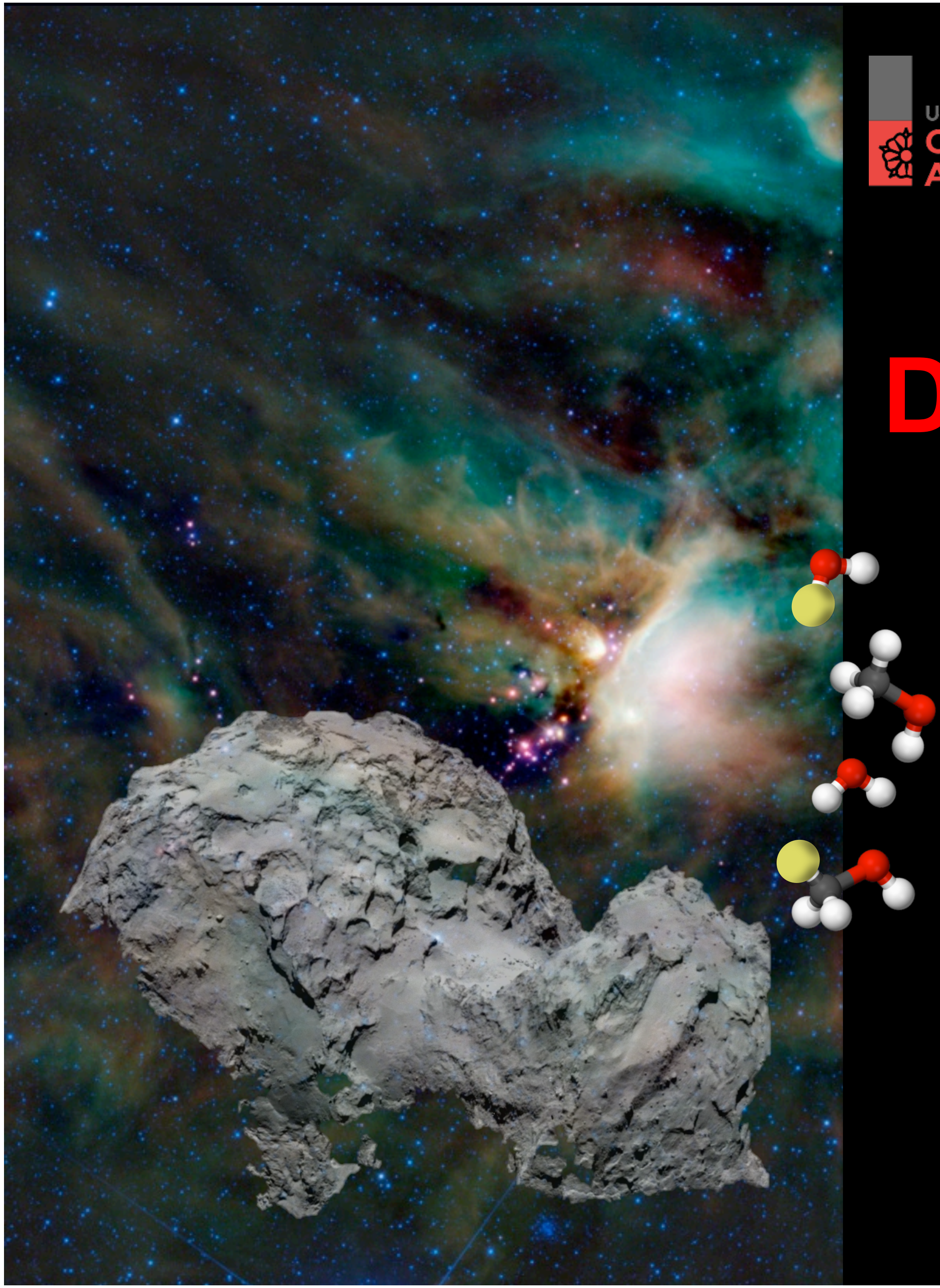

D/H equilibrium fractionation in ices

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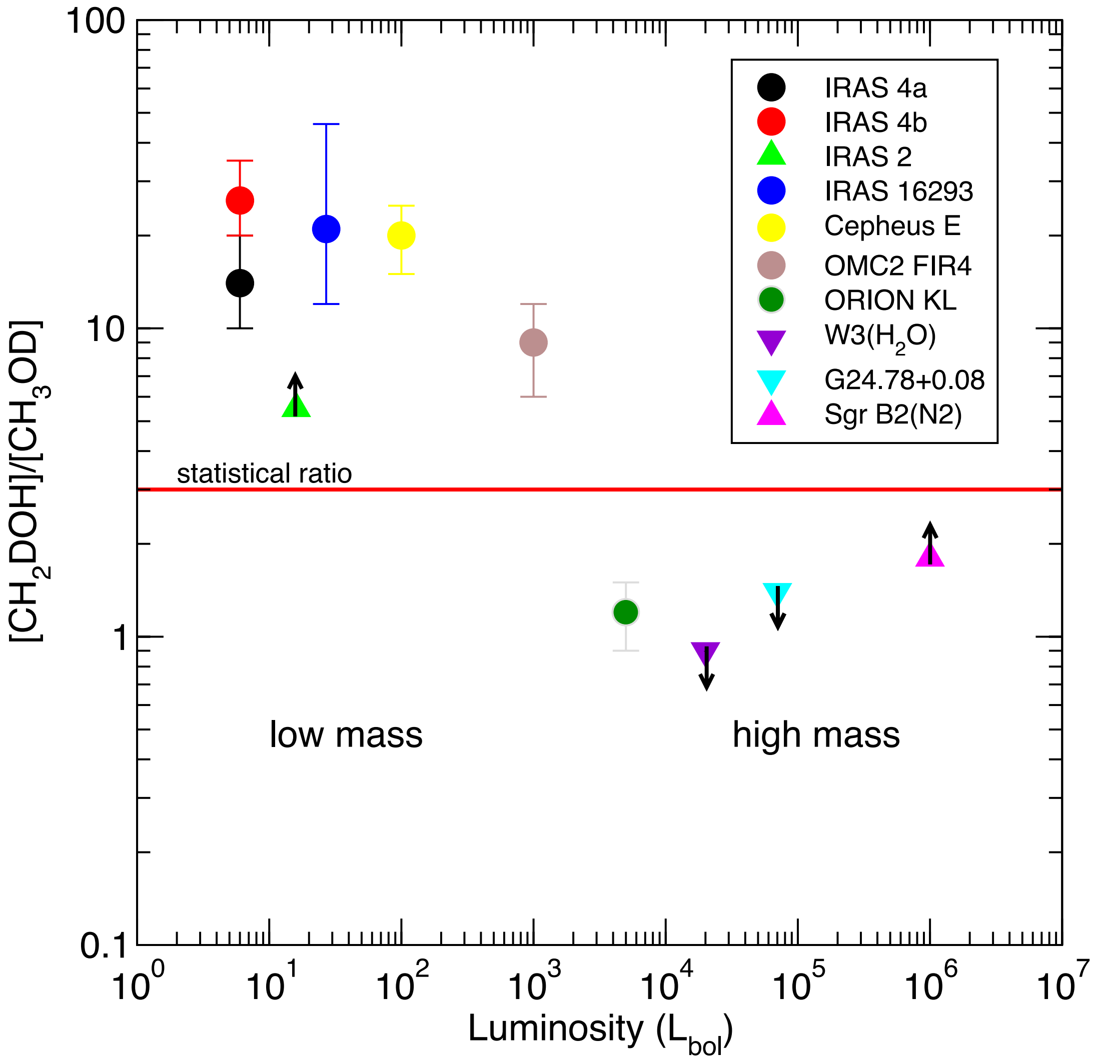
Fractionation of isotopes in space
Firenze, 10-13 october 2016

Outline

- The methanol puzzle
- Experiment
- Model
- Results
- Conclusions & perspectives

The methanol puzzle

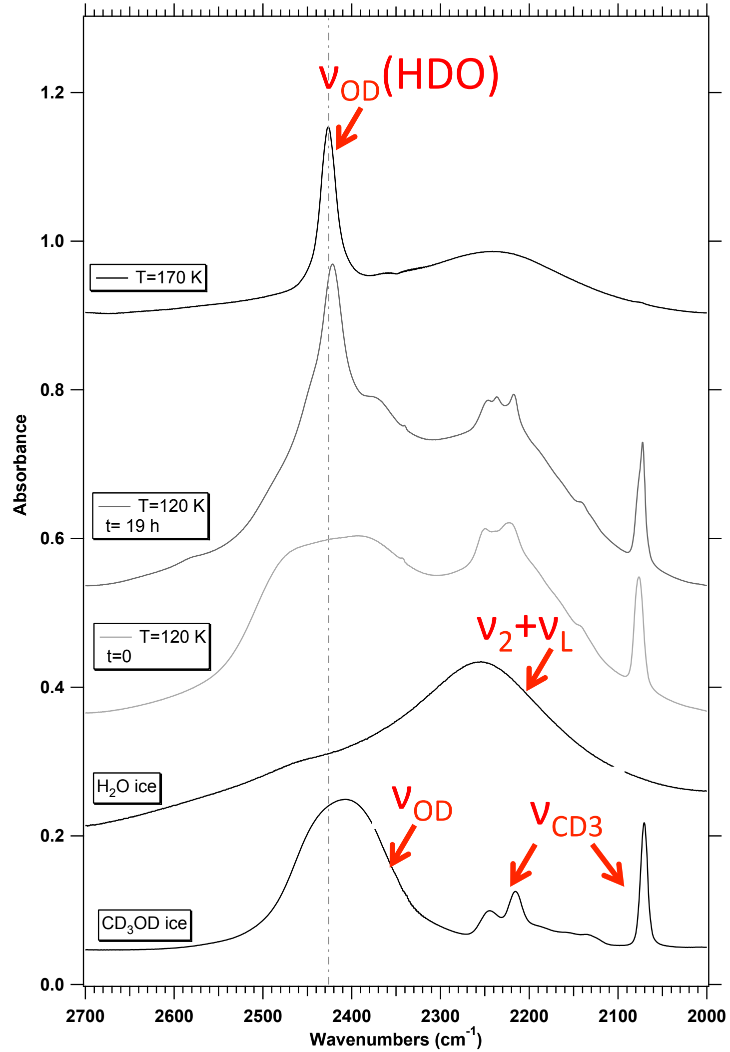
References:
Parise et al. (2006)
Ratajczak et al. (2011)
Neill et al. (2013)
Belloche et al. (2015)



Adapted from Ratajczak et al. A&A (2011)

H/D exchanges in ice

- Thin films (1 µm) of $H_2O:CD_3OD$ ice mixtures are monitored by FTIR spectroscopy
- Rapid (~ hrs) H/D exchanges are observed above *T*=120K on the -OH functional group

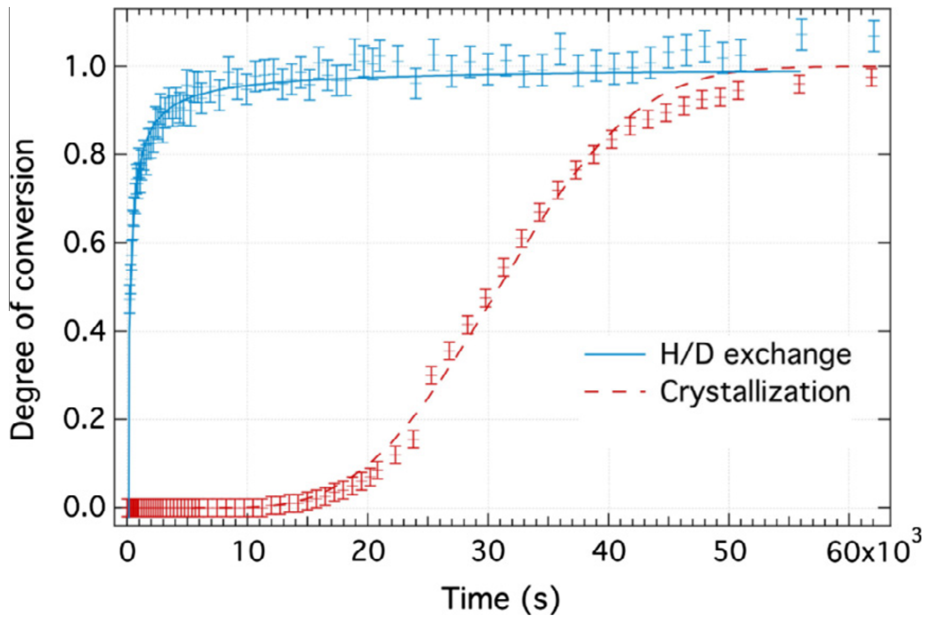


Ratajczak et al. A&A (2009)

Kinetics experiment

- Exchanges are observed in H_2O:CD_3OD and H_2O:CD_3ND_2, but not in D_2O:HCN
- Activation energies are similar for exchanges and crystallisation (~ 4000 K)

H_2O:CD_3ND_2 @ T=125K



[See Faure M. et al. *Icarus* **261** 14 (2015)]

The model

- Grain surface chemical model (rate equations) as in Hasegawa et al. ApJ (1992)
- Chemistry is limited to H/D exchanges + accretion + thermal sublimation
- No diffusion on grains and no post-evaporative gas-phase chemistry

Surface species considered:

- H_2O
- HDO
- D_2O
- CH_3OH, CH_3OD
- CH_2DOH, CHD_2OD
- CD_2HOH, CD_2HOD
- CD_3OH, CD_3OD

H/D exchange kinetics of $CH_3OD + H_2O = CH_3OH + HDO$

- Experimental data fitted to a 1st-order rate constant $k^{1st}(T)$ (Arrhenius type)

- BUT: rate equations require a 2nd-order rate constant

- Assuming a H_2O partial order of 1, we have:

$$k^{2nd}(T) = k^{1st}(T)/\ n(s\text{-}H_2O)$$

Reversibility predicts a relation between k^{1st} and k_b:

$$K(T) = k^{1st}/k_b = K^{stat} * \exp(-\Delta H/T)$$

where ΔH was measured in liquid phase (~ 50 K)

Ice composition

- See Öberg et al. (2011), Boogert et al. (2015)

- Low-mass protostars **IRAS 16293**
  - $[H_2O] = 5.\ 10^{-5}$ (relative to n_H)
  - $[CH_3OH]$ = 3% relative to $[H_2O]$

- High-mass protostars **Orion KL**
  - $[H_2O] = 5.\ 10^{-5}$ (relative to n_H)
  - $[CH_3OH]$ = 4% relative to $[H_2O]$

Statistical addition of H and D atoms to CO:

$[CH_2DOH]/[CH_3OH] = 3*(D/H)_m$

$[CH_3OD]/[CH_3OH] = (D/H)_m$

$[CD_2HOH]/[CH_3OH] = 3*(D/H)_m^2$

etc.

Initial conditions

- Accreting $(D/H)_m$ atomic ratio is fixed by CH_2DOH fractionation:
  - IRAS 16293: $(D/H)_m$ = 12%
  - Orion-KL: $(D/H)_m$ = 0.2%

- Water deuteration $(D/H)_w$ is our (unique) free parameter

- $n_H = 2 * 10^7$ cm^{-3}, $T_g = T_d$ = 100 K → instantaneous jump + steady-state solutions

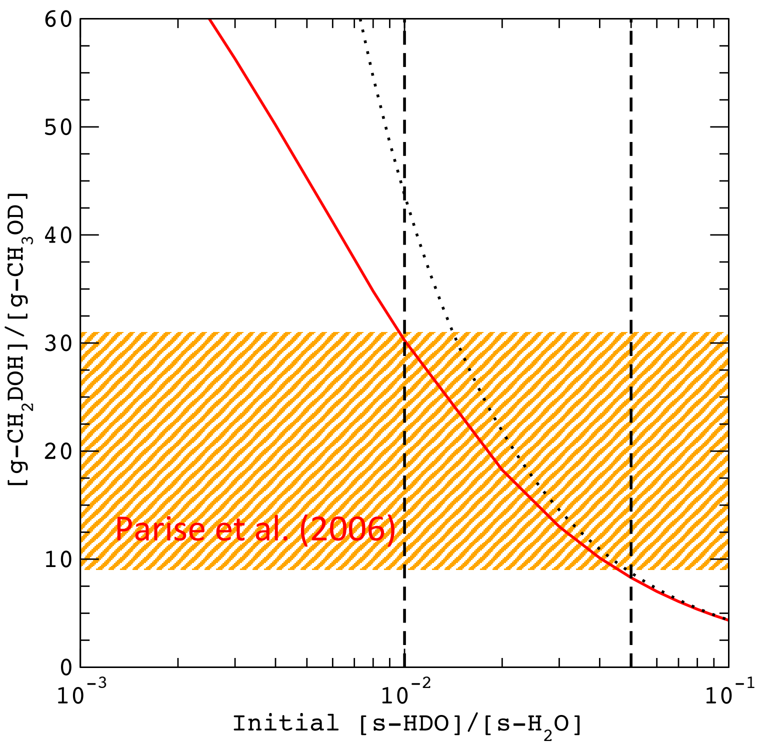
IRAS-16293

Species	Abundance	Isotopologue	Fractionation
H_2O	5.0(-5)	HDO	1.0(-4)–1.1(-1)
		D_2O	2.5(-9)–2.8(-3)
CH_3OH	1.5(-6)	CH_3OD	1.2(-1)
		CH_2DOH	3.6(-1)
		CH_2DOD	4.3(-2)
		CD_2HOH	4.3(-2)
		CD_2HOD	5.2(-3)
		CD_3OH	1.7(-3)
		CD_3OD	2.1(-4)

Orion-KL

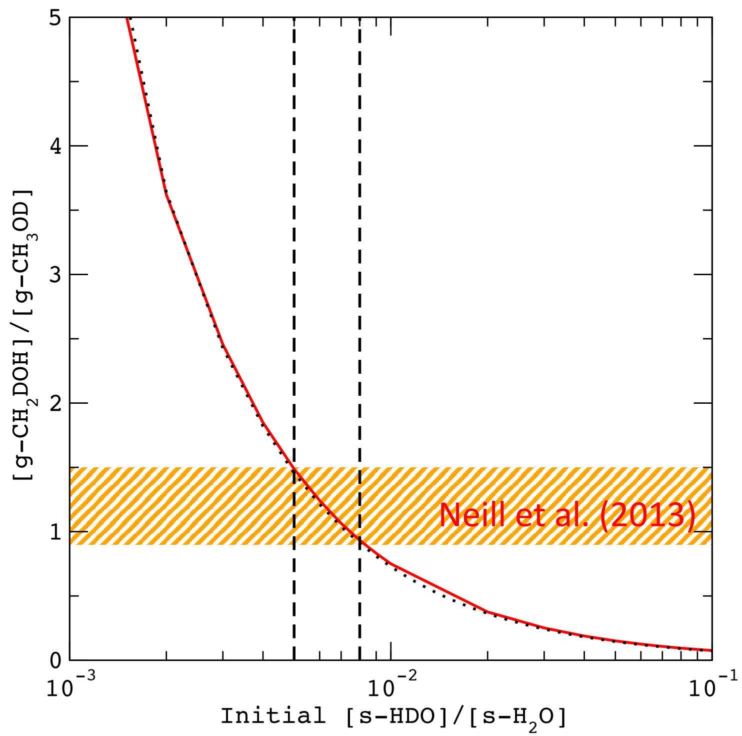
Species	Abundance	Isotopologue	Fractionation
H_2O	5.0(-5)	HDO	1.0(-4)–1.1(-1)
		D_2O	2.5(-9)–2.8(-3)
CH_3OH	2.0(-6)	CH_3OD	2.0(-3)
		CH_2DOH	6.0(-3)
		CH_2DOD	1.2(-5)
		CD_2HOH	1.2(-5)
		CD_2HOD	2.4(-8)
		CD_3OH	8.0(-9)
		CD_3OD	1.6(-11)

Gas-phase D-methanol



IRAS-16293

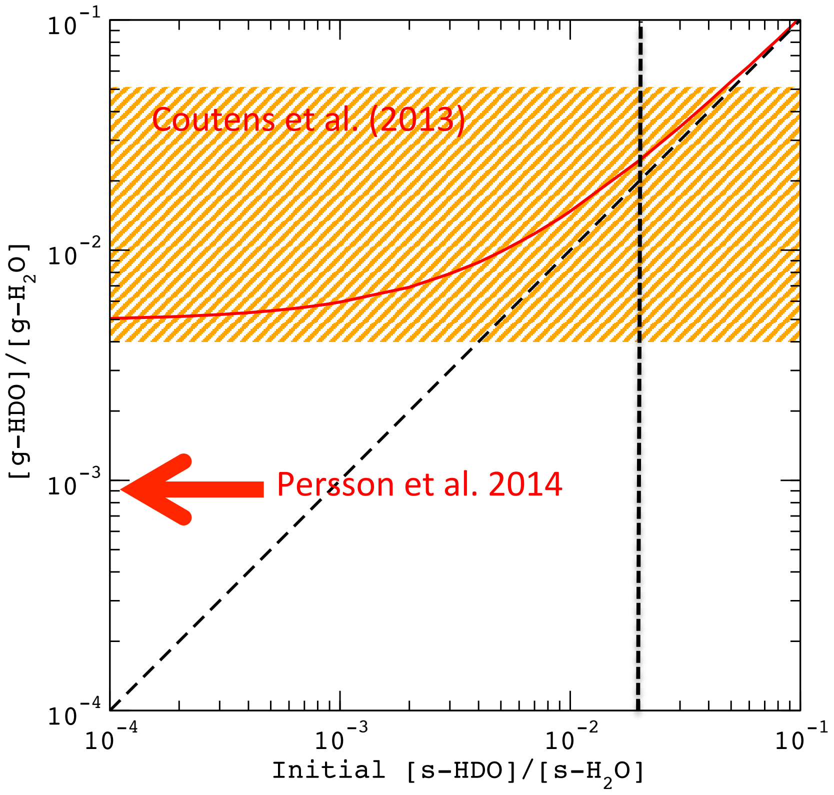
[s-HDO]/[s-H_2O] ~2%



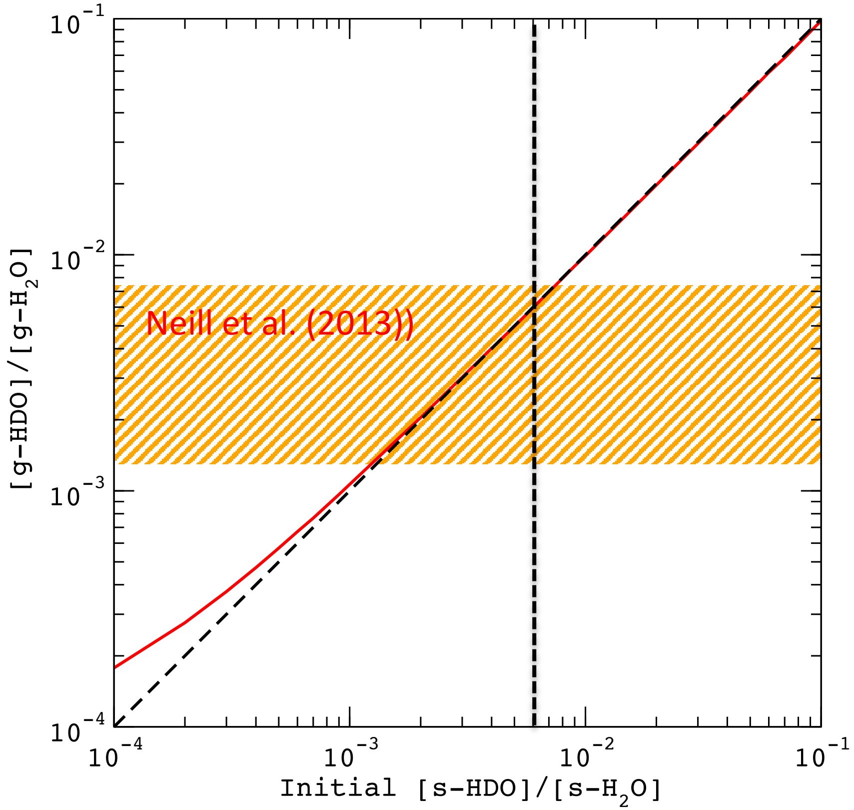
Orion-KL

[s-HDO]/[s-H_2O] ~ 0.6%

Gas-phase HDO



IRAS-16293



Orion-KL

Best-model

- Agreement between model and observations is within error bars.

- Next isotoplogue to be detected is CH_2DOD (but frequencies not available…)

IRAS 16293

Species	Best model	Observations	References
HDO	2.5(-2)	6.6(-4)-5.0(-2)	Coutens et al. (2013)
			Persson et al. (2014)
D_2O	1.7(-4)	≤3.0(-4)	Coutens et al. (2013)
CH_3OD	2.0(-2)	$1.8^{+2.2}_{-1.2}$(-2)	Parise et al. (2006)
CH_2DOH	3.6(-1)	$3.7^{+3.8}_{-1.9}$(-1)	Parise et al. (2006)
CH_2DOD	7.2(-3)	-	-
CD_2HOH	4.4(-2)	$7.4^{+8.4}_{-4.4}$(-2)	Parise et al. (2006)
CD_2HOD	8.8(-4)	-	-
CD_3OH	1.8(-3)	$8.0^{+6.0}_{-6.0}$(-3)	Parise et al. (2004)
CD_3OD	3.5(-5)	-	-

Orion-KL

Species	Best model	Observations	References
HDO	6.0(-3)	$3.8^{+3.6}_{-2.5}$(-3)	Neill et al. (2013)
D_2O	1.0(-5)	-	-
CH_3OD	4.9(-3)	$5.0^{+1.0}_{-1.0}$(-3)	Neill et al. (2013)
CH_2DOH	6.0(-3)	$5.8^{+1.2}_{-1.2}$(-3)	Neill et al. (2013)
CH_2DOD	2.9(-5)	-	-
CD_2HOH	1.2(-5)	-	-
CD_2HOD	2.5(-8)	-	-
CD_3OH	8.2(-9)	-	-
CD_3OD	1.7(-11)	-	-

Analytical solution

- Statistical deuteration

$$[CH_2DOH]/[CH_3OH] = 3*(D/H)_m$$

- Reversibility

$$[CH_3OH]/[CH_3OD] = 2*\exp(-\Delta H/T)*[H_2O]/[HDO]$$
$$= \exp(-\Delta H/T)/(D/H)_w$$

- D-methanol

$$[CH_2DOH]/[CH_3OD] = 3*(D/H)_m*\exp(-\Delta H/T)/(D/H)_w$$
$$\sim (D/H)_m/(D/H)_w$$

[See Faure et al. *A&A* **583** A98 (2015)]

Conclusions

- Molecules with –OD or –ND bonds (not –CD) can isotopically equilibrate with water ice
- D/H ratios measured in hot cores may not be representative of the original mantles
- D-methanol is a potential probe of water deuteration in the ice

Perspectives

- D-methanol in cold cores (Bizzocchi et al. 2014) and Sgr B2(N2) (Belloche et al. 2015)
- D-isotopologues of NH_2CHO and $CH_2OH-CHO$ recently detected with ALMA (talk by A. Coutens)
- Investigate other (non thermal) desorption mechanisms, i.e. UV and cosmic ray impact.