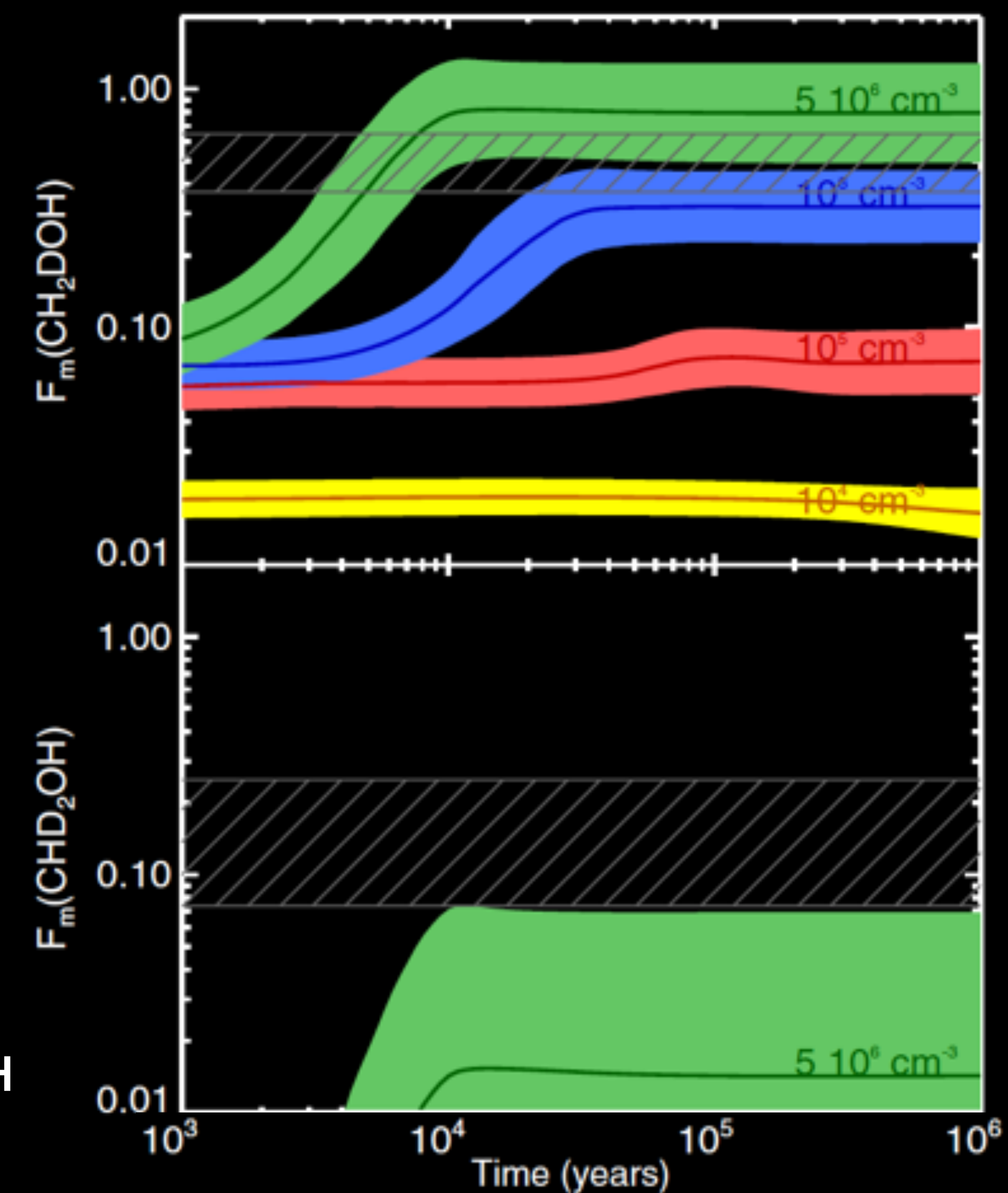
Furuya et al. (2015); see also Cazaux et al. (2011), Taquet et al. (2013)

Experiments: 1) O+H: Dulieu+ (2010), Jing+ (2011); 2) O_2+H: Miyauchi+ (2008), Ioppolo+ (2008, 2010), Cuppen+ (2010); 3) O_3+H: Mokrane+ (2009), Romanzin+ (2011); 4) OH+H_2: Oba+ (2011), Lamberts+ (2014)
Calculations: H_2O_2+H: Ellingson et al. (2007), Taquet et al. (2013); OH+H_2: Nguyen et al. (2011)

Methanol chemical network

Methanol and its deuterated isotopologues are formed through addition reactions from CO on ices…





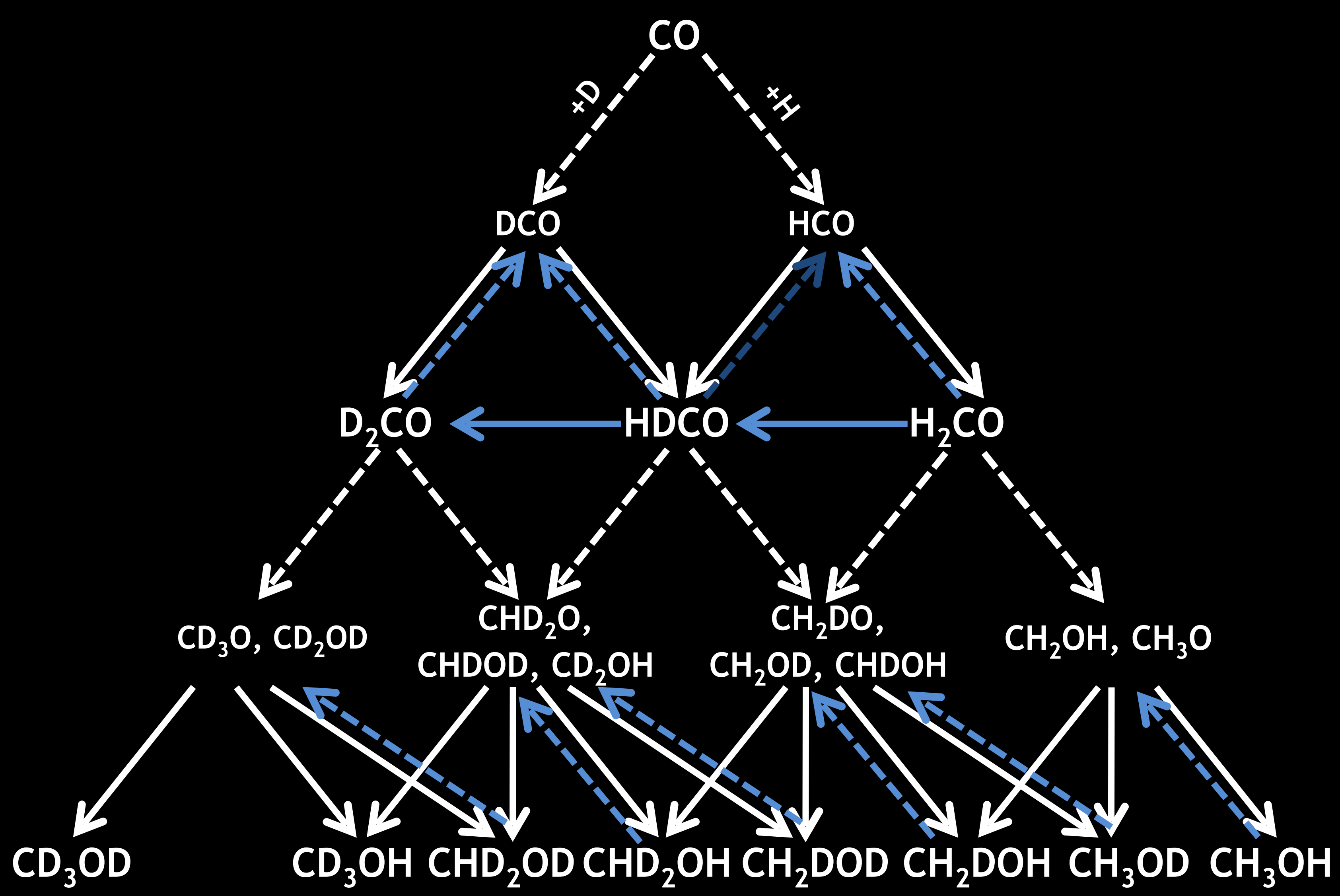
Taquet et al. (2012); see also Tielens (1983), Caselli et al. (2002),Cazaux et al. (2011)

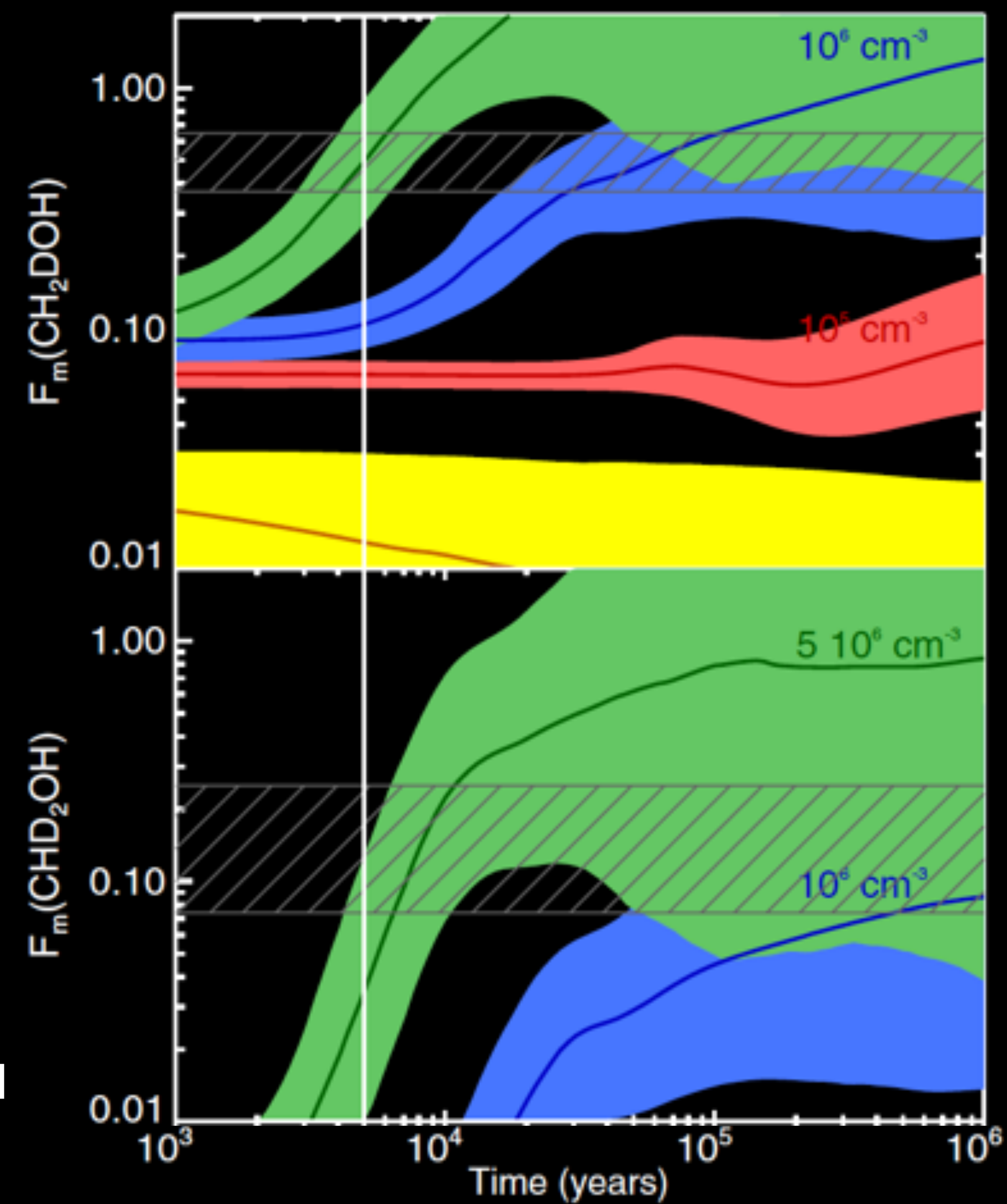
Experiments: Watanabe+ (2002, 2003, 2004, 2006), Nagaoka+ (2005, 2007), Hidaka+ (2007, 2009)

Calculations: Woon (2002), Andersson+ (2011), Peters+ (2013), Rimola+ (2014)

Methanol chemical network

… But substitution and abstraction reactions are also very efficient !
→ Increase of the methanol deuteration in ices





Taquet et al. (2012); see also Tielens (1983), Caselli et al. (2002),Cazaux et al. (2011)

Experiments: Watanabe+ (2002, 2003, 2004, 2006), Nagaoka+ (2005, 2007), Hidaka+ (2007, 2009)
Calculations: Woon (2002), Andersson+ (2011), Peters+ (2013), Rimola+ (2014)

Deuterium fractionation in interstellar ices

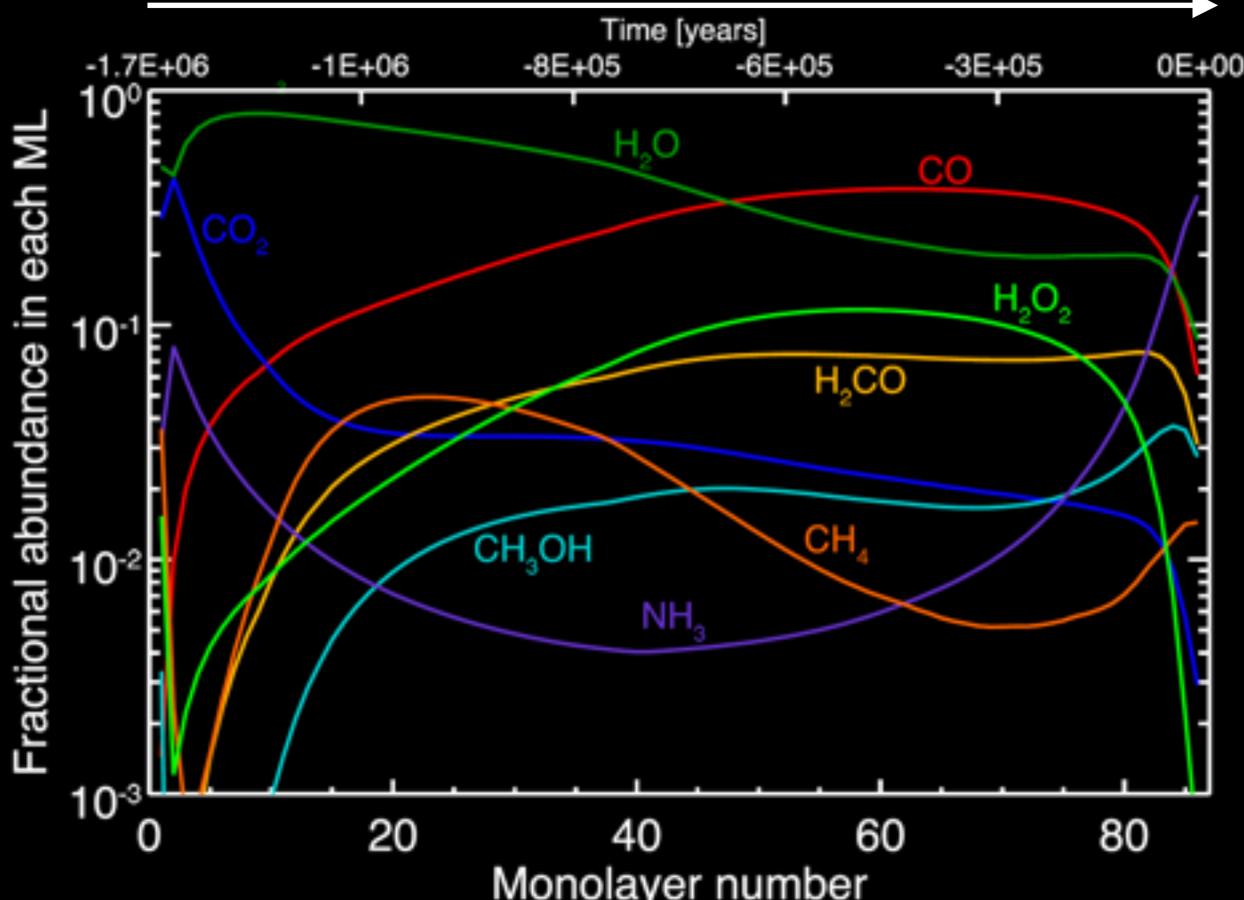
Interstellar ices slowly form from translucent clouds to prestellar cores:

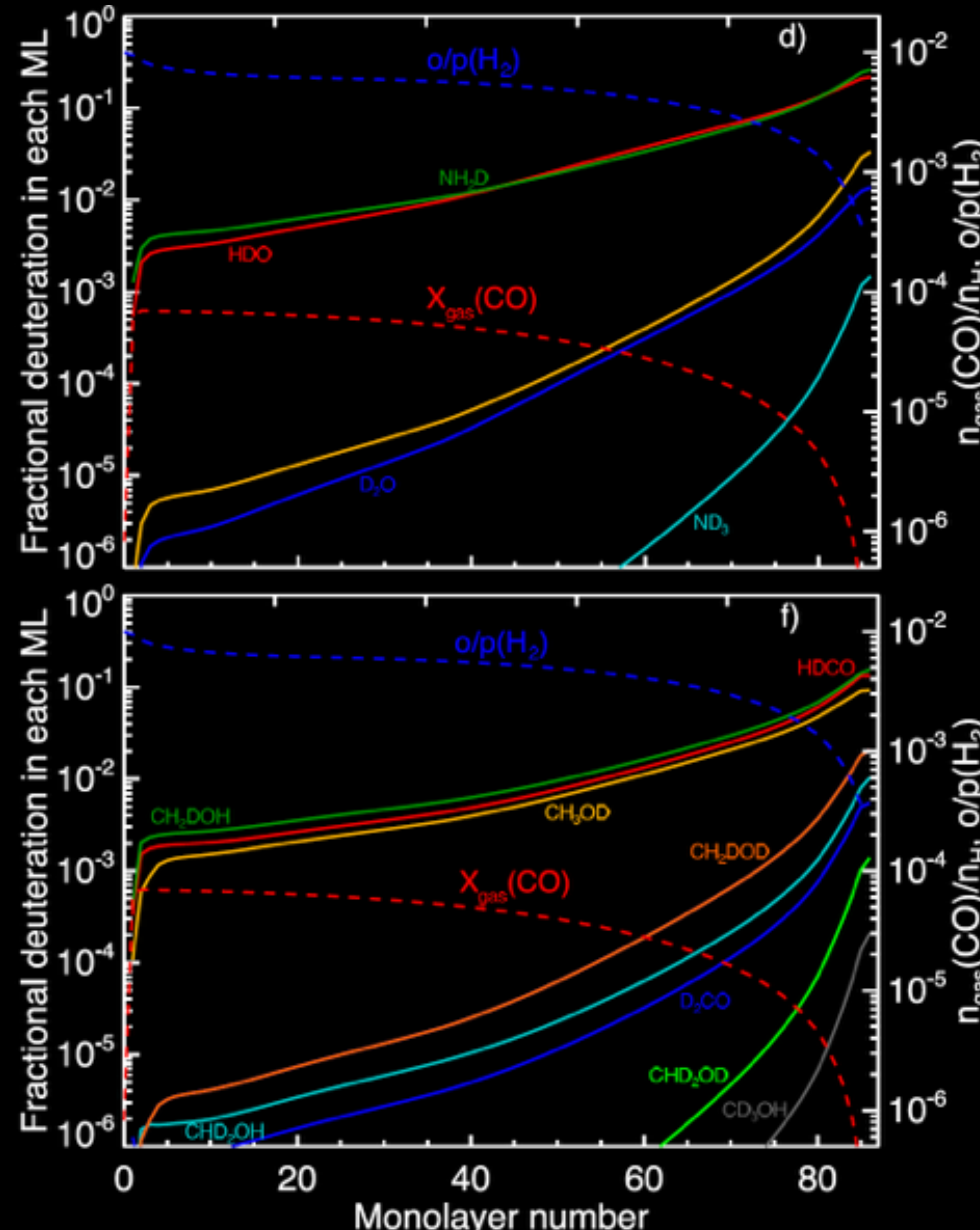
- **Ices are chemically heterogeneous**
  - H_2O and CO_2 mostly in the inner part of ices
  - CH_3OH mostly at the surface

- **Deuteration increases towards ice surface** due CO depletion and decrease of H_2 o/p

→ $F_D(H_2O) < F_D(NH_3) < F_D(H_2CO) < F_D(CH_3OH)$

T decreases, n_H increases →





Taquet et al. (2014); see also Furuya et al. (2016)

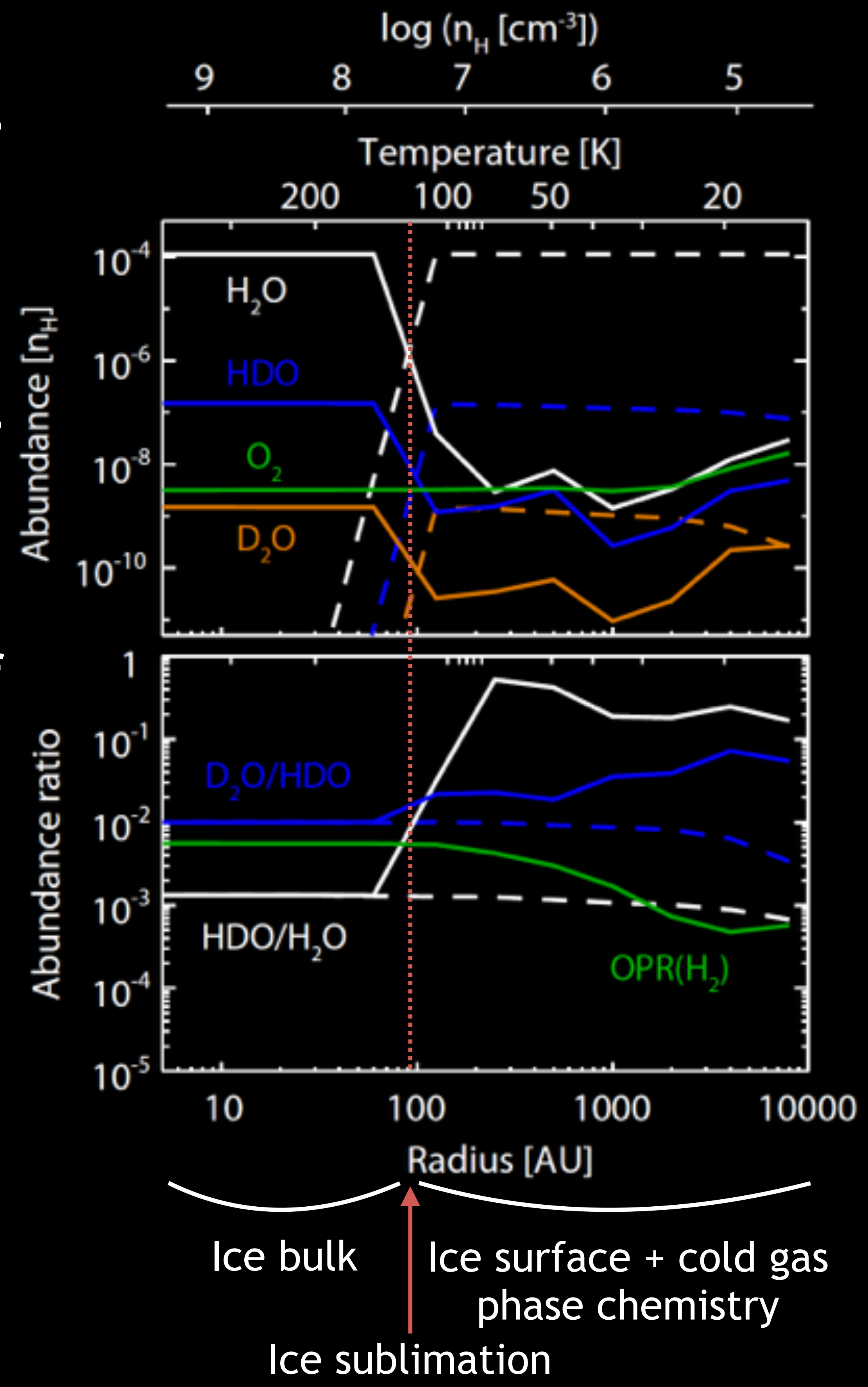
Impact of ice layering on the observed deuteration

Deuteration gradient in ices induces an increase of the water deuteration in the gas from the inner to the outer envelope:

- $HDO/H_2O_{warm} \approx 0.1 - 1$ %
- $HDO/H_2O_{cold} \approx 10$ %

→ consistent with *Herschel* observations by Coutens et al. (2013)

HDO and D_2O only produced at the surface of ices while H_2O mostly in the inner part
→ **explain $[D_2O]/[HDO] = 7\ [HDO]/[H_2O]$**



Furuya et al. (2016); see also Aikawa et al. (2012), Taquet et al. (2014), Wakelam et al. (2014)

H/D exchange in warm ices

Models presented so far assume that deuteration of cold ices remains unchanged until their evaporation at T > 100 K…

But H/D exchanges can occur in warm ices !

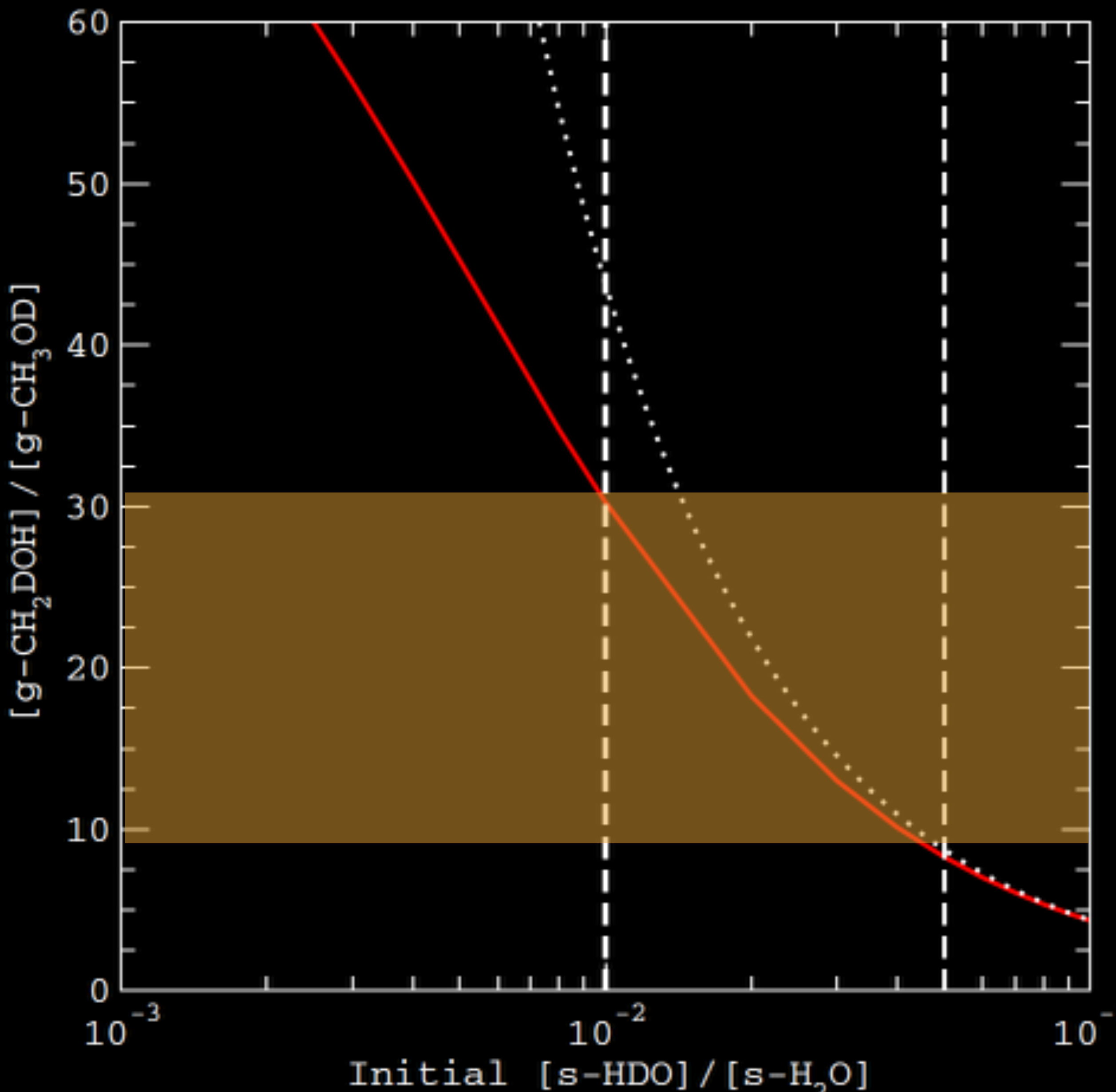
$CH_3OD + H_2O \rightleftarrows CH_3OH + HDO$; Ea = 4100 K (Ratajczak et al. 2009, Faure et al. 2015)

$H_2O + D_2O \rightleftarrows 2\ HDO$; Ea = 3840 K (Lamberts et al. 2015)

H/D exchange can naturally explain the high $[CH_2DOH]/[CH_3OD]$ ~ 20 observed in low-mass protostars

(But need to start with a high initial $[CH_2DOH]/[CH_3OH]$ = 40 %)

See A. Faure's talk !



Faure et al. (2016)

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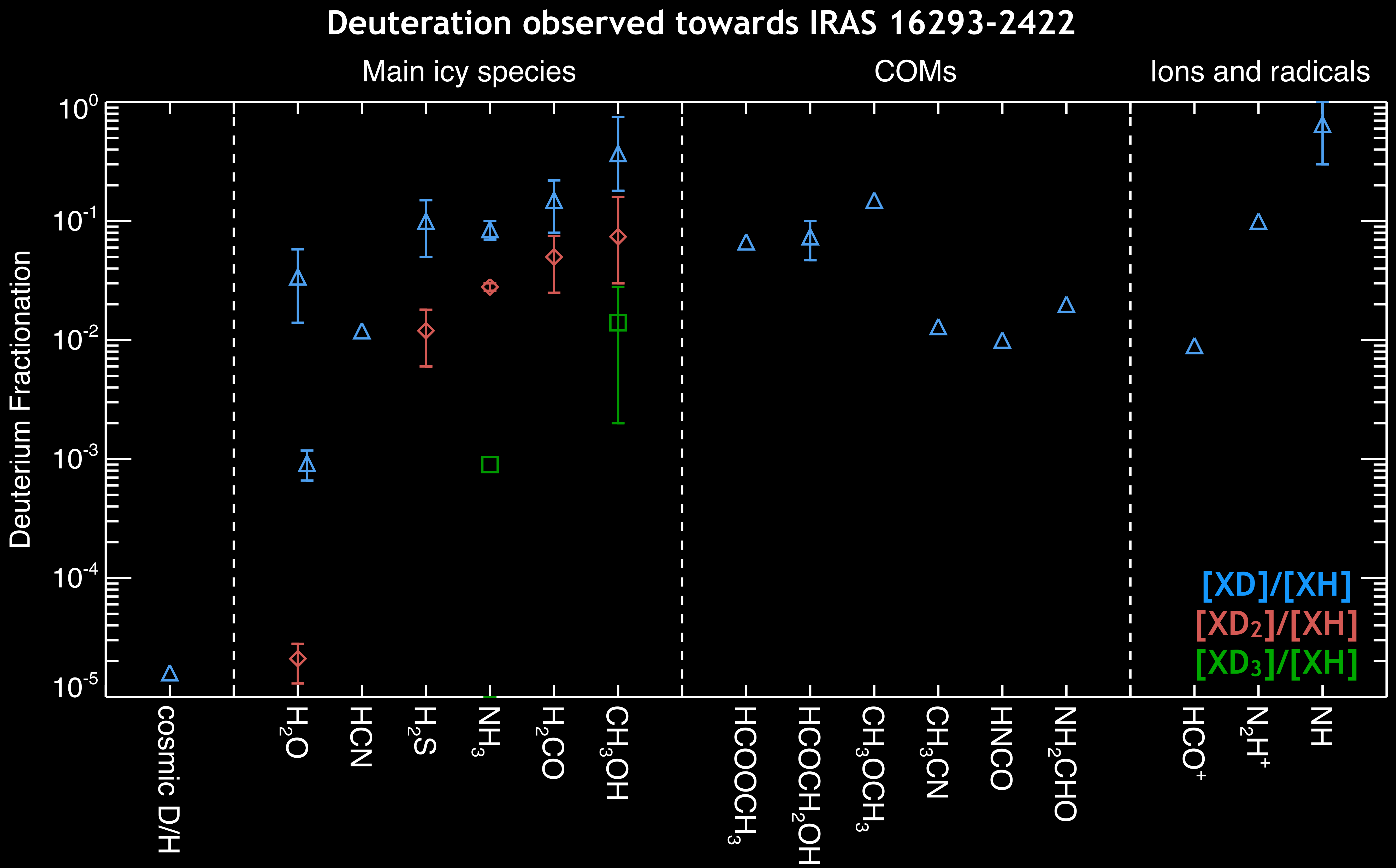
Deuteration in low-mass YSOs

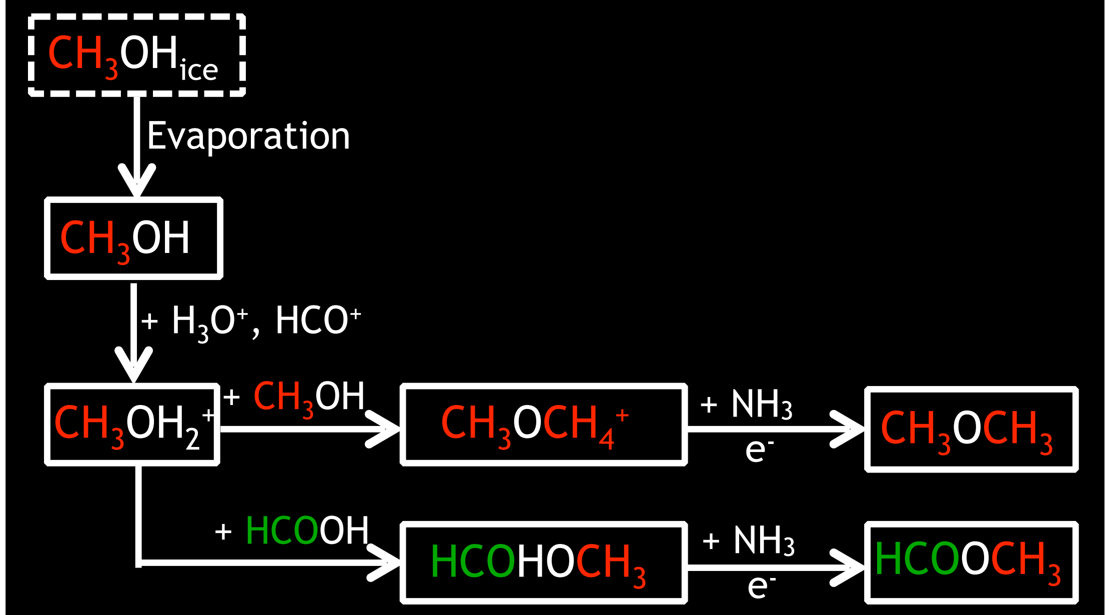


$HCOOCH_3$: Demyk et al. (2010); **$HCOCH_2OH$:** Jørgensen et al. (2016); **CH_3OCH_3:** Richard et al. (2013); **CH_3CN:** C. Kahane (priv. com.); **HNCO and NH_2CHO:** Coutens et al. (2016); **NH:** Bacmann et al. (2010)

Deuteration of O-bearing complex organics

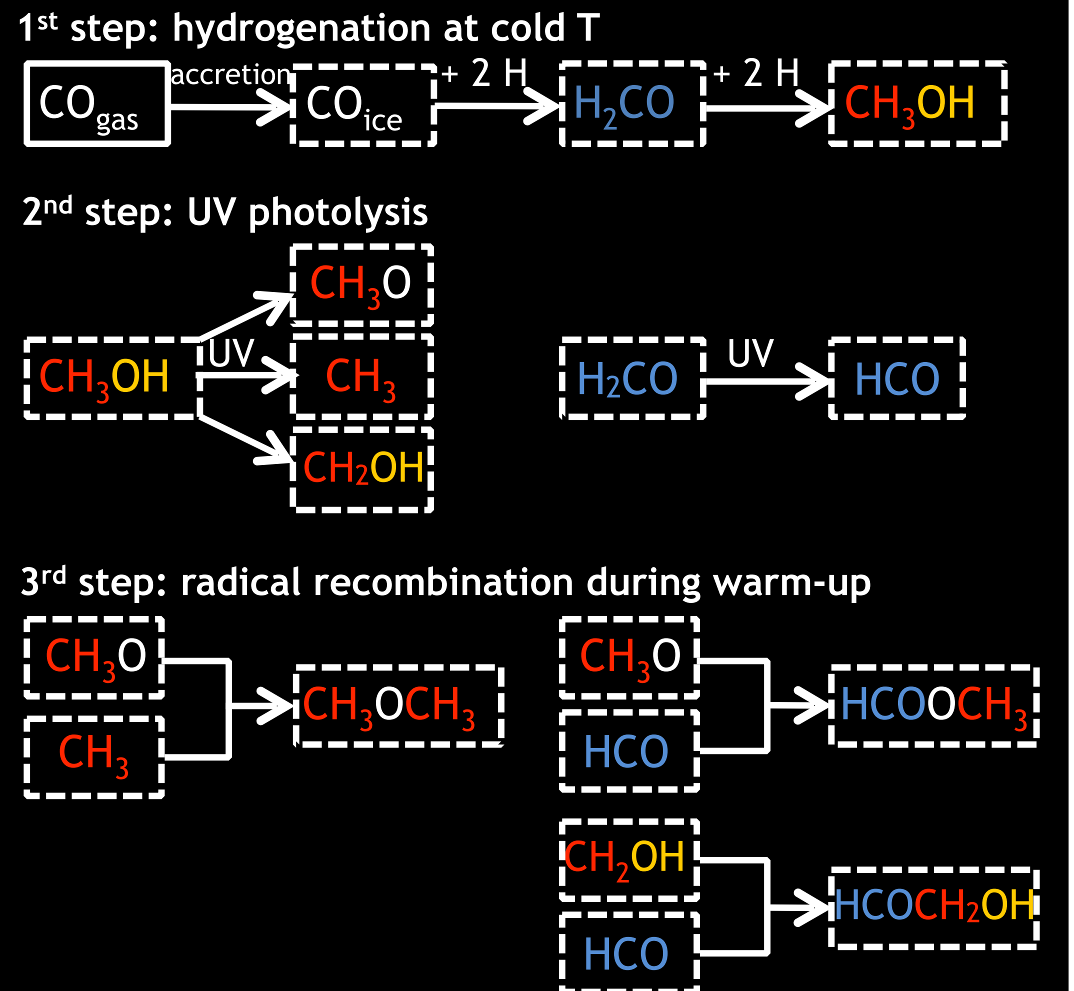
Deuteration should allow us to distinguish between gas phase and grain surface formations → need to have consistent D/H for all molecules

Gas phase chemistry



→ $CH_2DOCH_3/CH_3OCH_3 \approx CH_2DOH/CH_3OH$
→ $HCOOCH_2D/HCOOCH_3 \approx CH_2DOH/CH_3OH$
→ $DCOOCH_3/HCOOCH_3 \approx DCOOH/HCOOH$

Grain surface chemistry



→ $CH_2DOCH_3/CH_3OCH_3 \approx CH_2DOH/CH_3OH$
→ $HCOOCH_2D/HCOOCH_3 \approx CH_2DOH/CH_3OH$
→ $DCOOCH_3/HCOOCH_3 \approx HDCO/H_2CO$
→ $HCOCHDOH/HCOCH_2OH \approx CH_2DOH/CH_3OH$
→ $HCOCH_2OD/HCOCH_2OH \approx CH_3OD/CH_3OH$
→ $DCOCH_2OH/HCOCH_2OH \approx HDCO/H_2CO$

Deuteration of O-bearing complex organics

Deuteration should allow us to distinguish between gas phase and grain surface formations → need to have consistent D/H for all molecules

Deuteration (%)	Predictions by Taquet+ (2014)	Observations	Telescope	Reference
HDCO	4.1	15	IRAM 30m	Parise et al. (2006)
CH_2DOH	5.5	37	IRAM 30m	Parise et al. (2006)
CH_3OD	3.5	1.8	IRAM 30m	Parise et al. (2006)
DCOOH	2.3	/	/	/
HCOOD	1.0	/	/	/
CH_2DOCH_3	20	15	IRAM 30m	Richard et al. (2013)
$DCOOCH_3$	9.2	6	IRAM 30m	Demyk et al. (2010)
$HCOOCH_2D$	21	/	/	/
$DCOCH_2OH$	9.2	5.2	ALMA	Jørgensen et al. (2016)
HCOCHDOH	13.1	10	ALMA	Jørgensen et al. (2016)
$HCOCH_2OD$	13.4	4.7	ALMA	Jørgensen et al. (2016)

See A. Coutens's talk for deuteration of N-bearing COMs !

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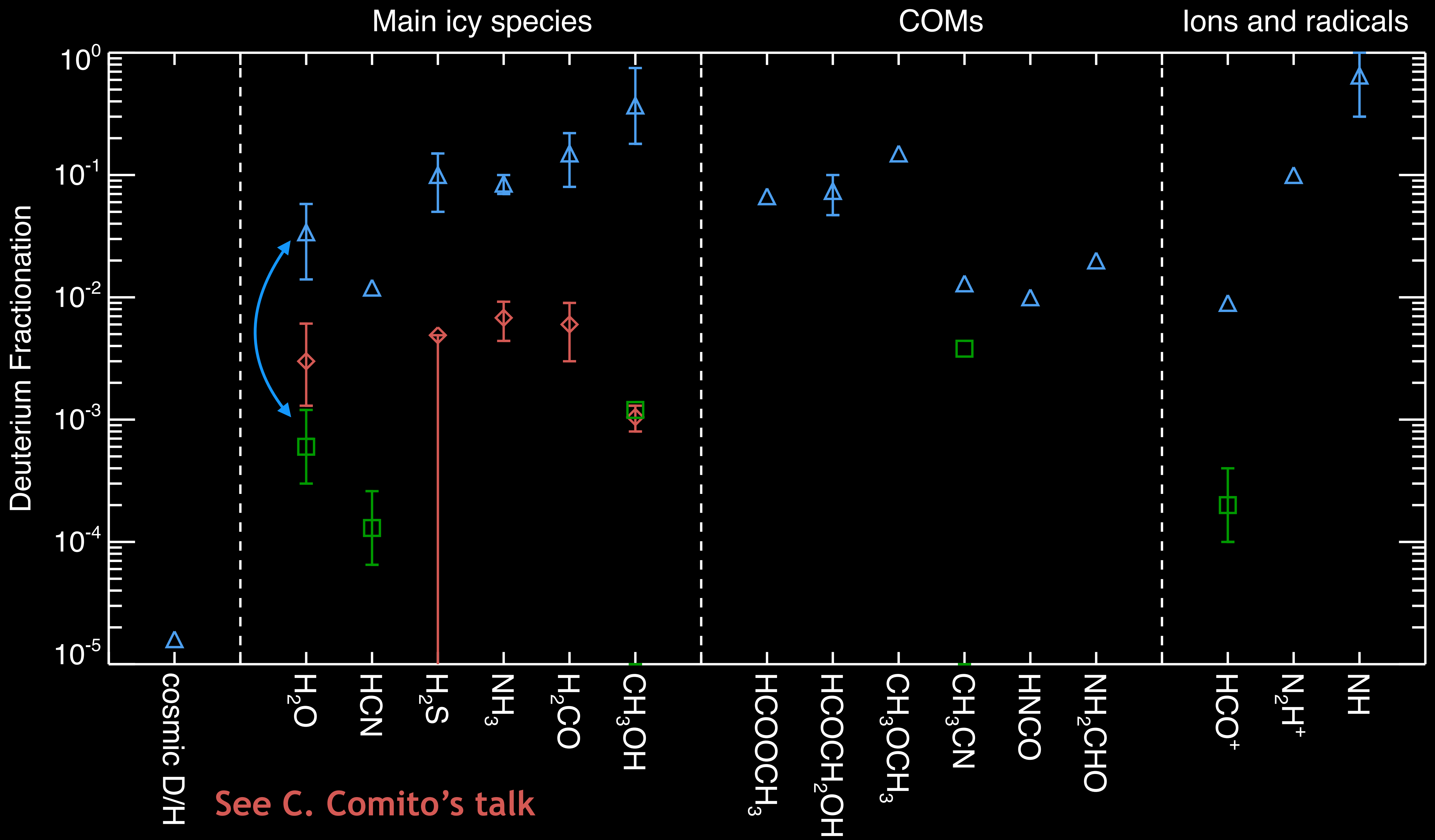
Deuteration: low-mass vs high-mass YSOs

Deuteration observed towards IRAS 16293-2422, Orion KL, and Sgr B2

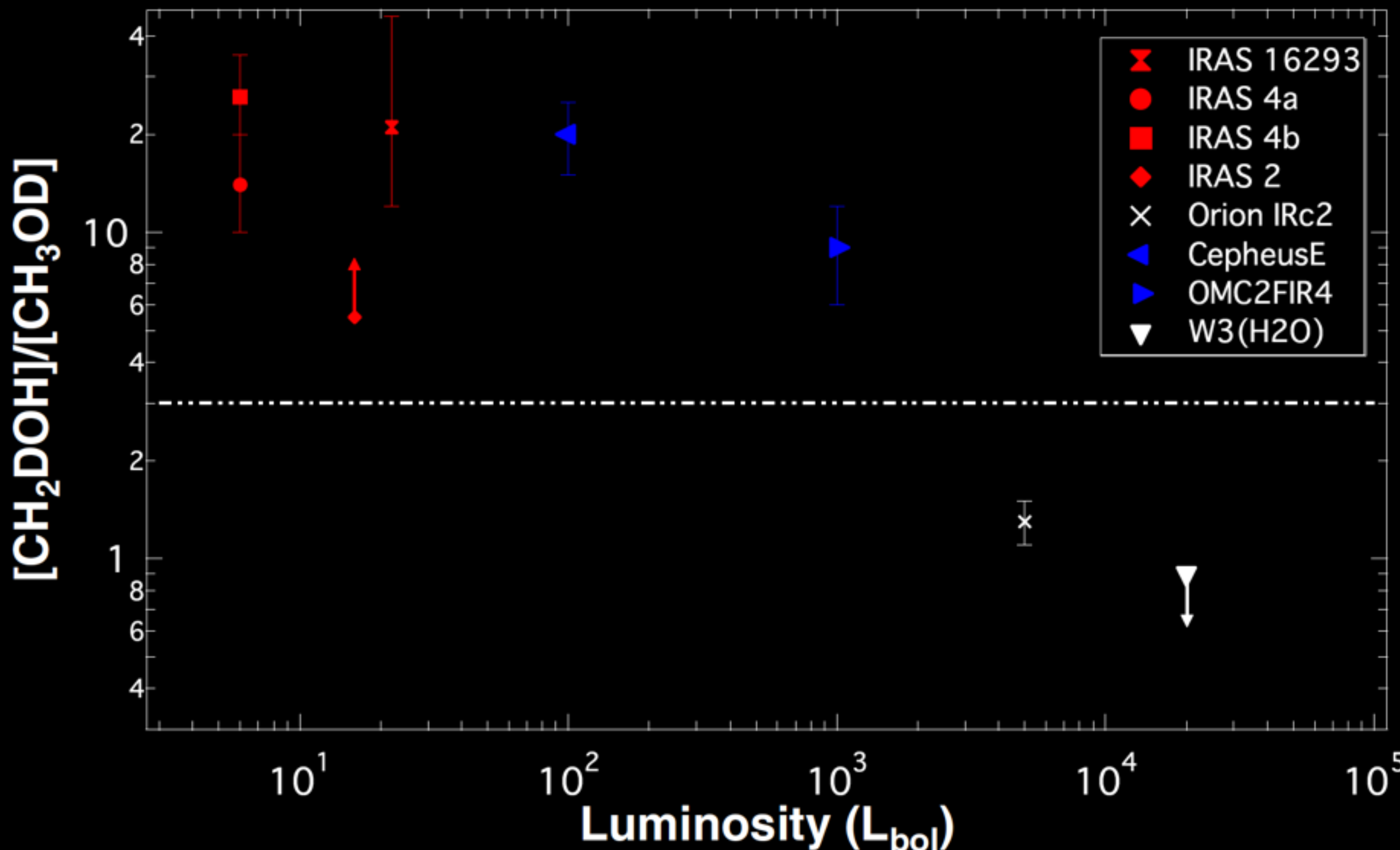


See C. Comito's talk

Orion KL: Peng et al. (2012), Neill et al. (2013), Favre et al. (2014); Sgr B2: Jacq et al. (1999), Comito et al. (2003), Belloche et al. (2013)

Deuteration: low-mass vs high-mass YSOs

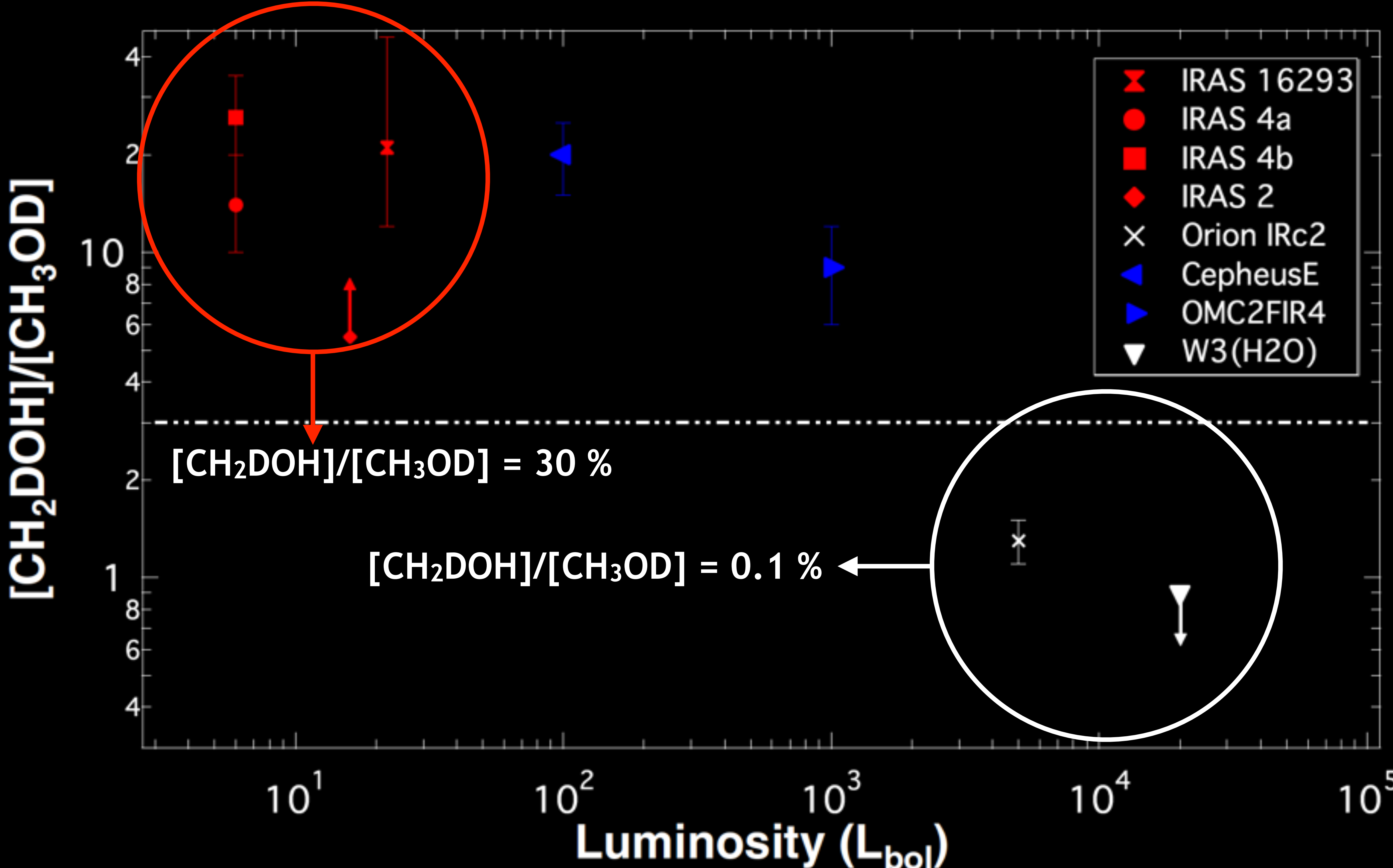
Evolution of the $[CH_2DOH]/[CH_3OD]$ with the protostellar luminosity



Low-mass: Parise et al. (2006); **Intermediate-mass:** Ratajczak et al. (2011); **High-mass:** Jacq et al. (1990), Ratajczak et al. (2011)

Deuteration: low-mass vs high-mass YSOs

Evolution of the [CH_2DOH]/[CH_3OD] with the protostellar luminosity



Low-mass: Parise et al. (2006); **Intermediate-mass:** Ratajczak et al. (2011); **High-mass:** Jacq et al. (1990), Ratajczak et al. (2011)

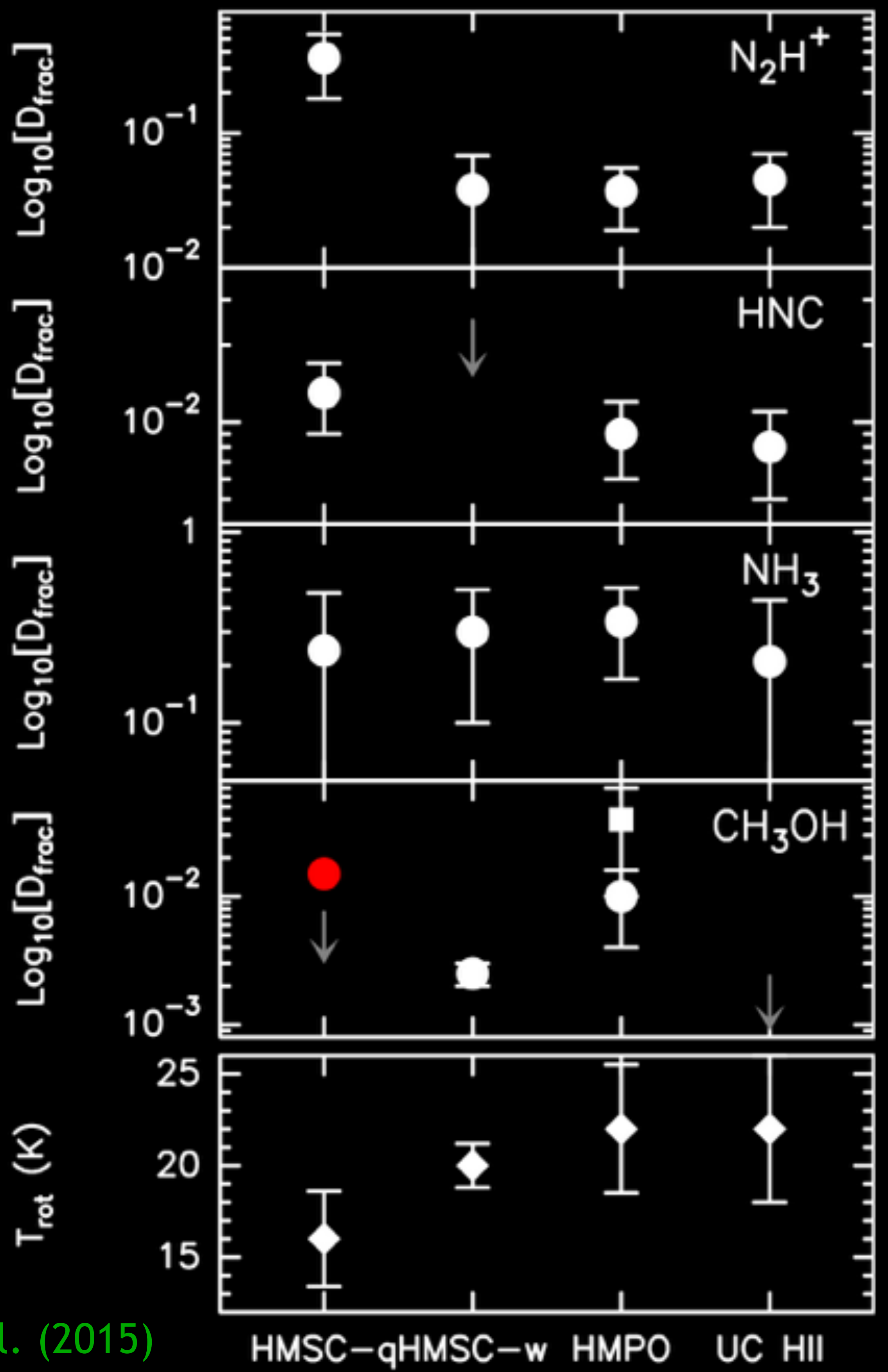
Deuteration: low-mass vs high-mass YSOs

High deuteration of NH_3 (and of CH_3OH) has been observed towards other massive protostars:

- Low deuteration observed towards Orion KL and Sgr B2 could be specific
→ close to bright older sources that could have warmed up the cloud to T > 20 K

- T > 20 K → [D]/[H] < 1 %
→ abstraction reactions are not efficient
→ $[CH_2DOH]/[CH_3OD] = 1$

Correlation between $[CH_2DOH]/[CH_3OD]$ and $[CH_2DOH]/[CH_3OH]$?



Fontani et al. (2015)

Conclusions

- Ion deuteration is sensitive to current physical conditions
  → tracer of evolutionary stage

- Deuteration of neutral species observed towards low-mass YSOs:
  tracer of their past formation in dark clouds on ices

- Deuteration could be useful to constrain formation mechanisms of COMs
  → need for new models and consistent observations

- Massive protostars show different chemical behaviour for neutral species than low-mass YSOs:
  due to warmer prestellar stage or more active warm chemistry ?