Oxygen Chemistry on Dust Grains

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WHERE DISCOVERIES BEGIN

Outline

- Introduction
  - Oxygen in space: the abundance puzzle
  - Oxygen chemistry on grains

- Oxygen on dust grains: recent experiments and theoretical simulations
  1. Water formation on grains
  2. Atomic oxygen on dust grains
  3. Formation of precursors to amino acids

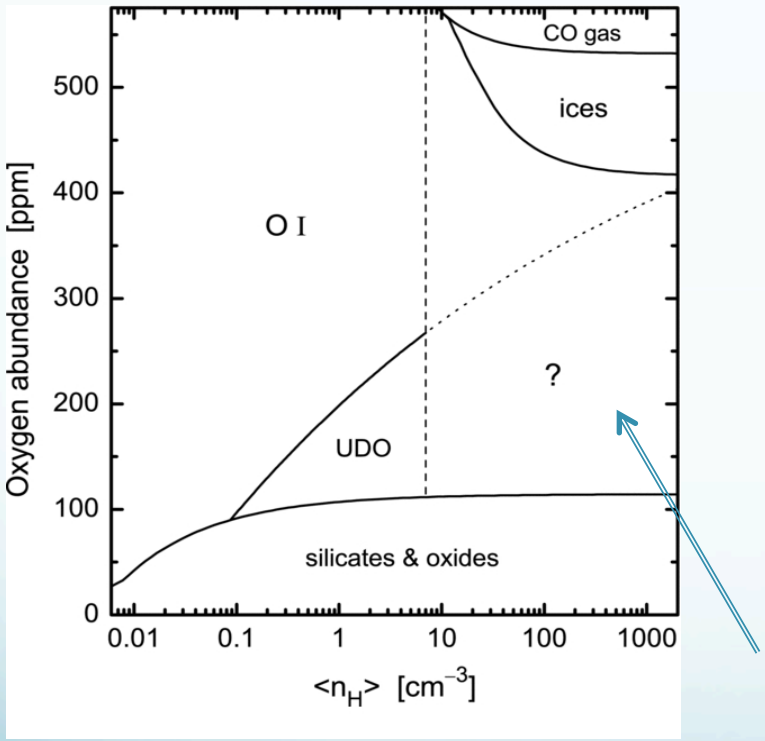
Molecular oxygen in dense clouds

- Gas-phase models for O_2: 7×10^{-5} (Woodall et al 2007)
- Observations
  - $< 10^{-7}$ Odin dark clouds (Pagani et al. 2003; Larsson et al. 2007)
  - $< 6\ 10^{-9}$ Herschel WIFI low mass protostar (Yildiz et al 2013)
  - 5×10^{-8} ρ Oph A (Larsson et al. 2007; Liseau et al. 2012)
  - No detection towards the Orion Bar (Melnick et al. 2012)

Oxygen in the Universe

- X(O)/X(H)=550 ppm (solar)

Figure 3 from Oxygen Depletion in the Interstellar Medium: Implications for Grain Models and the Distribution of Elemental Oxygen
D. C. B. Whittet 2010 ApJ 710 1009

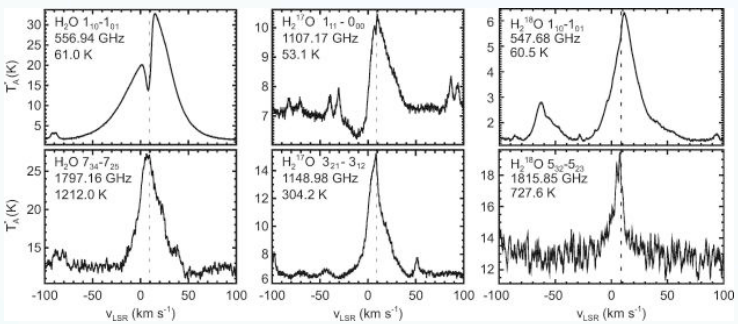


- O, O_2 the gas-phase; (CO, CO_2)
- Oxygen in grains (silicates)
- Oxygen in water ice on grains

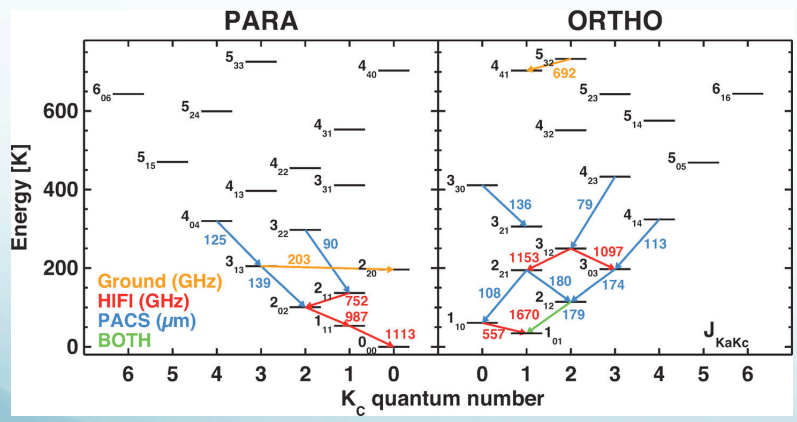
- *Hydrated silicates*
- *On large grains (>1 μm)*
- *O on/in carbonaceous grains (Whittet 2010)*
- …

Observation of Water in Space

Interstellar Water Chemistry: From Laboratory to Observations
Ewine F. van Dishoeck, Eric Herbst, and David A. Neufeld
Chemical Reviews (2013) 113, 9043



Rotational lines, towards Orion KL MC
Melnick, G. J.; et al. A&A. 2010, 521, L27



van Dishoeck, E. F.; et al. Publ. Astron. Soc. Pac. 2011, 123, 138.

Choi et al. A&A 572, L10 (2015)
OPR<1 in Orion PDR

Yabishita et al., ApJ, 699, L80 (2009)

Formation of Water in Space: 3 Routes

1. Gas-phase at low temperature (<250 K) - cold molecular clouds

$$H_3O^+ + e^- \rightarrow H + H_2O$$
$$\rightarrow OH + H_2$$
$$\rightarrow OH + 2H$$
$$\rightarrow O + H + H_2$$

($H + O \rightarrow OH$
$OH + H \rightarrow O_2 + H$)

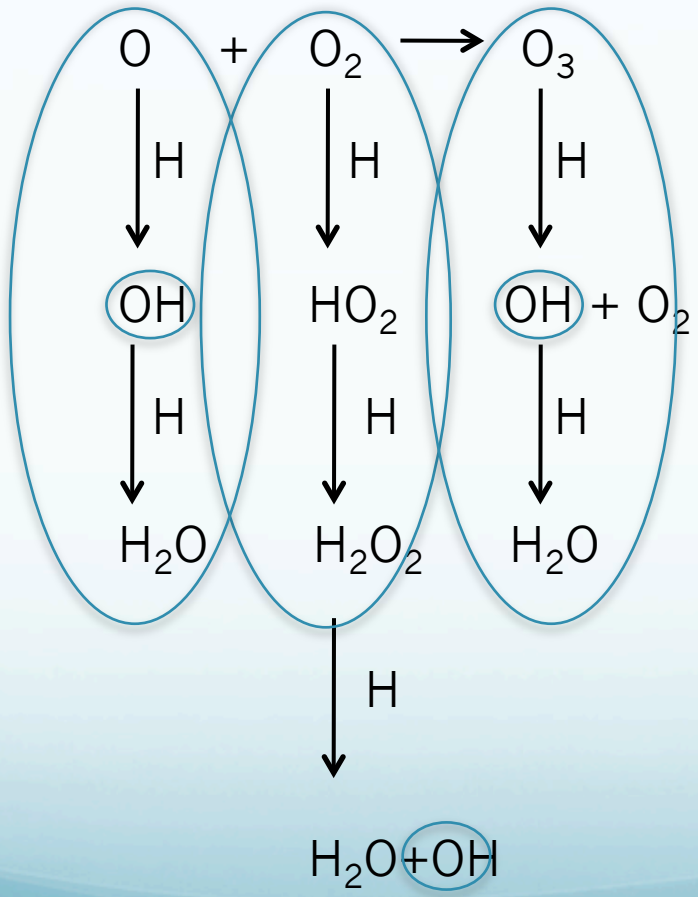
2. Gas phase at high temperature (>300 K) – inner parts of protoplanetary disks, shocks

$$O + H_2 \rightarrow OH + H \ (E_a = 3{,}160K)$$
$$OH + H_2 \rightarrow H_2O + H \ (E_a = 1{,}660K)$$

- But these reactions are not efficient enough to explain the abundance of water and ices

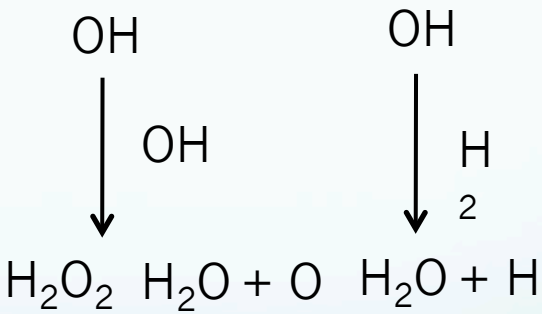
Formation of Water in Space

- 3. Formation of water on dust grains



Watson & Salpeter, Ap.J (1972) 174, 321

Tielens and Hagen (1982)
Astron. & Astrophys. 114, 245



Earlier investigations in the laboratory: Prior experiments (see also Vidali, J. Low Temp. Phys. (2013) 170, 1; T. Hama & N.Watanabe Chem. Rev. 113, 8783 (2013))

- **O_2 Channel**
  - Miyauchi et al. (2008) 456 (2008) 27: $H+O_2$ at 10 K gives H_2O and H_2O_2; H flux of 2 10^{14} atoms/s/cm^2 on 8 ML of O_2.
  - Ioppolo et al., ApJ 686, 1474 (2008); PCCP 12, 12065 (2010); $H+O_2$ at 12-28 K gives H_2O and H_2O_2 and O_3; H flux 2.5 10^{12} atoms/cm^2/s on 15ML of O_2.

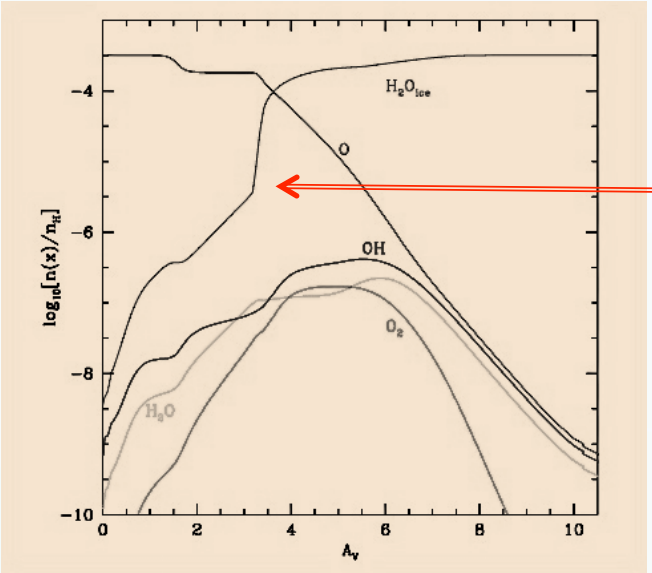
- **O_3 channel**
  - Mokrane et al. ApJ 795, L195 (2009) H_2O formation with H reacting with O_3 on non-porous amorphous ice
  - Romanzin et al. JCP 134, 084594 (2011) $O_2 + O \rightarrow O_3$; $O_3+H \rightarrow H_2O+O_2$ (25 to 50 K) H flux of 8 10^{13} atoms/cm^2/s; O_3 is deposited.
  - Bennett & Kaiser: 5 keV e beam in ice

- **OH channel**
  - Oba et al., PCCP 13, 15792 (2011); ApJ 749, 12 (2012) H_2O dissociation: OH $+H_2$ $+H$ $+O+O_2$; OH + OH ➔ H_2O + O; OH $+H_2$ tunneling at 10 K; flux ~10^{13} atoms/s/cm^2 on Al (?) substrate at 10 – 50 K

- **O channel**
  - Dulieu et al. A&A 512, 30 (2010) H+O on porous amorphous water ice at 10 K
  - Jing et al. ApJ 741, L9 (2011) H+O on a bare amorphous silicate surface at 15K

Simulation of ISM chemistry

Steady-state PDR (Hollenbach et al. 2009)



onset of ices on grains

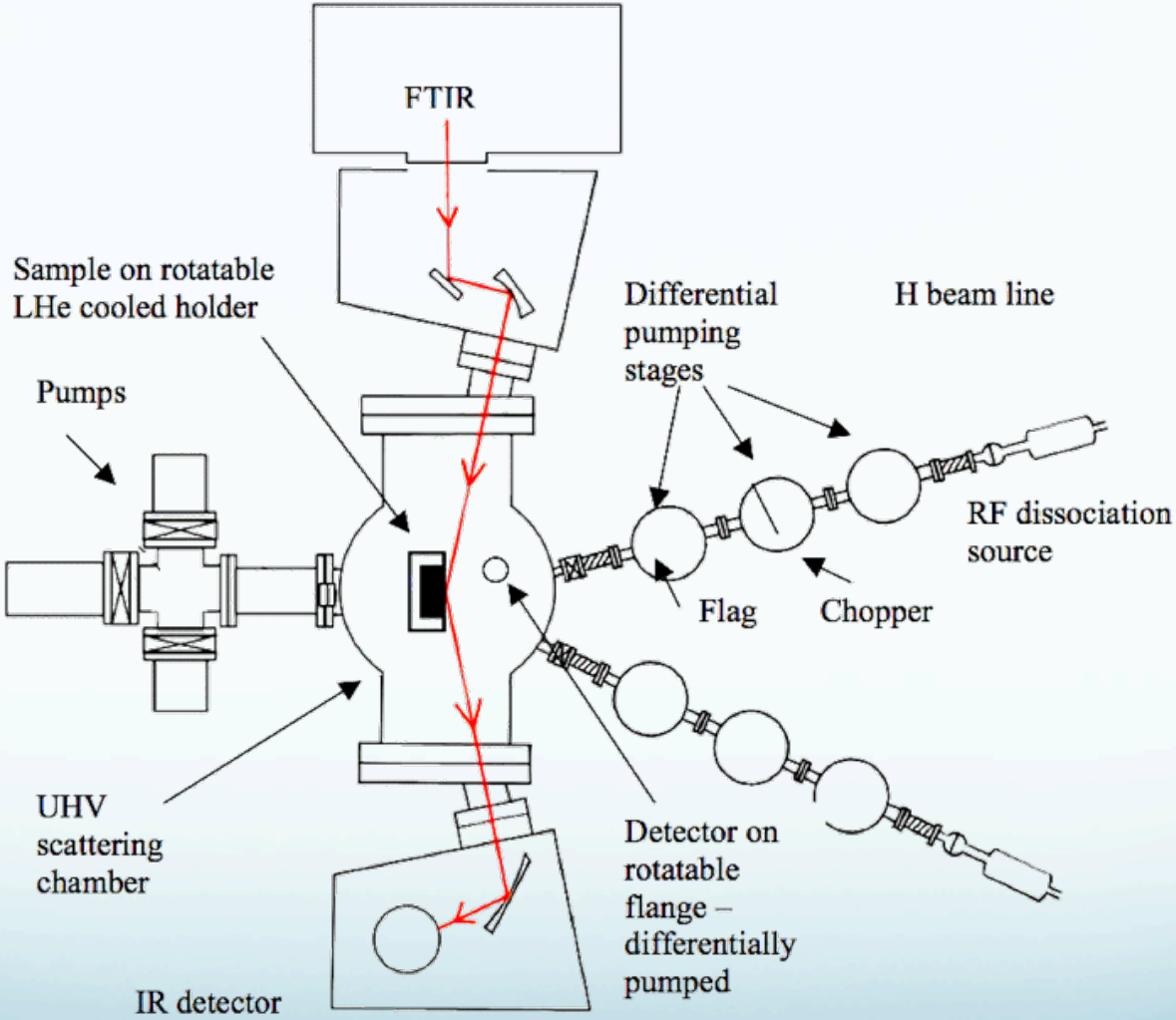
Formation of water on warm grains

- Ices form in regions with A_v>2-3
- In Av<3 regions, T_{grain}>25 K; no O_2 on surface // Glassgold et al. 2012

  → Water forms by hydrogenation of O
  - $O+H \rightarrow OH$ $OH+H \rightarrow H_2O$

  or O_3,
  - $O_3+H \rightarrow OH+O_2$ $OH+O \rightarrow H_2O$
- What's the residence time of O, OH and O_3? $t \sim \tau_0 e^{E/kT}$
- Program at Syracuse University:
  - Study water formation at T_{grain}>25K via O+H, O_3+H
  - What's the residence time of O, OH and O_3? $t \sim \tau_0 e^{E/kT}$ → Measure E_b for O, OH,O_3

Apparatus at Syracuse University



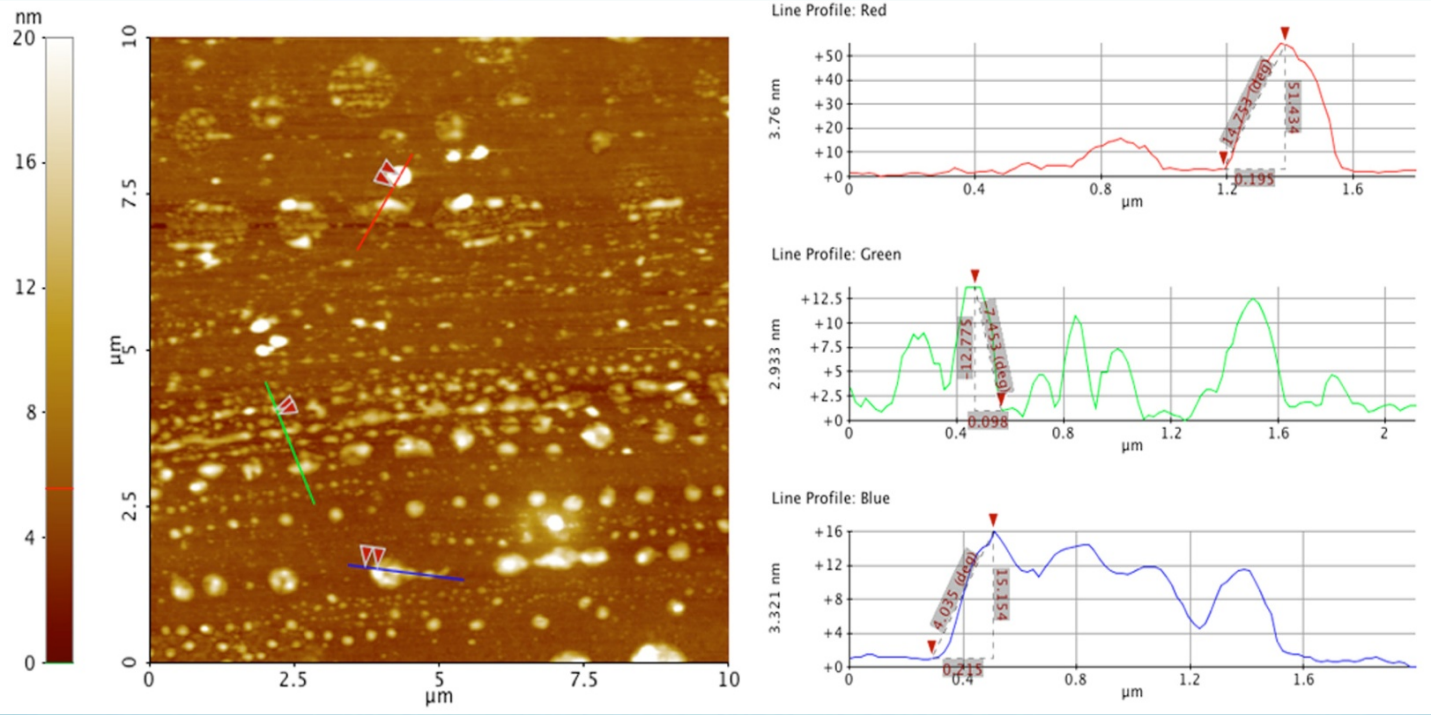
Water Formation on Dust Grains

Apparatus Highlights

- Main Chamber: Ultra-High vacuum as low as 5 x 10^{-11} Torr; operating pressure 1-2 x10^{-10} torr
- Sample temperature adjustable from 6K to 400K; rotatable sample
- Two highly collimated beam lines allowing studies of complex reactions with the operating pressure in the main chamber in the low 10^{-10} torr
- Reflection-adsorption-infrared-spectroscopy (RAIRS)
- Rotatable Quadrupole mass spectrometer (QMS) to measure in-coming reactants and out-going products
- Sputter Gun
- Auger
- Low energy electron diffraction (LEED)

Sample Preparation and Characterization

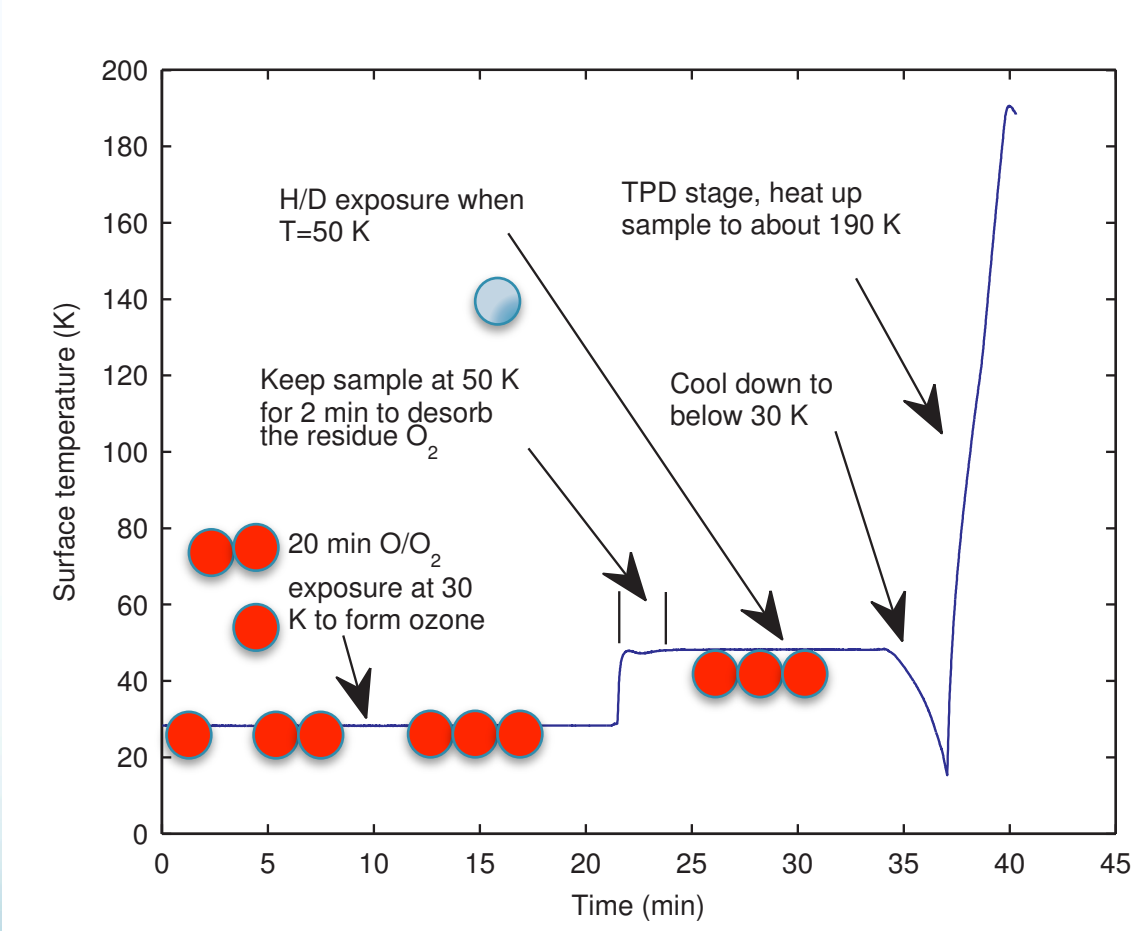
Amorphous silicate prepared and characterized by Dr. Brucato (Astrophys. Obs. Arcetri) EB-PVD



Study of cleaning by sputtering

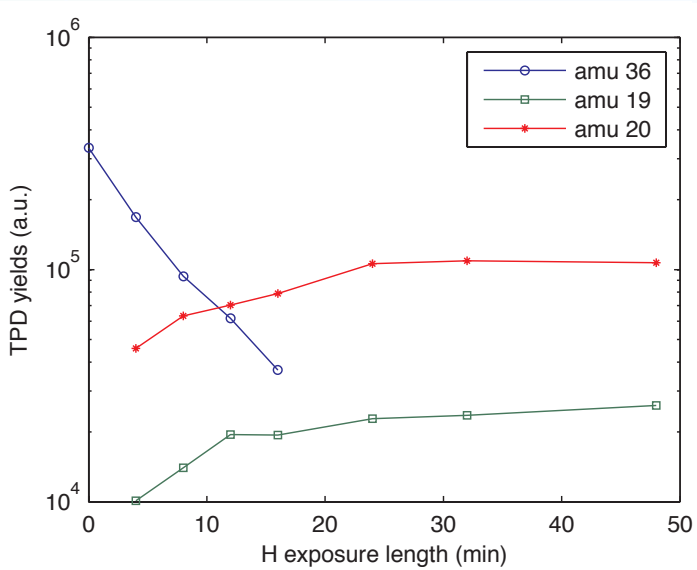
Jing et al. J.Phys.Chem. A117, 3009 (2013)

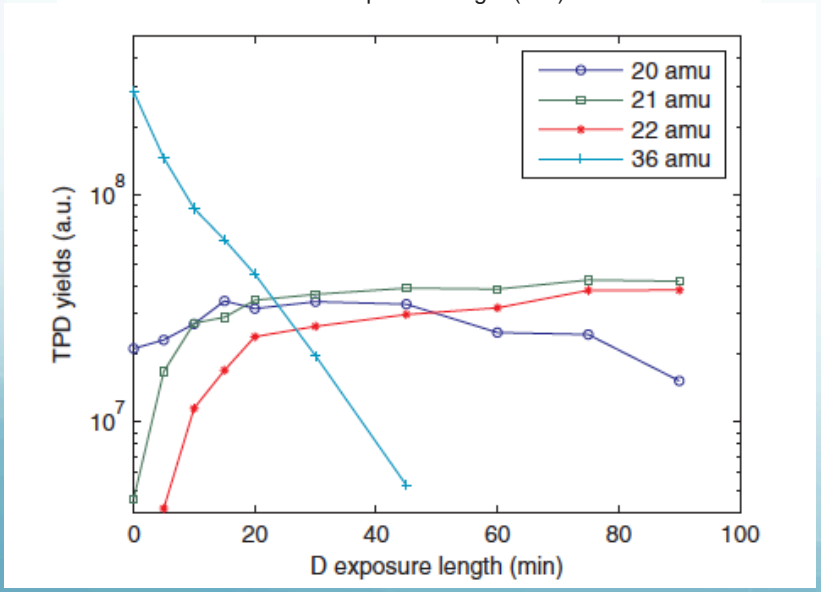
Water Formation via H/D + O_3 Reaction at 50 K

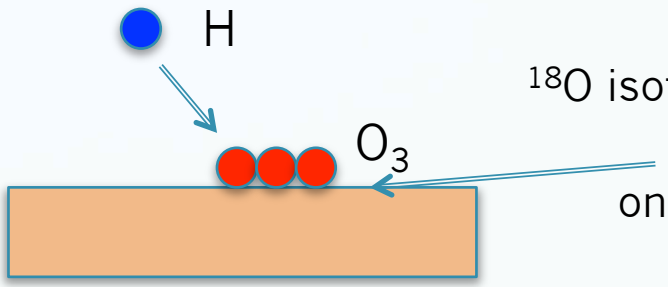


J.He & G.Vidali ApJ 788, 50 (2014)

Water formation







^{18}O isotope is used

one layer of O_3

- $H+O_3 \rightarrow OH+O_2$ $\quad OH+H \rightarrow H_2O$
  - mass 20: H_2O from OH+H, $OH+H_2$
  - mass 19: OH from $OH+O_2$ and H_2O frag.
- $D+O_3 \rightarrow OD+O_2$
  - mass 22: D_2O from OD+D, $OD+D_2$
  - mass 20: OD from $OD+O_2$ and D_2O frag.
  - mass 21: HDO from $OD+H_2$

mass 36: O_2 and O_3 from break-up of ozone in ionizer

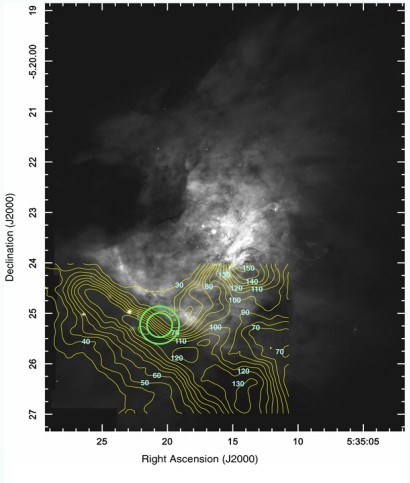
Results

- H on O_3 experiment: $H+O_3 \rightarrow OH+O_2$ and OH is readily converted to water

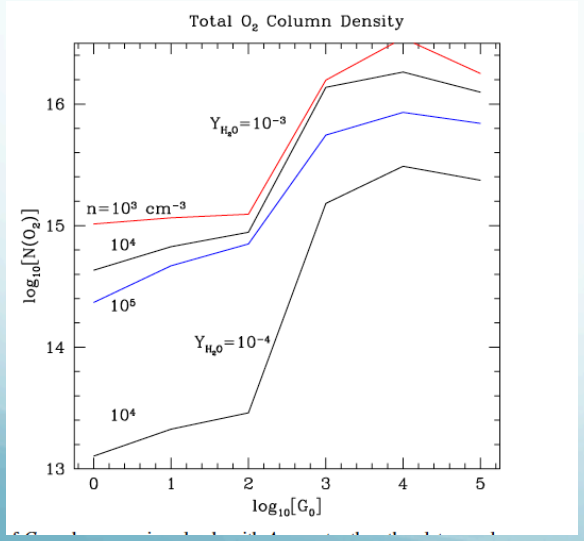
- D on O_3 experiment: slower conversion of OD to D_2O → isotope effect

Oxygen Chemistry in Space: the abundance puzzle

O_2 toward the Orion Bar



- Non detection of O_2 ($<10^{-7}$) in search toward the Orion Bar (Melnick et al. Ap.J 752, 56 (2012))
- Steady-state PDR model (Hollenbach et al. Ap.J 690, 1497 (2009))
  - They used: binding energy of O on grains E_b=800K (Tielens and Hagen, 1987)
- For $G_0 \geq 10^3$ thermal desorption of O yields too high a $N(O_2)$ (10^{-5}), contrary to observations
- → O_2 formation is suppressed if O is more tightly held on grains, E(O) ~1600K



G_0=multiplier of average radiation field

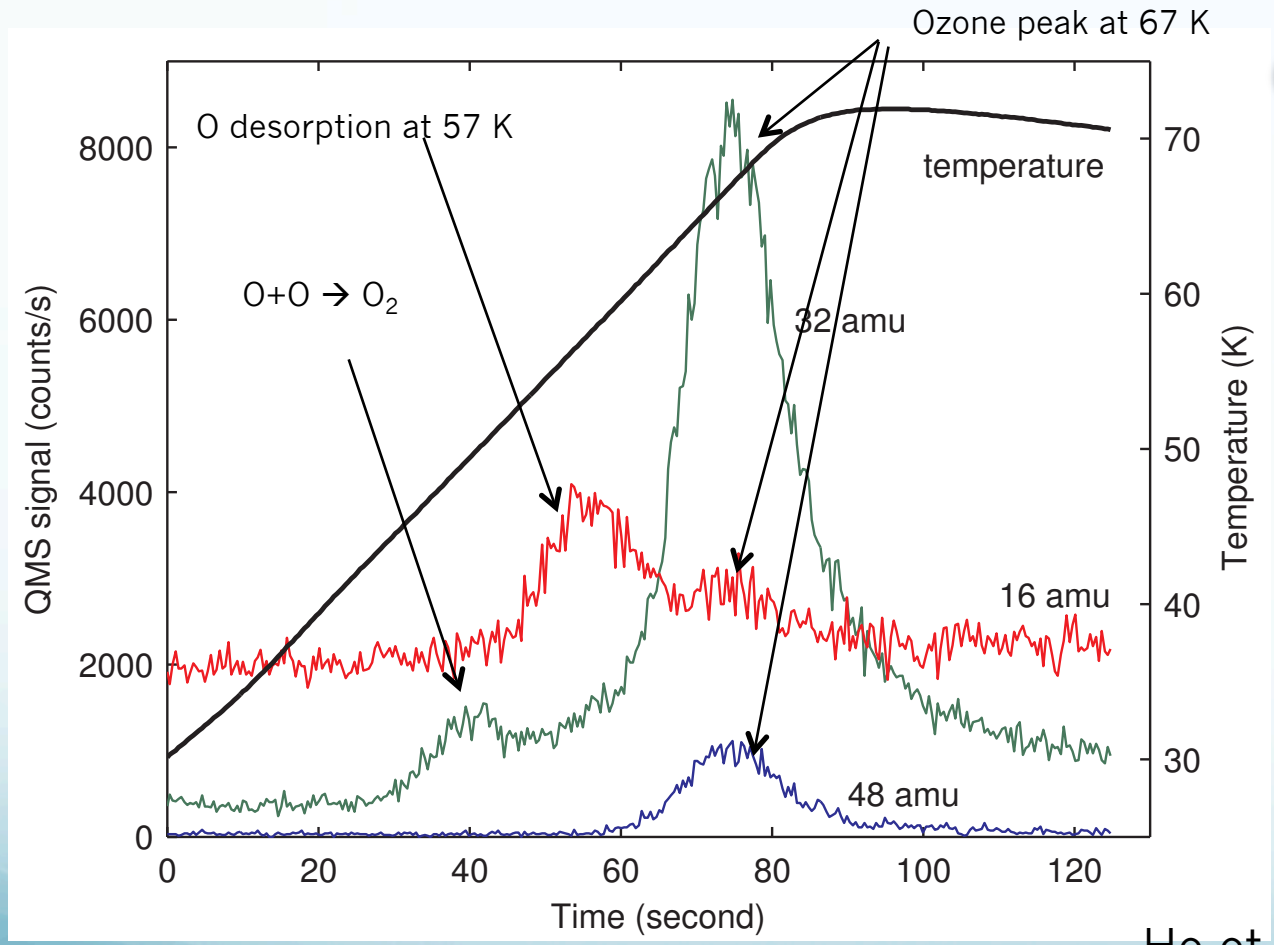
→ What is the binding energy of O on grains?

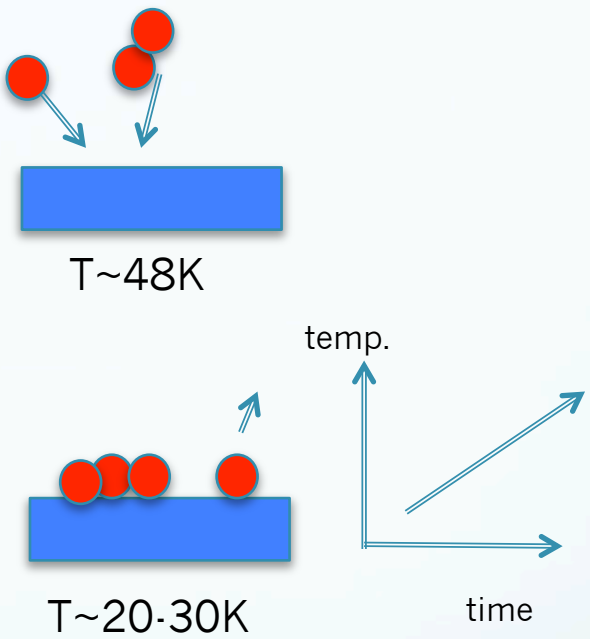
Oxygen on dust grains

- Formation of OH, H_2O, etc. depends on O residence time on grains
- What is the binding energy of O on grains?
- No prior <u>direct</u> measurement; values adopted in simulations of ISM chemistry are <u>estimates</u> only
  - 800K Tielens and Hagen ApJ (1982)

Atomic Oxygen on Dust Grains

Measurement of O Desorption from Porous Water Ice

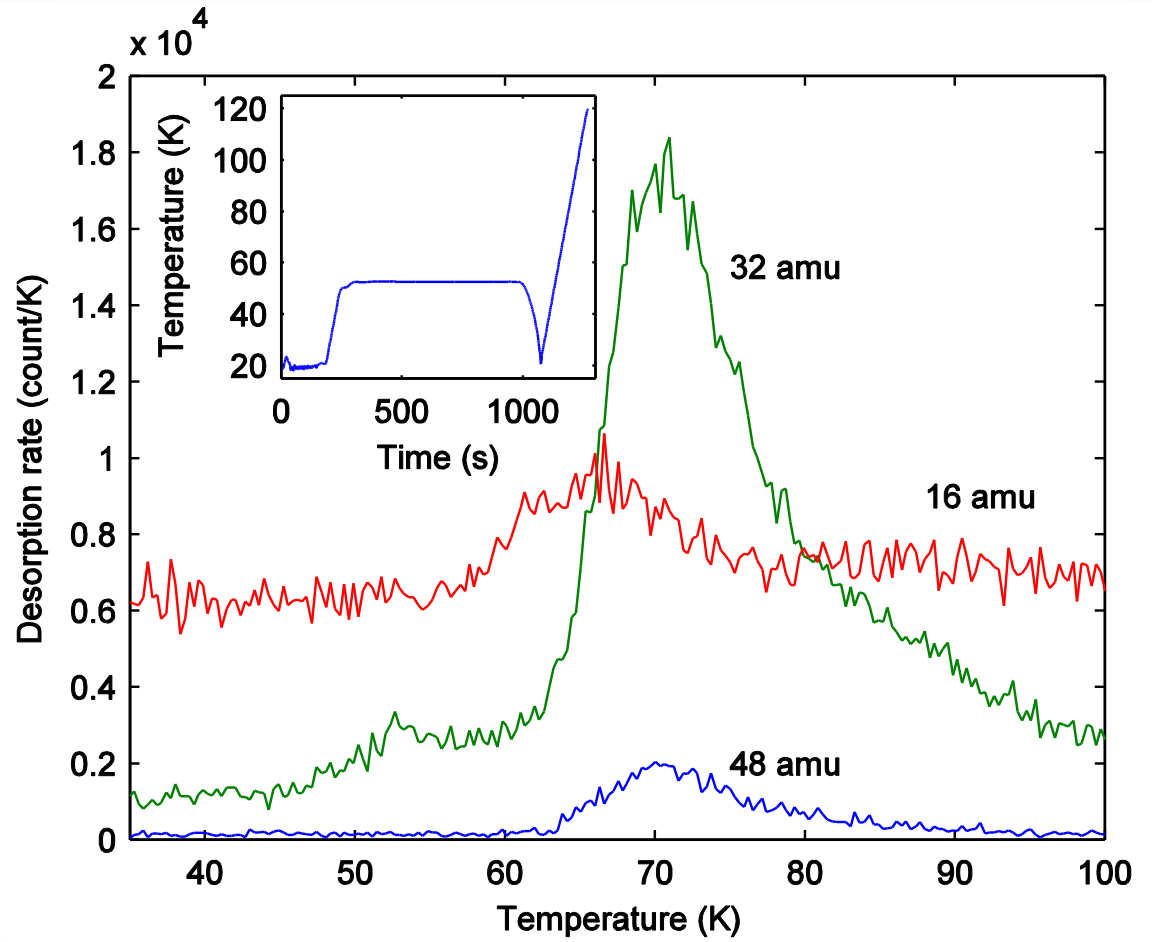




porous amorphous water

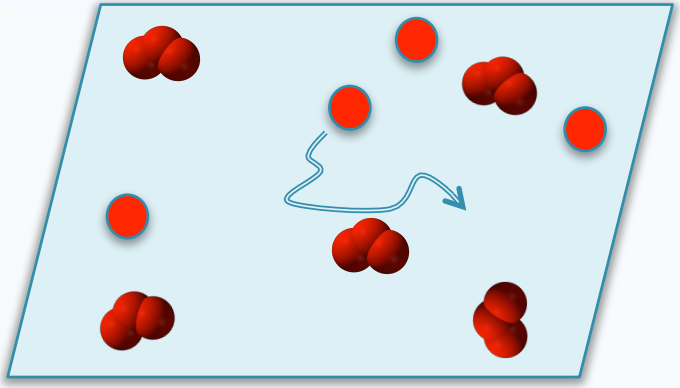
He et al., ApJ (2015) in press

Measurement of O Desorption from an Amorphous Silicate Film



He et al., ApJ (2015) in press

- silicate pre-coated with O_3 to prevent O+O reactions



O Desorption from an Amorphous Silicate Film with O_3 on it

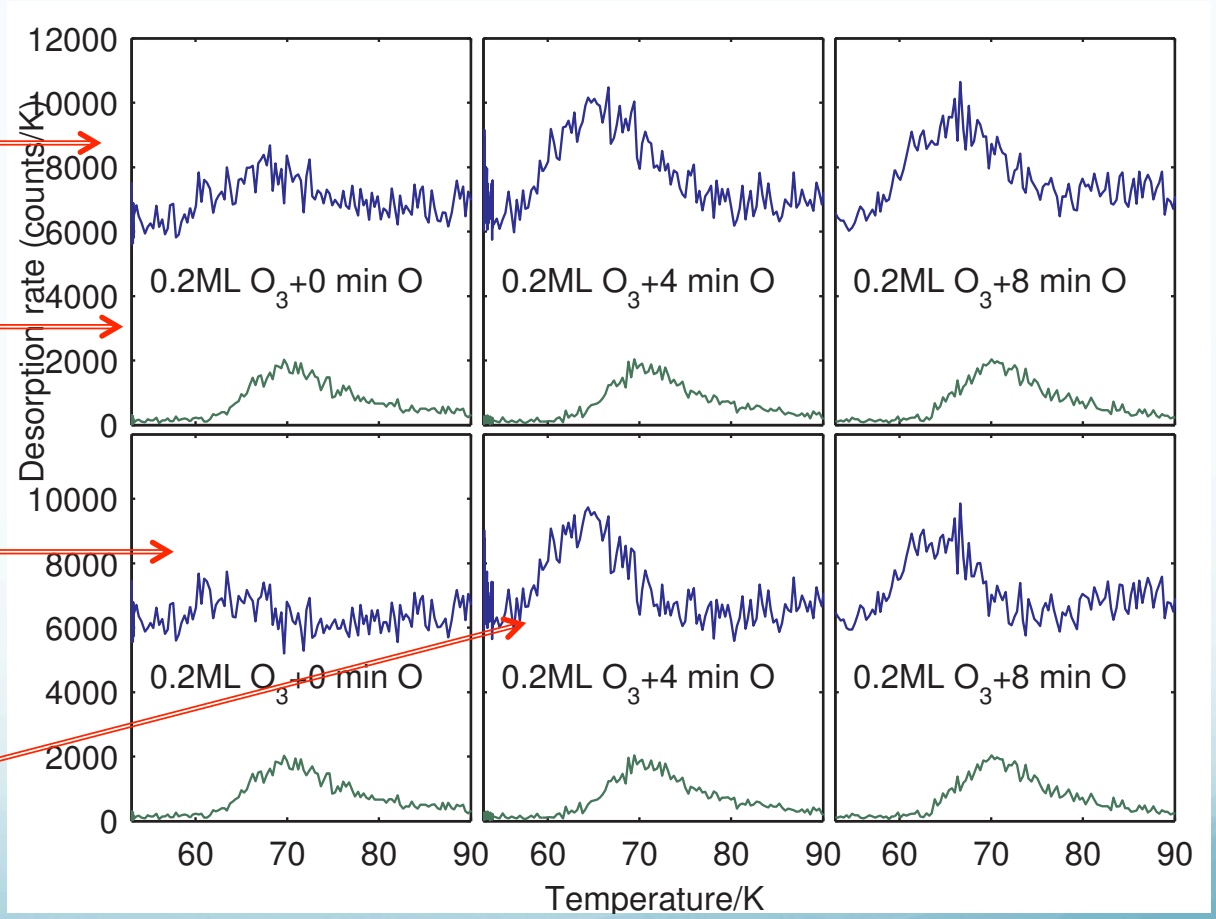
He et al., ApJ (2015) in press

mass 16
raw data

mass 32
ozone (fract.)

ozone subtracted

atomic oxygen
desorption



Atom - molecule	E_{des} (estimates) (K)	E_{des} (rate eqs. & observ.) (K)	Prior estimates/ measurements (K)	Direct measurement – this work (K)
O	800 [a]	1764 [b] 1800 [c]	1100 [e] 1680	1660±60 on a-H_2O ice 1850±90 on a-silicate
OH	1260 [a]	1650-4760 [d]		
O_2	1210 [a]		904 [b] 1200-1400 [ef] 910 [g] 900 [h]	
O_3			1820 – 2240 [j]	

a Estimate from various authors (see: Stantcheva et al. A&A 391, 1069)

b rate eqs. fit to data: He et al. PCCP 16, 3493 (2014)

c to satisfy observations: Melnick et al. ApJ 752, 26 (2012)

d He & Vidali ApJ 788, 50 (2014)

e O/silicate (Dulieu et al. Sci.Rep.3, 1318 (2013)); O/graphite (Kimber et al. Faraday Disc. 2014)

f O_2/graphite (Ulbricht et al., Carbon 44, 2931 (2012))

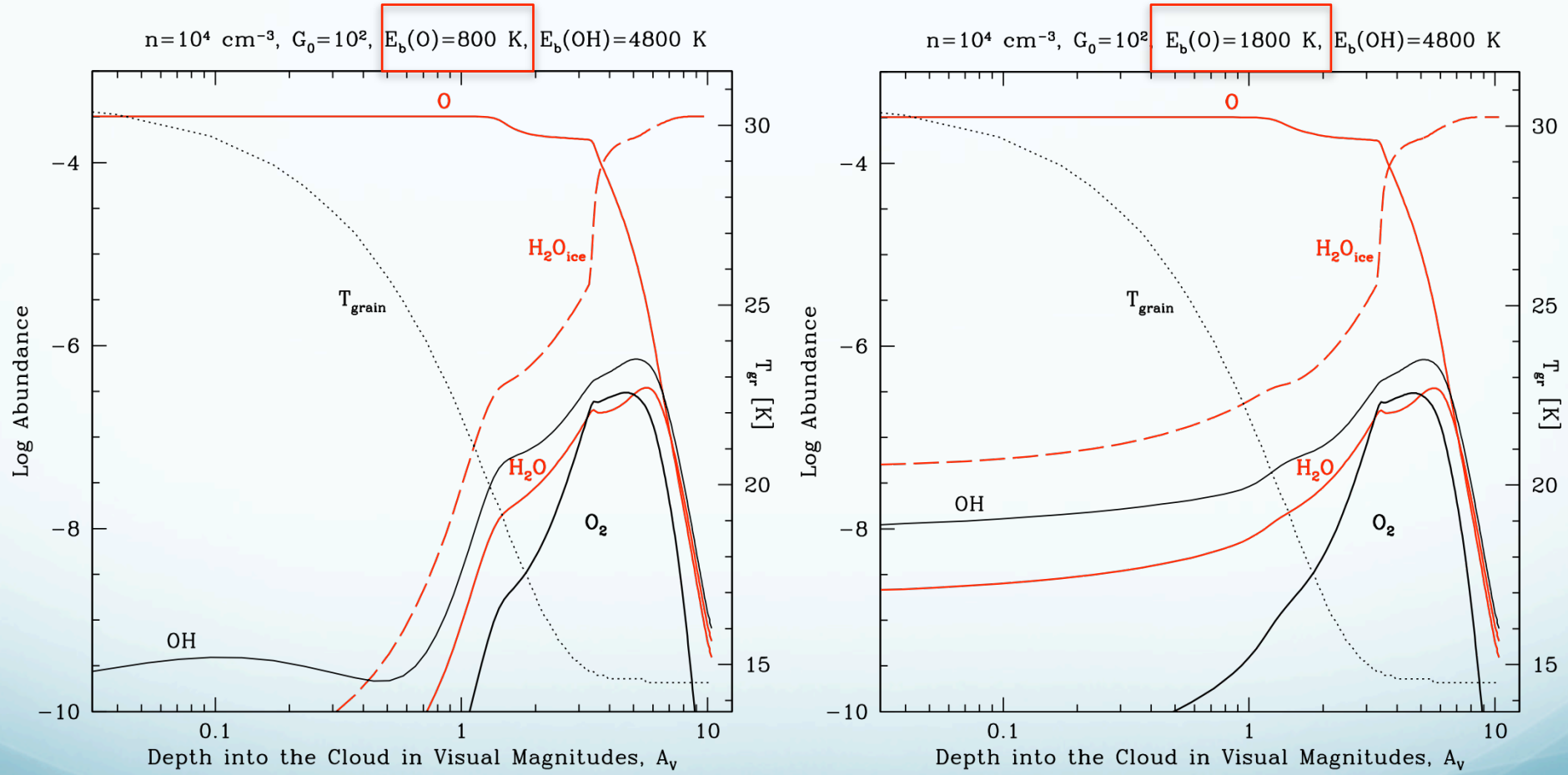
g O_2/O_2 ice (calculation) Acharyya A& A 466, 1005 (2007)

h O_2/H_20 ice Noble et al., NMRAS 421, (68 (202)); (calc.)(Lee-Meuwly Faraday Disc. 2014); tunneling for T<15K (Minissale et al. PRL 2013)

j Mokrane et al., 2009, Romanzin et al. 2011, He & Vidali 2014

Simulation

static PDR Hollenbach et al.(2009)



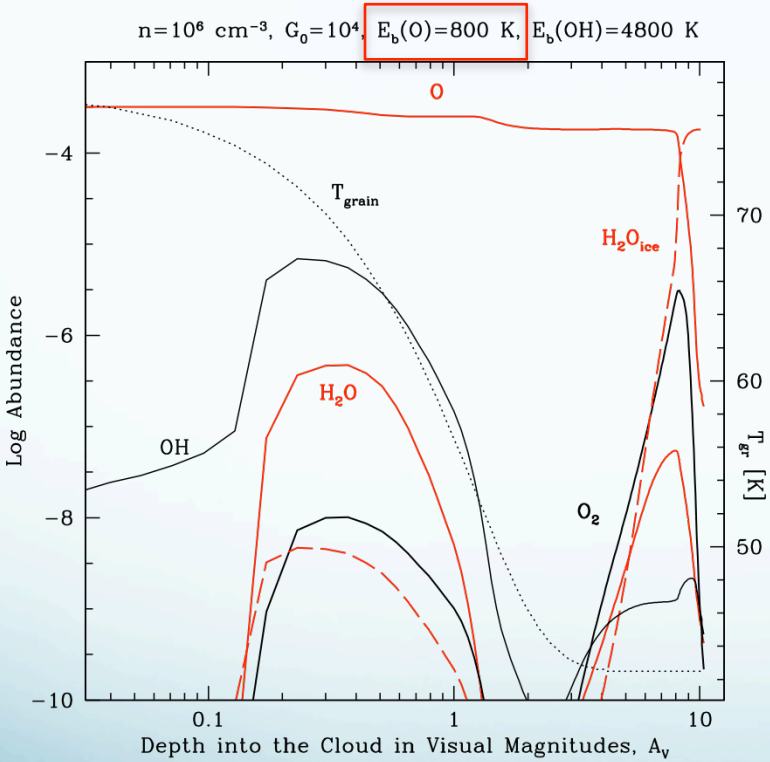
He et al., ApJ (2015) in press

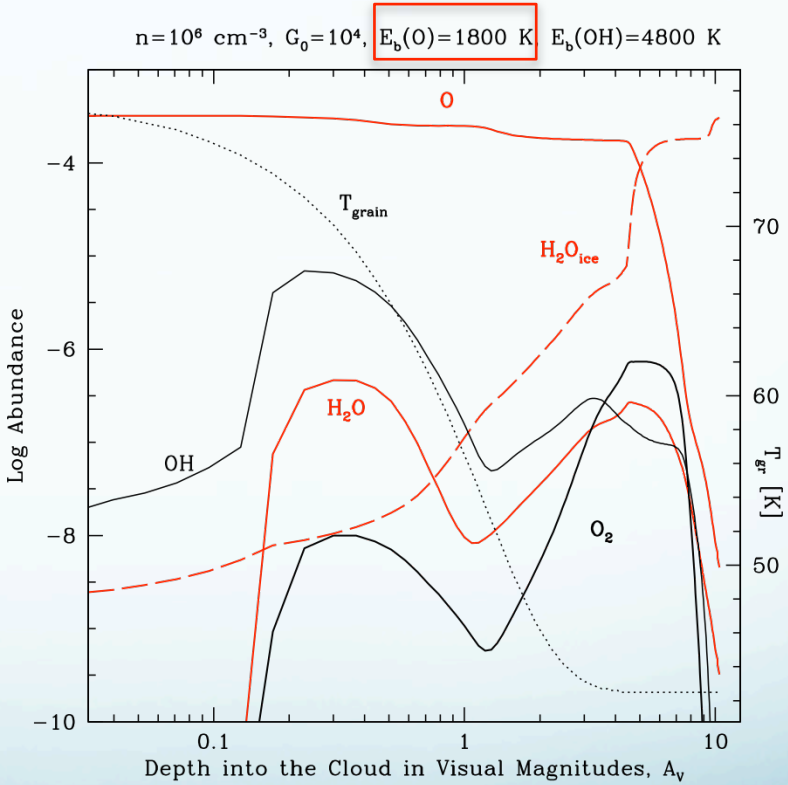
M.Kaufman

Atomic Oxygen on Dust Grains

Simulation

static PDR Hollenbach et al.(2009)





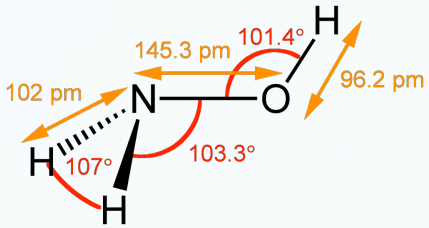
He et al., ApJ (2015) in press

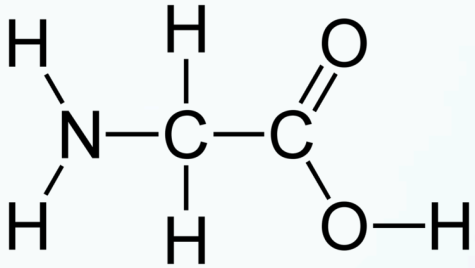
M.Kaufman

Implications of Results for H_2O and O chemistry in the ISM

- Formation of OH, H_2O on warm grains depends on availability of oxygen on the grain surfaces
- Residence time $t \sim t_0 e^{E/kT}$
- Higher E_b for O → more OH and H_2O formation on grains
  - Old E_b used in simulations:
    - for O: $E_b \sim 800K$ and T=50K → t ~ tens of microseconds
    - for OH: $E_b \sim 1{,}260K$ and T=50K → t ~ a few seconds
  - New values:
    - for O: $E_b \sim 1{,}800K$, $t \sim 10^3 - 10^4$ sec.
    - for OH: $E_b \sim 1{,}700\text{-}4{,}800K$, $t > 10^3$ sec
- Eventually H_2O is desorbed by FUV → more H_2O and less O_2 in the gas phase →consequences for gas-phase chemistry

Hydroxylamine



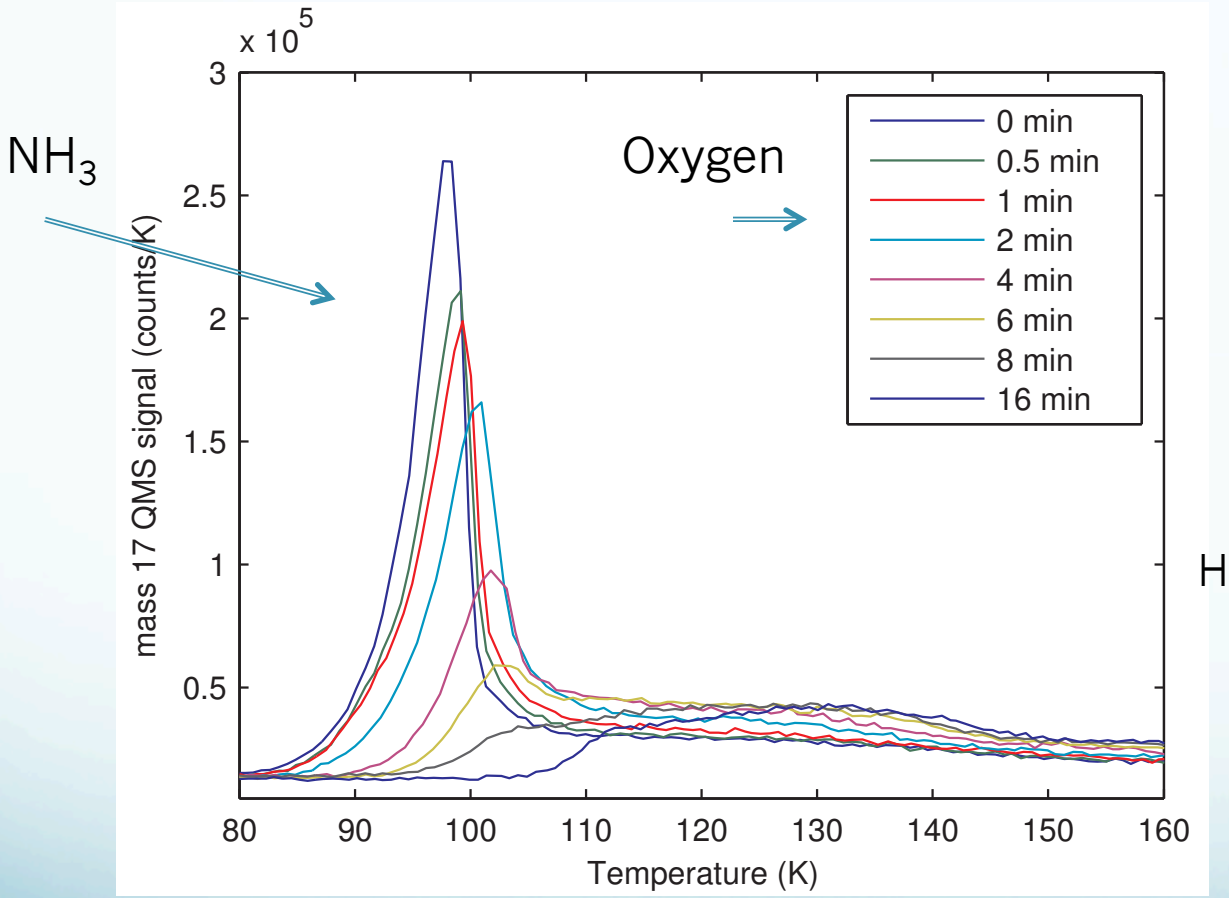


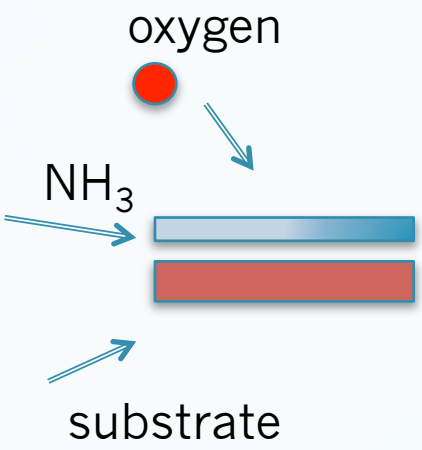
- NH_2OH hydroxylamine
- Precursor to glycine (NH_2CH_2COOH)
- It has not been detected yet in space
- Experiments
  - UV on NH_3+H_2O ice at 80-130 K (Nishi et al., 1984);
  - 5keV electrons on NH_3+H_2O ice at 10 K (Zheng & Kaiser 2010)
  - NO_{grain}+H+H+H (Congiu et al. 2012; Fedoseev et al. 2012)

J.He, G.Vidali, J-L Lemaire, & R.Garrod, Ap.J. 799, 49 (2015)

Formation of Precursors to Amino Acids

Ammonia Oxidation



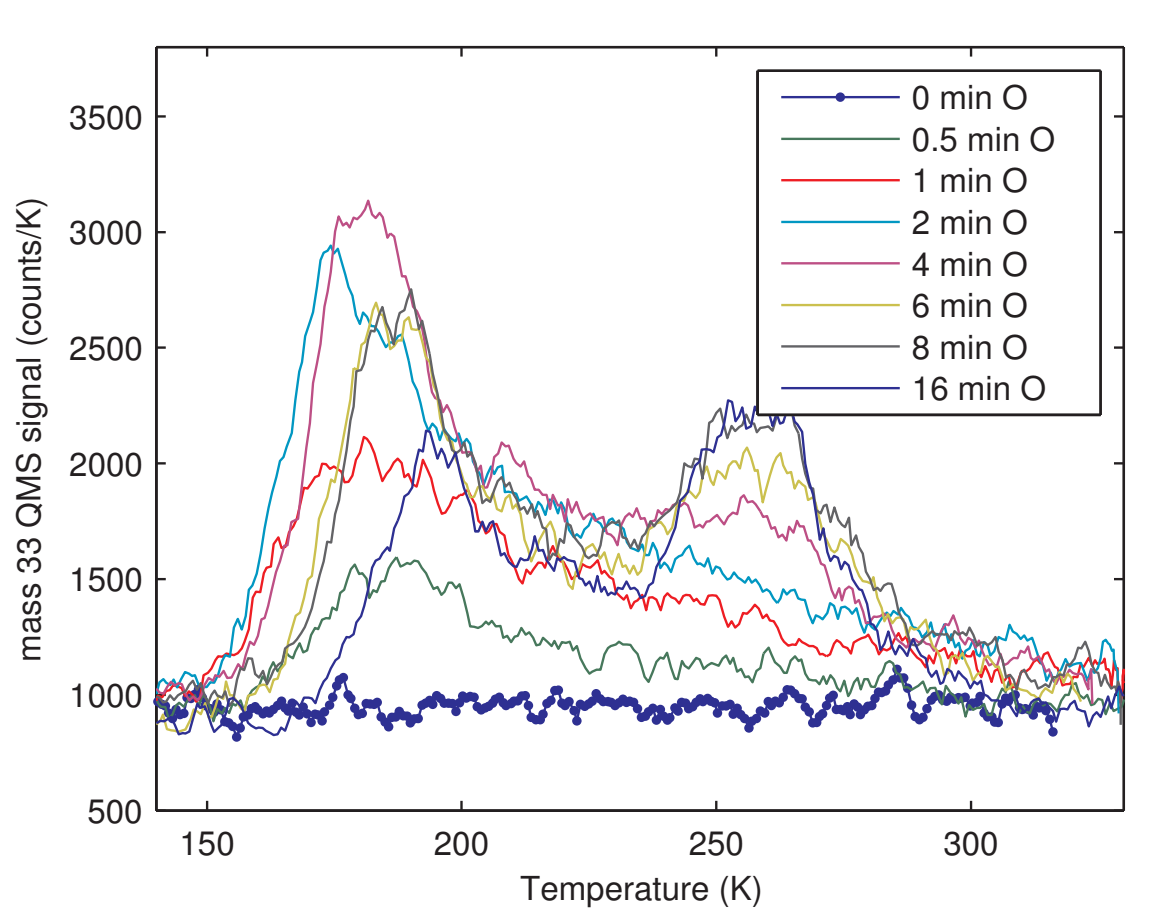


He et al., ApJ 799, 49 (2015)

NH_3 depletion vs. O exposure

Formation of Precursors to Amino Acids

Ammonia Oxidation



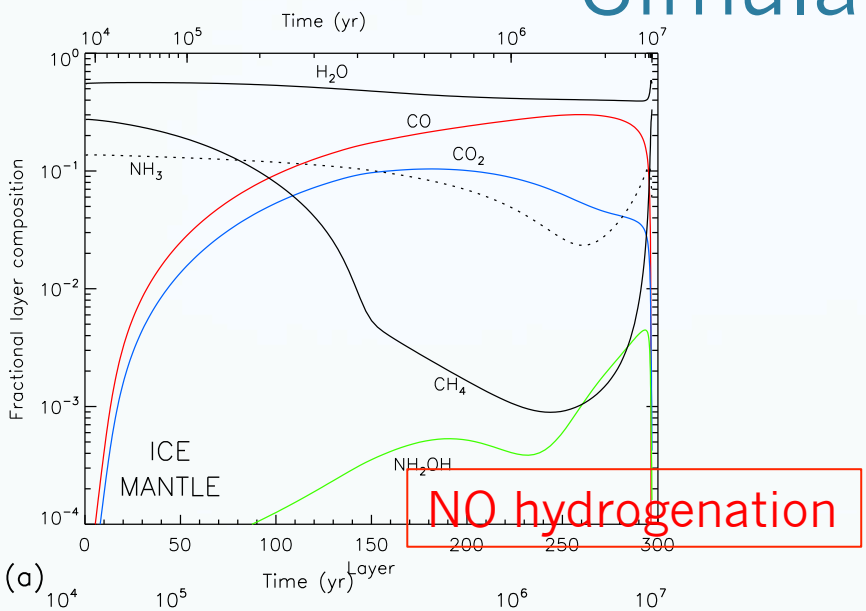
2ML of NH_3

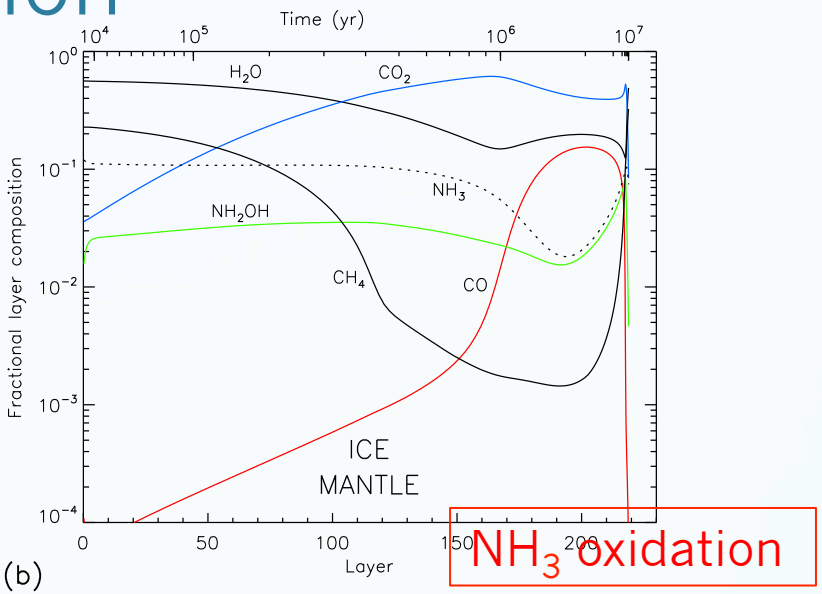
Mass 33 (NH_2OH) desorption for different O exposures at 70K

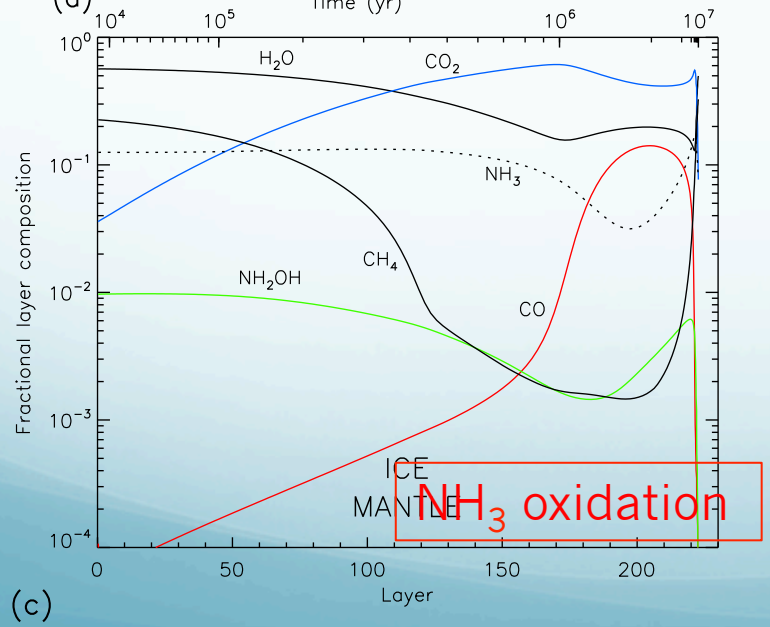
He et al., ApJ 799, 49 (2015)

Formation of Precursors to Amino Acids

Simulation







Fractional composition of ices within each layer as a function of depth into the ice

(a) E_A for the $O+NH_3$ reaction is 0 K; T ice =10 K.

(b) E_A=1000 K and T=14 K.

(c) E_A=2000 K and T=14 K

n_H=2 10^4 cm_{-3}; Av=10 $E_b(O)$=1500K

E_{diff}=0.35 $E_{\mathbf{b}}$

R.Garrod 3-phase gas-grain MAGICKAL

He et al., ApJ 799. 49 (2015)

Summary

- Formation of water on warm grains via $H+O_3$ reaction
- Binding energy of O on porous water ice and amorphous silicate film higher than previous estimate
  - From simulations: OH and H_2O formation on grains enhanced in molecular cloud edge in star forming regions in Orion
    - FUV photodesorption/photodissociaiton of OH and H_2O

    → Consequence for oxygen chemistry in the gas-phase
- Formation of hydroxylamine via oxidation of ammonia ice on grains
  - From simulations: triple hydrogenation of NO at T<12K; NH_3 oxidation is dominant at T>14K
    - NH_3 oxidation relevant in hot core/corino away from the core (cold regions)
    - Detection can be tricky because of the timing of the release of NH_2OH in the gas phase
    - ALMA!

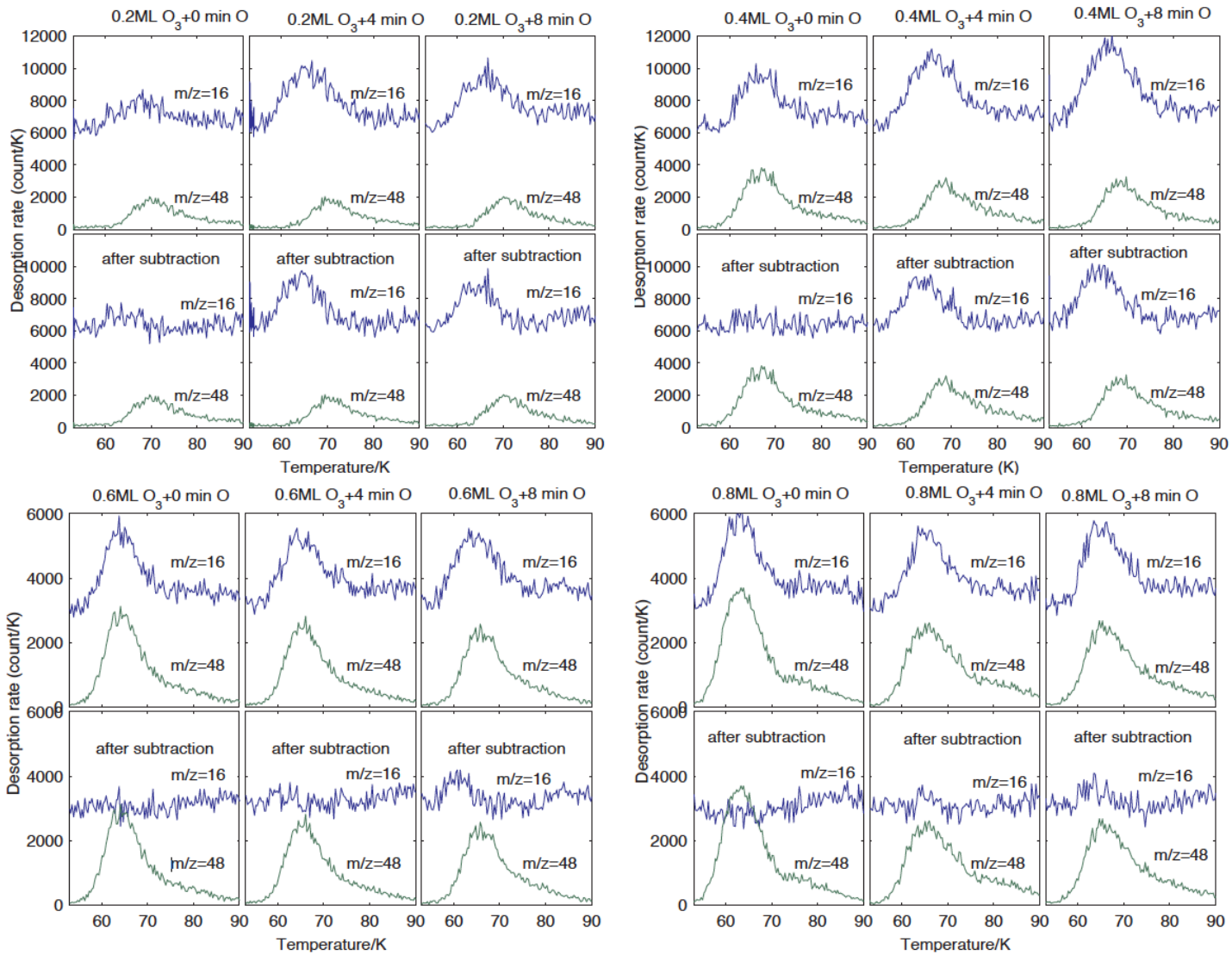
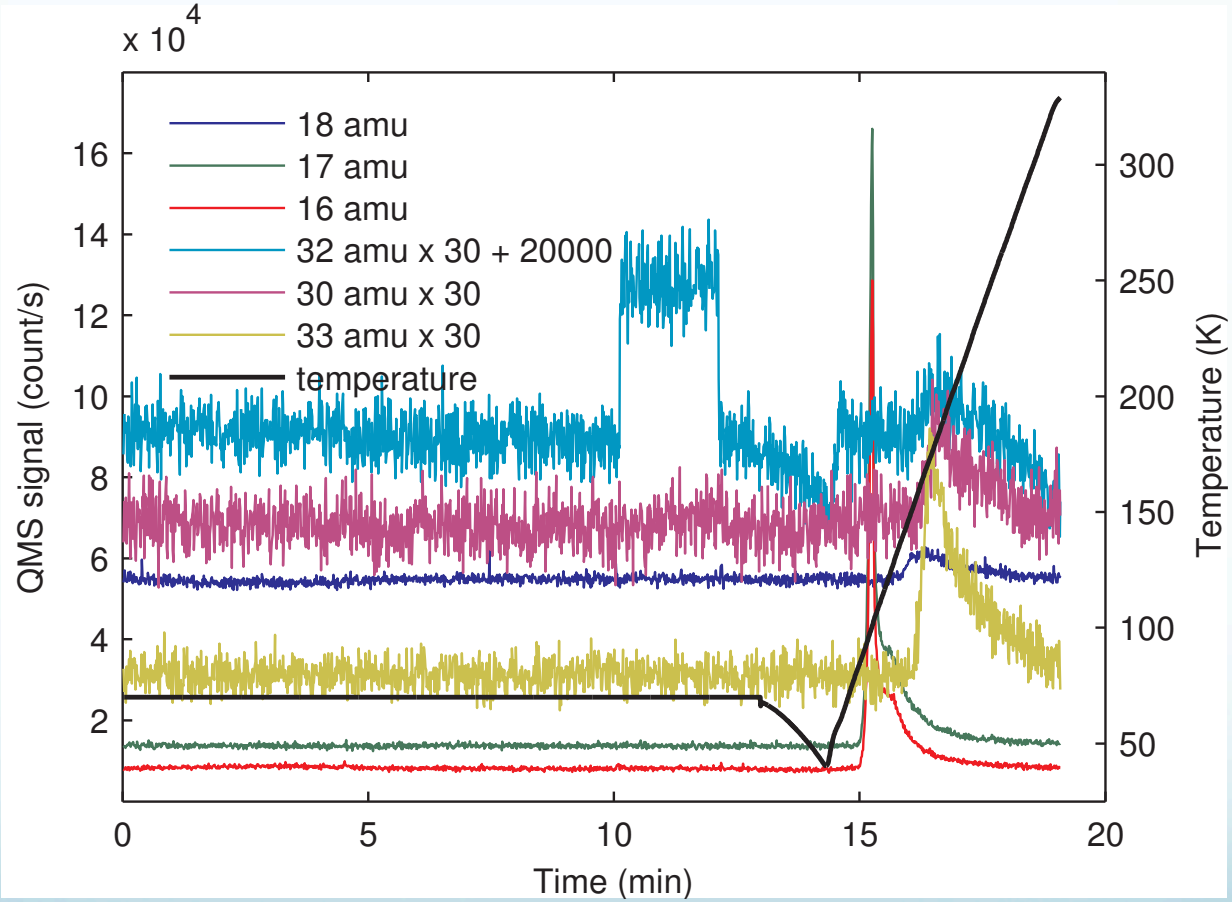


Figure 3. TPD traces of mass 16 amu (blue) and mass 48 amu (green) after deposition of 0 seconds, 240 seconds, and 480 seconds of O/O_2 on 0.2 ML, 0.4 ML, 0.6 ML, and 0.8 ML of O_3 pre-coated amorphous silicate. The heating ramp is 0.5 K s^{-1}. The top row of each panel has the original TPD traces while in the bottom row the contribution of O_3^+ fragmentation to the signal of mass 16 amu has been subtracted.

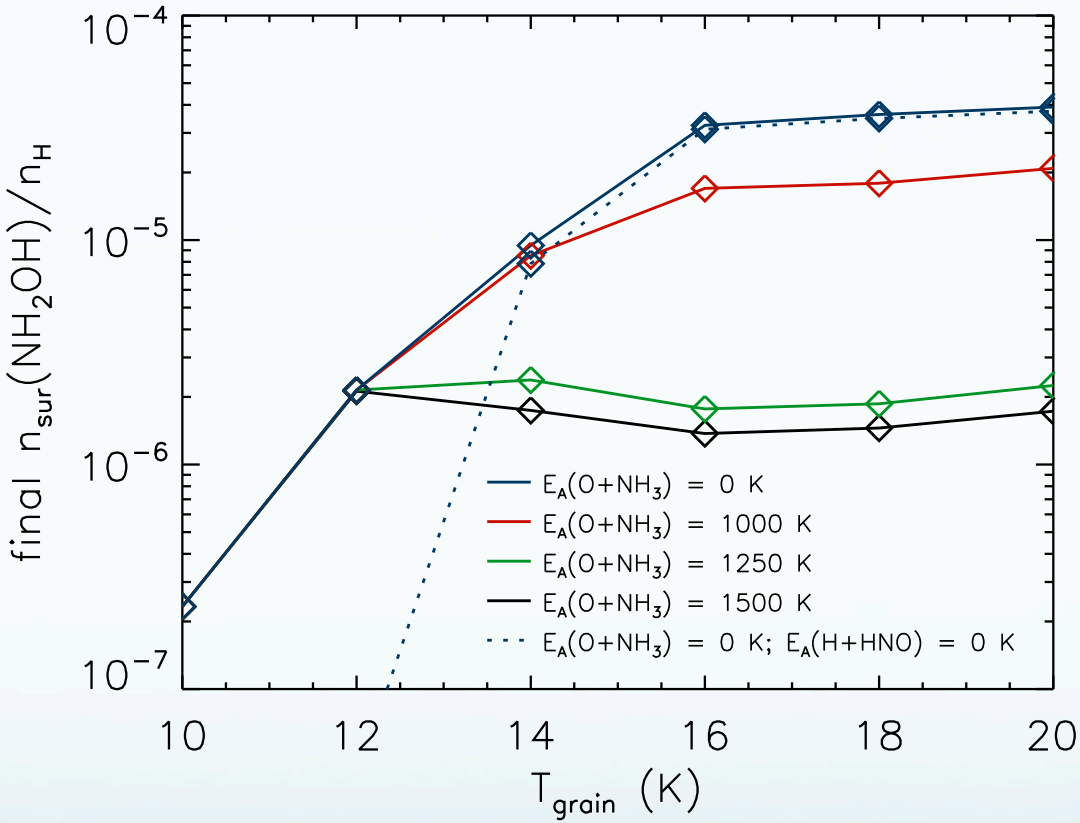
Formation of Precursors to Amino Acids

Ammonia Oxidation



He et al., ApJ submitted (2014b)

NH_2OH abundance



The dashed line shows the results assuming no barrier for either the NH3 + O →NH_2OH or H + HNOH→ HNHOH reactions.

He et al., ApJ submitted (2014b)

- Collaborators
  - at SU: Dr. Jianming Shi, Dr. Jiao He, Tyler Hopkins, Zhou Zhang
  - at Paris Observatoire: Prof. Jean Louis Lemaire
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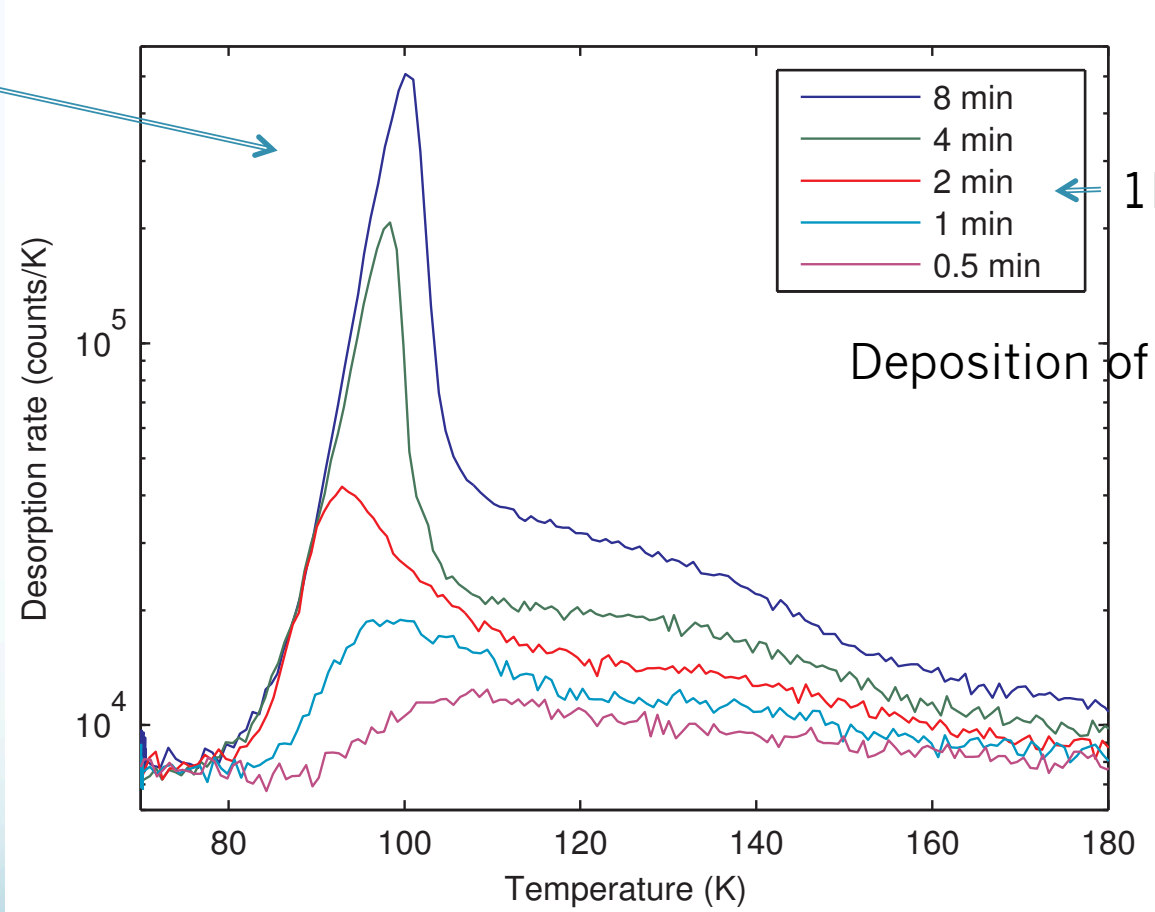
  - at San Jose' University: Prof. Michael Kaufman
  - at Arcetri Obs.: Dr. John Brucato

  - Funding:
    - National Science Foundation Astronomy and Astrophysics Division

Formation of Precursors to Amino Acids

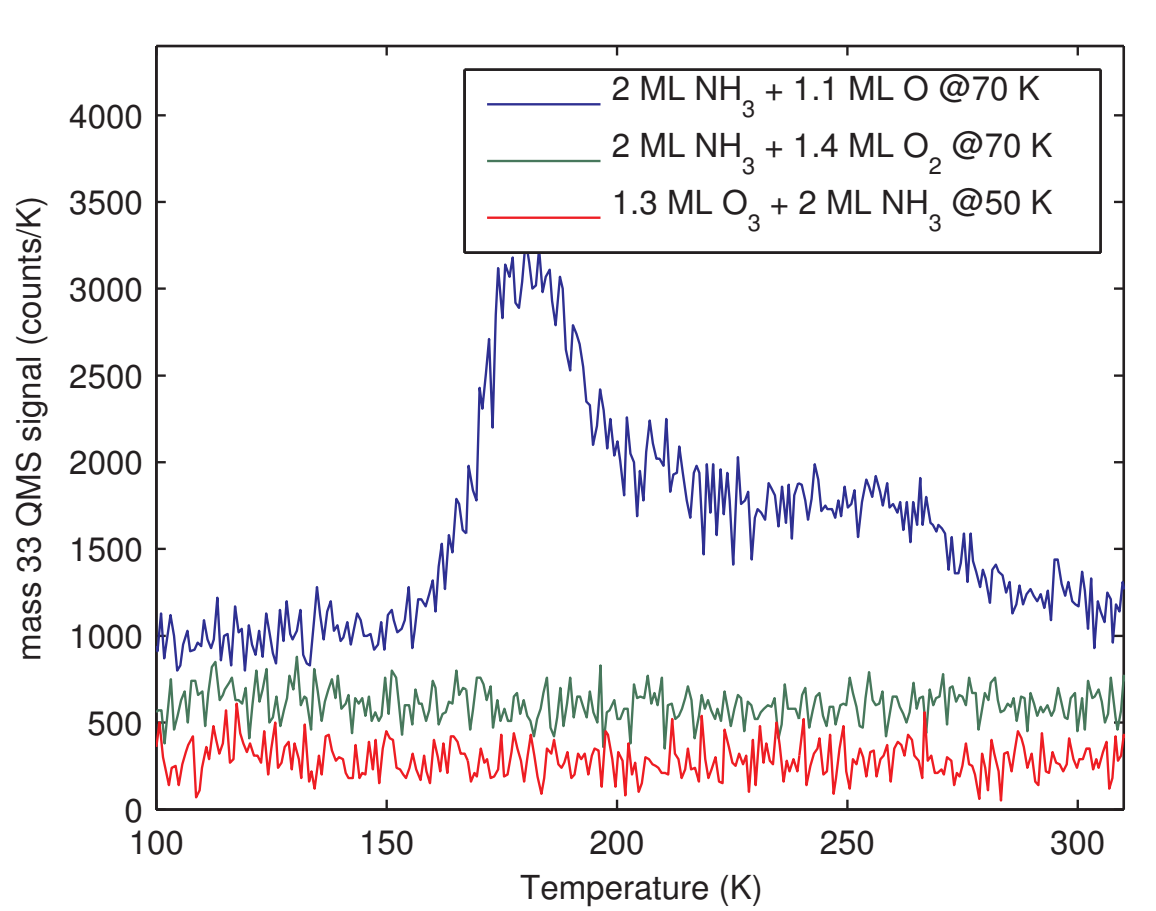
Ammonia (NH_3) Desorption

ammonia



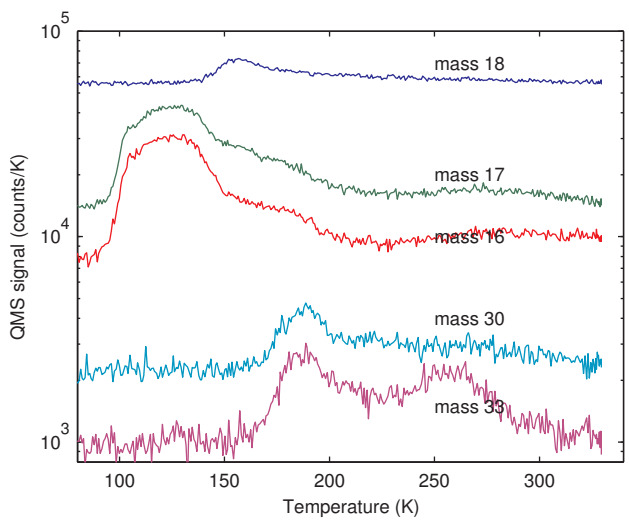
He et al., ApJ submitted (2014b)

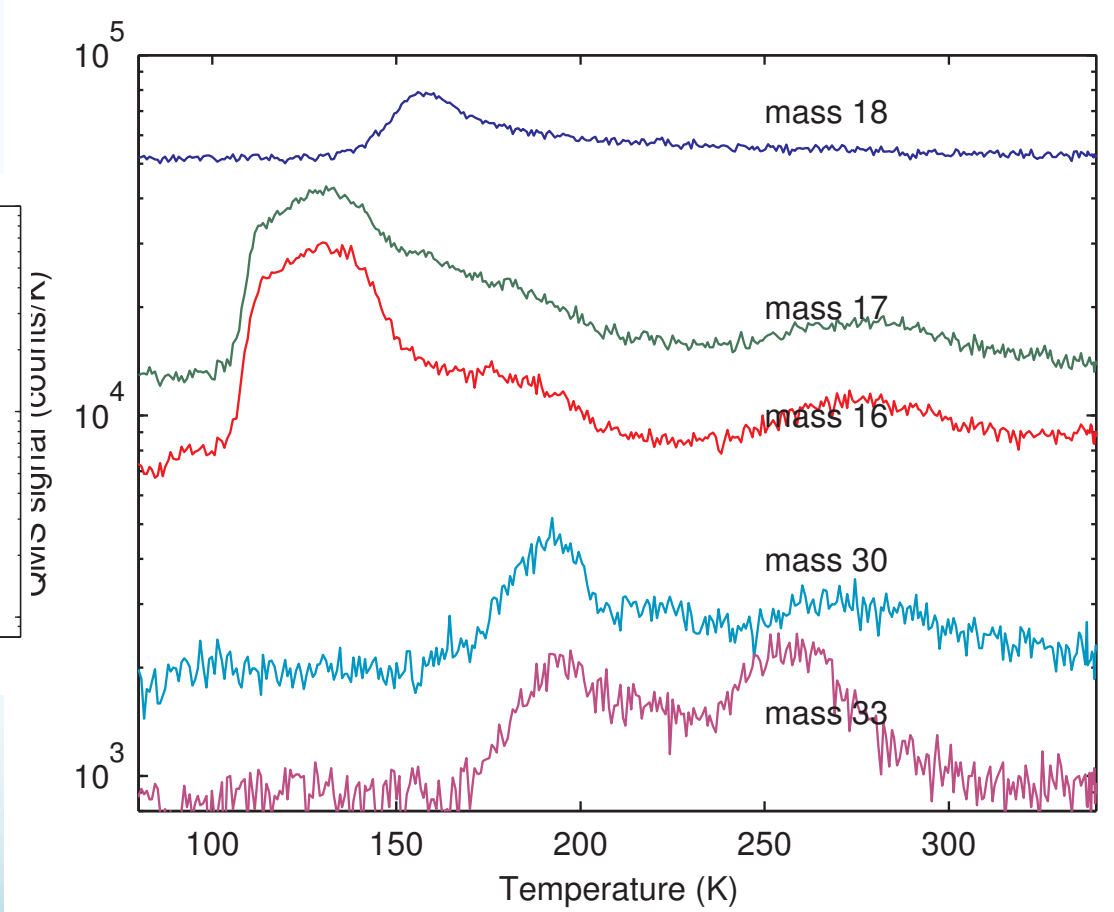
Control Experiments

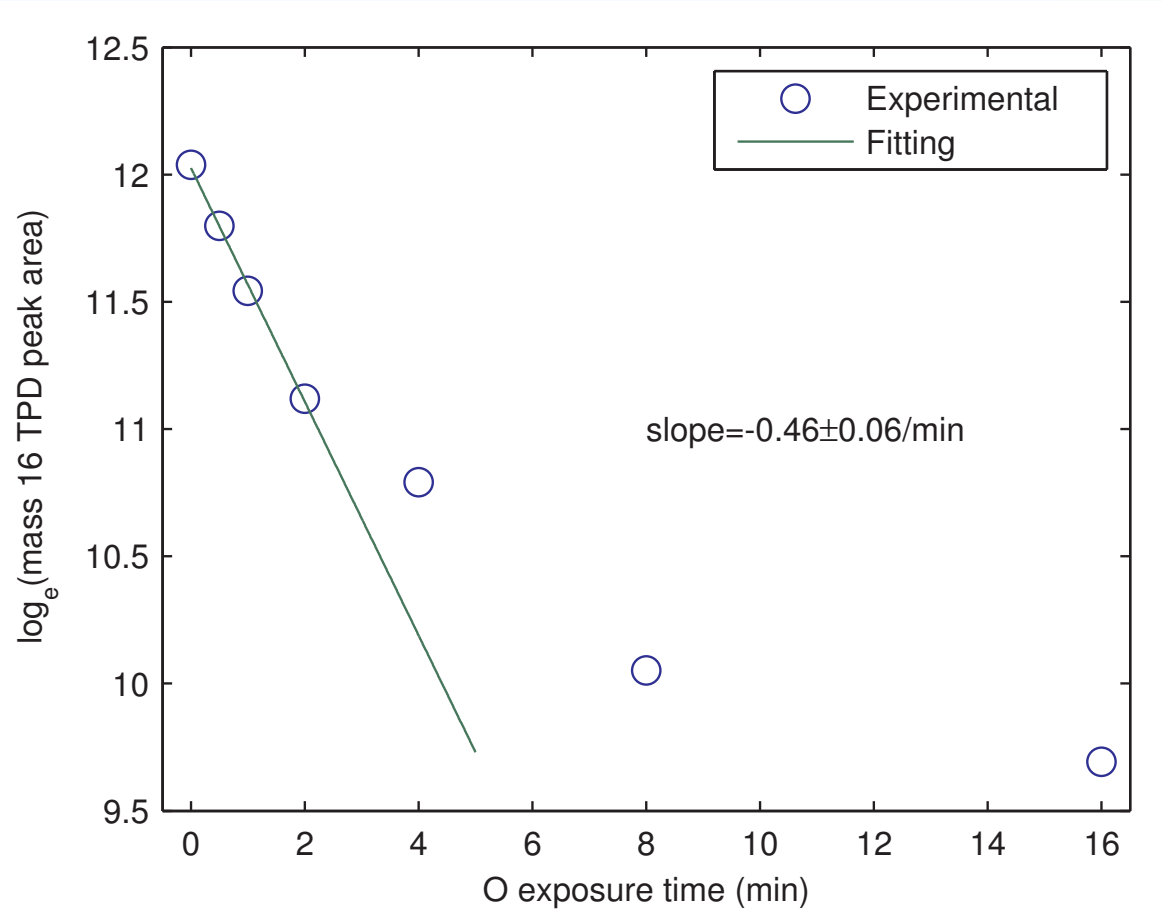


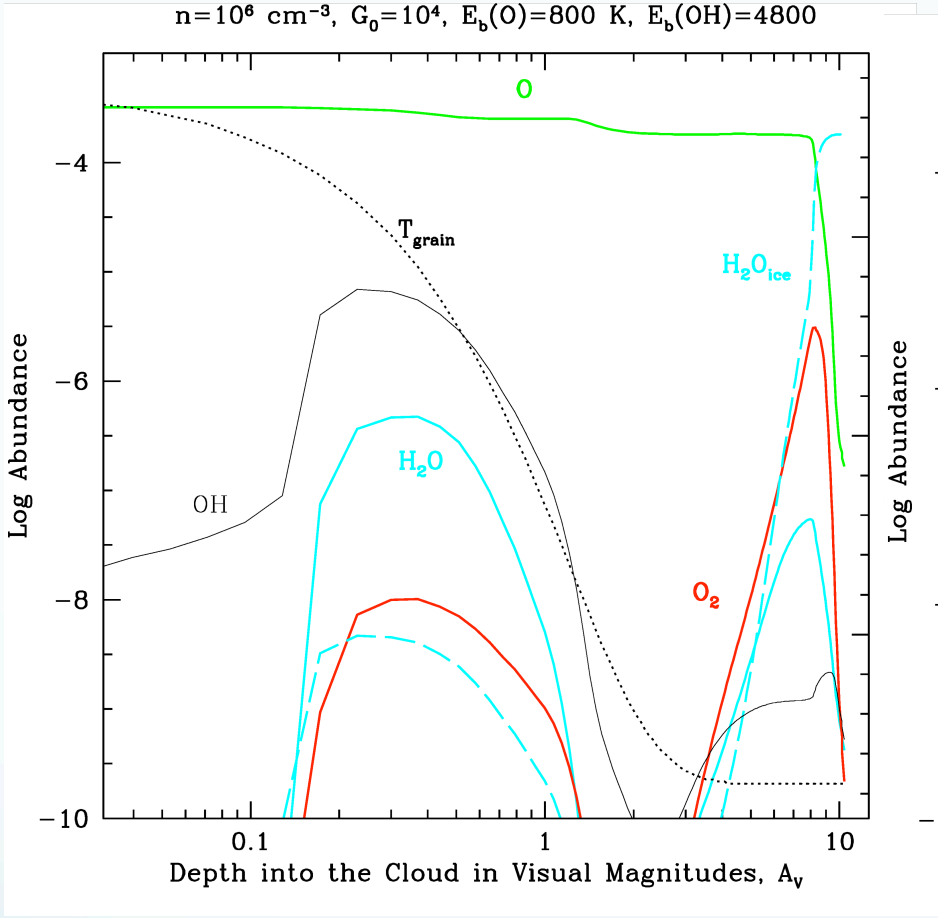
No NH_3 +O_2 and NH_3+O_3 reactions

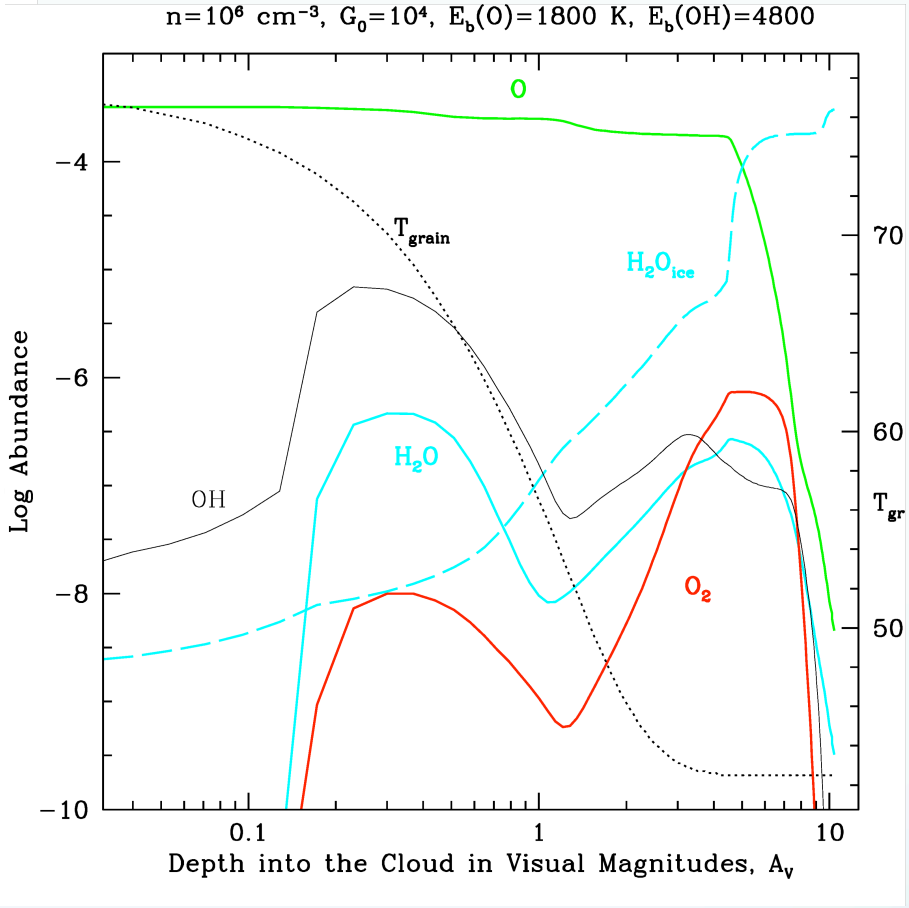
He et al., ApJ submitted (2014b)


QMS signal (counts/K)
Temperature (K)
mass 18
mass 17
mass 16
mass 30
mass 33


QMS signal (counts/K)
Temperature (K)
mass 18
mass 17
mass 16
mass 30
mass 33


Experimental
Fitting
slope=-0.46±0.06/min
12.5
12
11.5
11
10.5
10
9.5
0
2
4
6
8
10
12
14
16
log$_e$(mass 16 TPD peak area)
O exposure time (min)


n=10⁶ cm⁻³, G₀=10⁴, E_b(O)=800 K, E_b(OH)=4800
O
T_grain
H₂O_ice
H₂O
OH
O₂
Log Abundance
−4
−6
−8
−10
0.1
1
10
Depth into the Cloud in Visual Magnitudes, A_V


n=10⁶ cm⁻³, G₀=10⁴, E_b(O)=1800 K, E_b(OH)=4800
O
T_grain
H₂O_ice
H₂O
OH
O₂
Log Abundance
−4
−6
−8
−10
70
60
50
T_gr
0.1
1
10
Depth into the Cloud in Visual Magnitudes, A_V

Cross-section of $H+O_{3grain}$ reaction

$I \sim e^{-\phi\sigma t}$ ϕ=flux σ=cross-section

$\sigma_H = 1.6 +/- 0.27\ A^2$

$\sigma_D = 0.94 +/- 0.09\ A^2$