VUV AND EUV IRRADIATION OF CH_4 + NH_3 ICE MIXTURES

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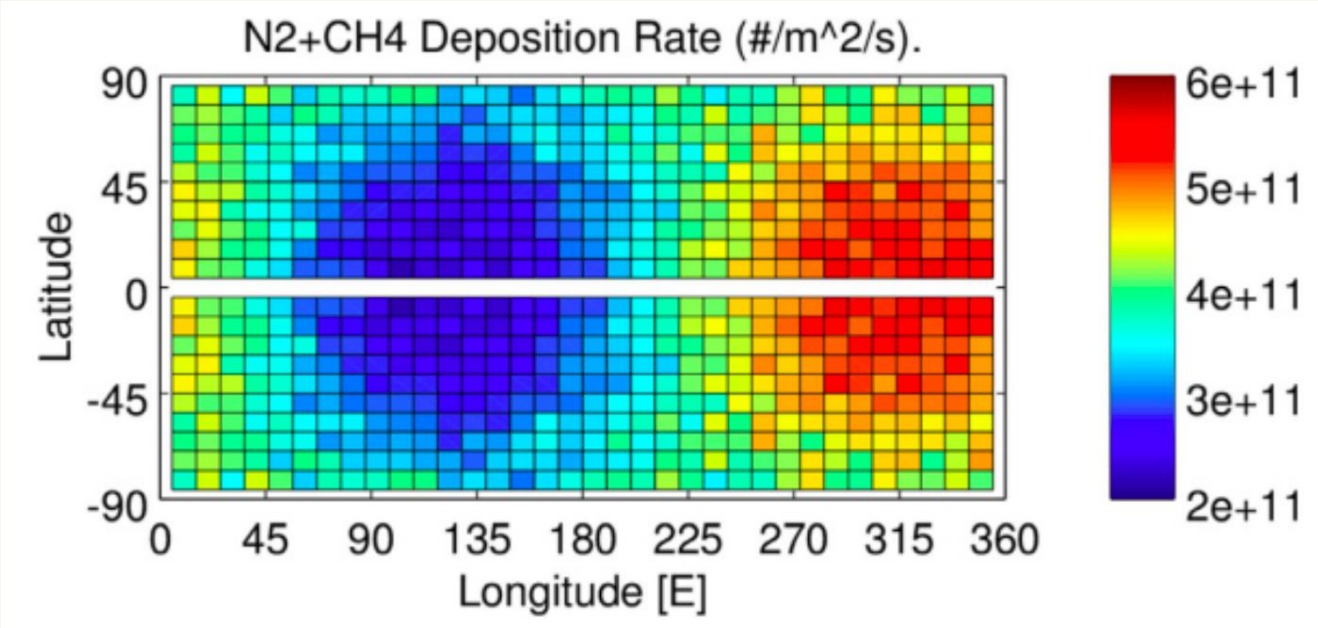
Contents

Introduction

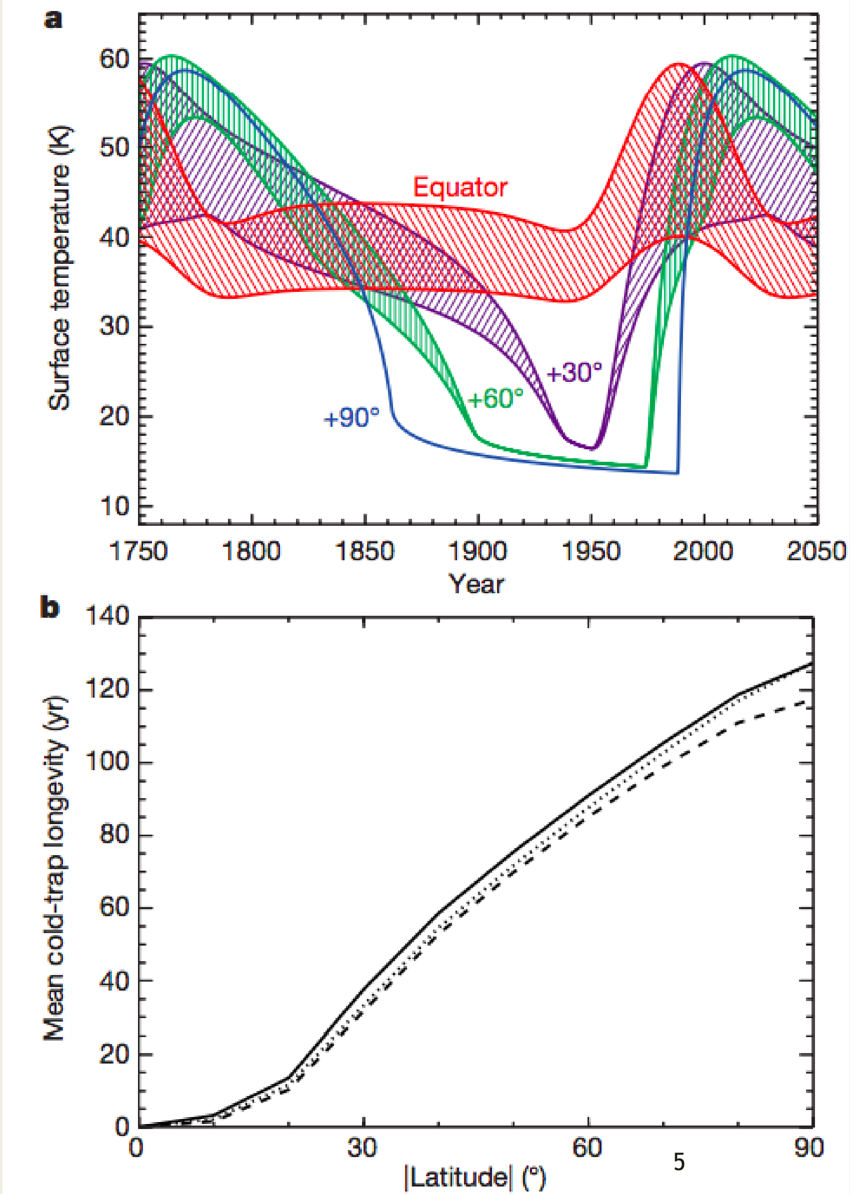
Deposition rate of methane on Charon



quoted from Hoey et al. (2017)

Surface temperatures at different latitudes

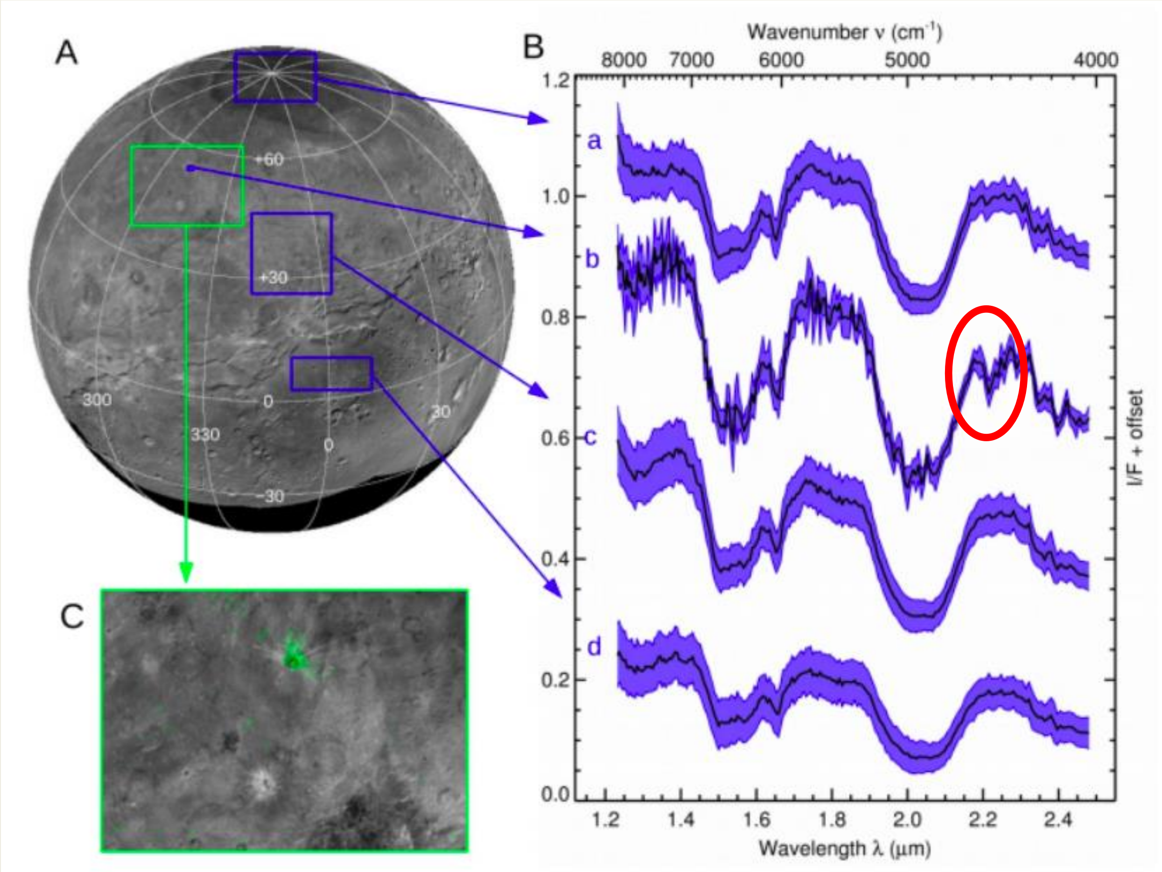
- Thermal model from Grundy et al. (2016) shows the pole position is below 25 K for 130 years
- Methane can condense on those positions where the temperature is below 25 K.



Quoted from Grundy et al. (2016)

Ammonia on Organa Crater

- *Ammonia was detected all over the surfaces, especially on Organa Crater*



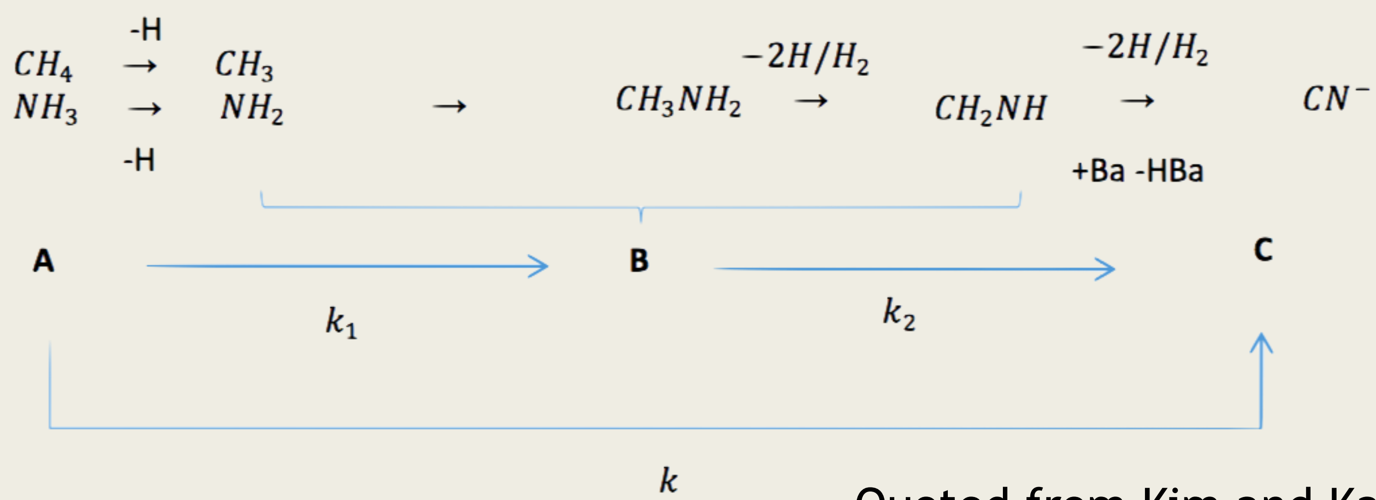
from Grundy et al. (2016)

Production mechanism of CN^-

Enthalpy of CH_3NH_2 formation

$$CH_3 + NH_2 \rightarrow CH_3NH_2 \ \ \Delta H = -3.64\ eV$$

Quoted from Kundu et al. (2017)



Quoted from Kim and Kaiser (2011)

Production mechanism of CN^-

Attempts to detect CH_3NH_2:

- Different results from 2 e^- irradiating experiments
  - *5 keV e^- by Kim and Kaiser (2011):*
    - The intermediate CH_3NH_2 was detected by TPD
  - *1- 90 eV e^- experiment by Kundu et al.(2017)*
    - The intermediate CH_3NH_2 cannot be detected by TPD

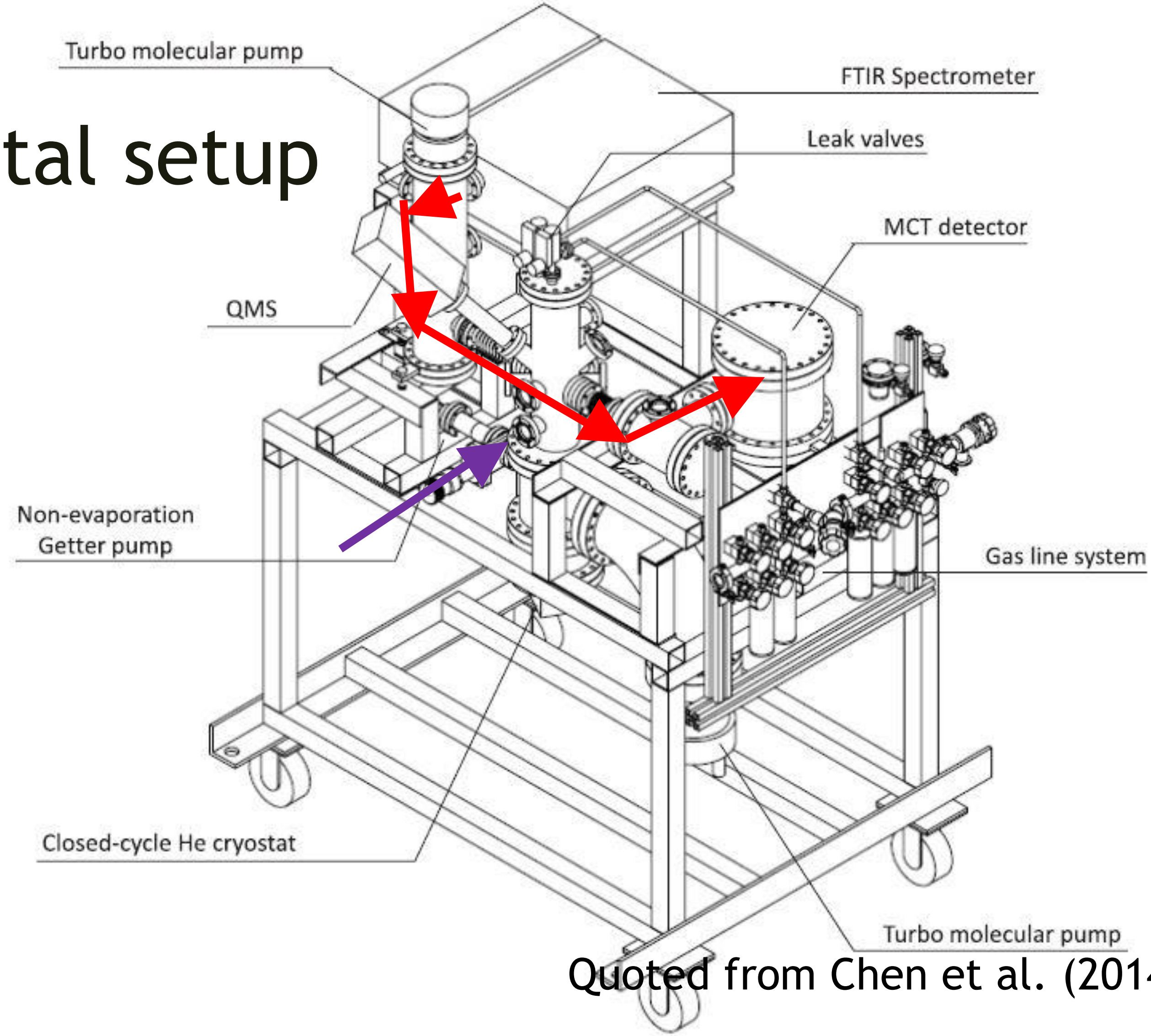
- How about photons?

Motivation

- 1. To compare with previous studies
  - *Experiment: CH_4+NH_3 = 3:2*
  - *Confirm mechanism of CN^-*
- 2. To simulate the surface of Charon
  - *Experiment: CH_4+NH_3 =1:5, 1:10, 1:20*
  - *Variation of photon sources: from VUV to EUV*

Methodology

Experimental setup



IR path

VUV/EUV path

Quoted from Chen et al. (2014)

Experimental Protocol

KBr substrate is pre-cooled to 15 K (1 x 10 $^{-10}$ torr) from 300 K (8 x 10 $^{-10}$ torr)

↓

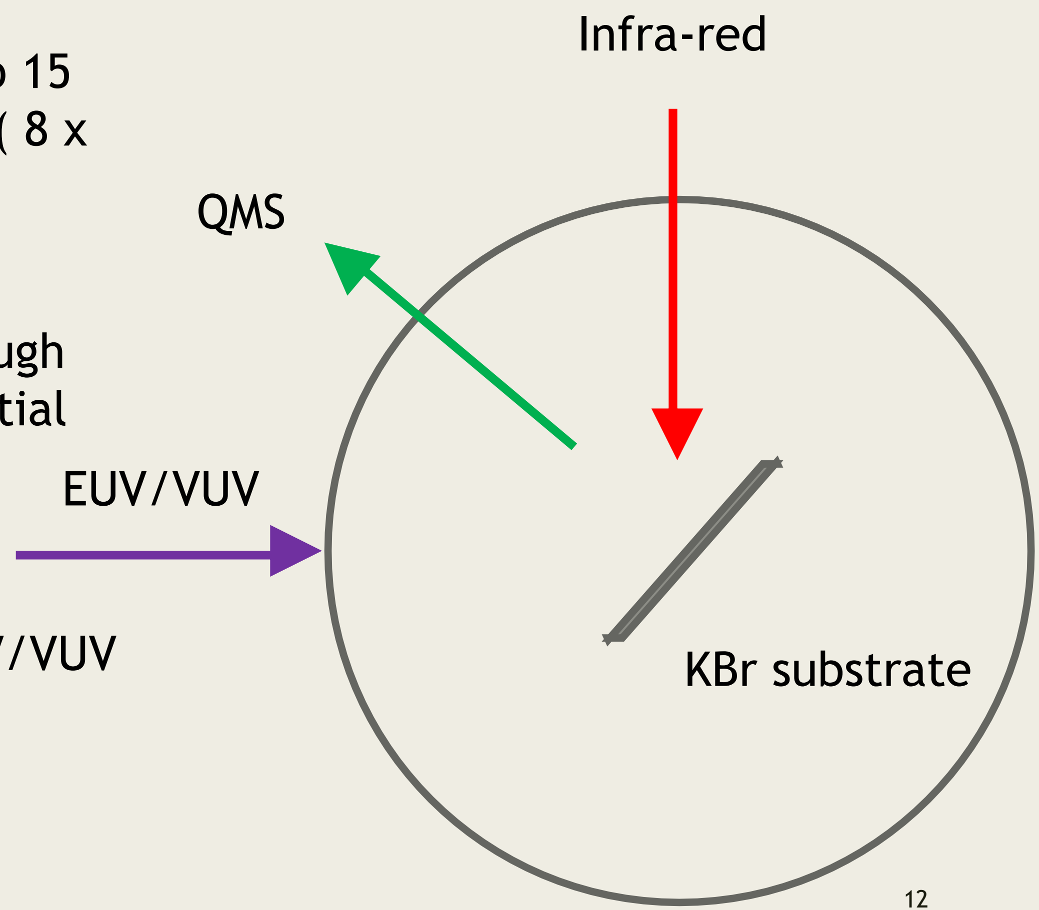
Deposit the ice mixtures through leak valve, with different partial pressures of CH_4 and NH_3

↓

Irradiate the samples by EUV/VUV

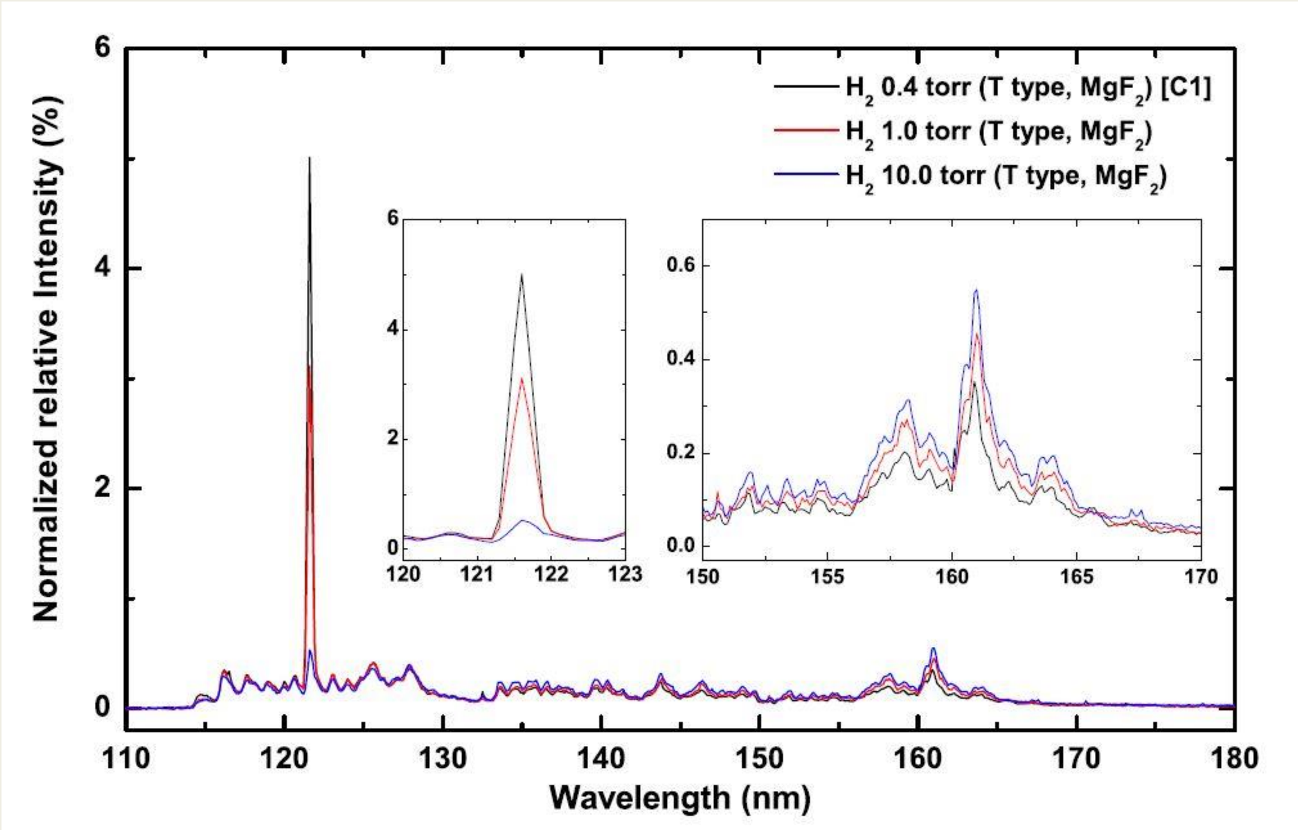
↓

Warm-up with 1 K/min



The spectrum of VUV (MDHL) energy source

- H_2 0.4 torr was adopted
- 19.1% is Ly-α
- average photon energy is 9.27 eV



Quoted from Chen et al. (2014)

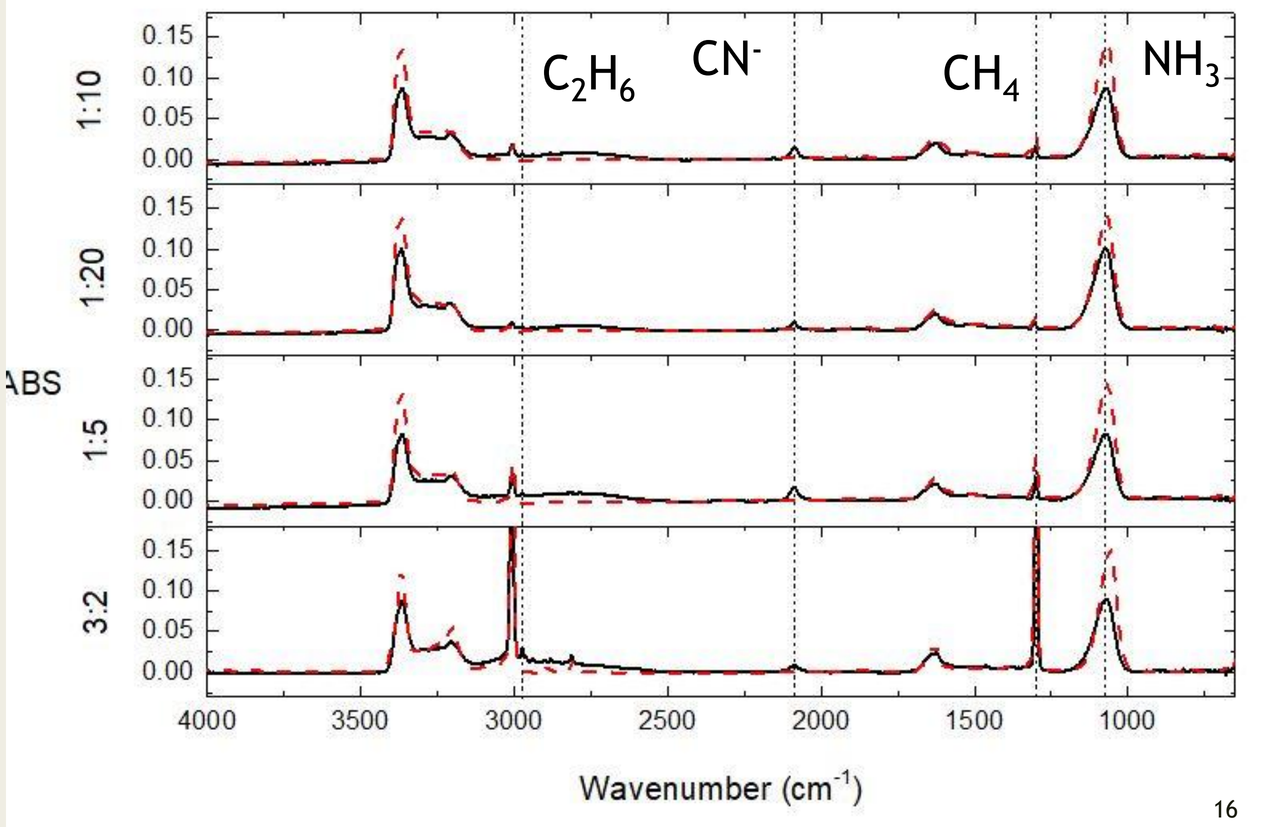
Experimental Configurations

Energetic Source	constituent	Column Density (x10 ^{15} molecules cm^{-2})			
		3:2	1:5	1:10	1:20
VUV (MDHL)	CH_4	900	120	60	30
	NH_3	600	600	600	600
EUV (30.4 nm)	CH_4	900	120	--	--
	NH_3	600	600	--	--

Results

Infra-red spectra

- Infra-red spectra before (red dotted lines) and after (black solid lines) VUV irradiation
- CN^-, C_2H_6 and C_3H_8 are formed after VUV irradiation



From Beer’s Law

Transmittance $T(v)$*is defined by:*

- $T(v) = \frac{I(v)}{I_o(v)}$

Absorbance $a(v)$ *is defined by:*

- $a(v) = -lnT = -\ln\left(\frac{I(v)}{I_o(v)}\right) = nl\sigma(v)$

Where n is number density (molecules cm^{-3}) l is the path length (cm) and $\sigma(v)$ is the cross-section (cm^{2} molecules $^{-1}$)

Column density N *is defined by:*

- $N = \frac{\int a(v)dv}{A(v)}$

Where$N$ is column density (molecules cm^{-2}) $A(v)$ is the absorption strength (A-value) (cm molecule^{-1}) from literatures

1. Production of CN-

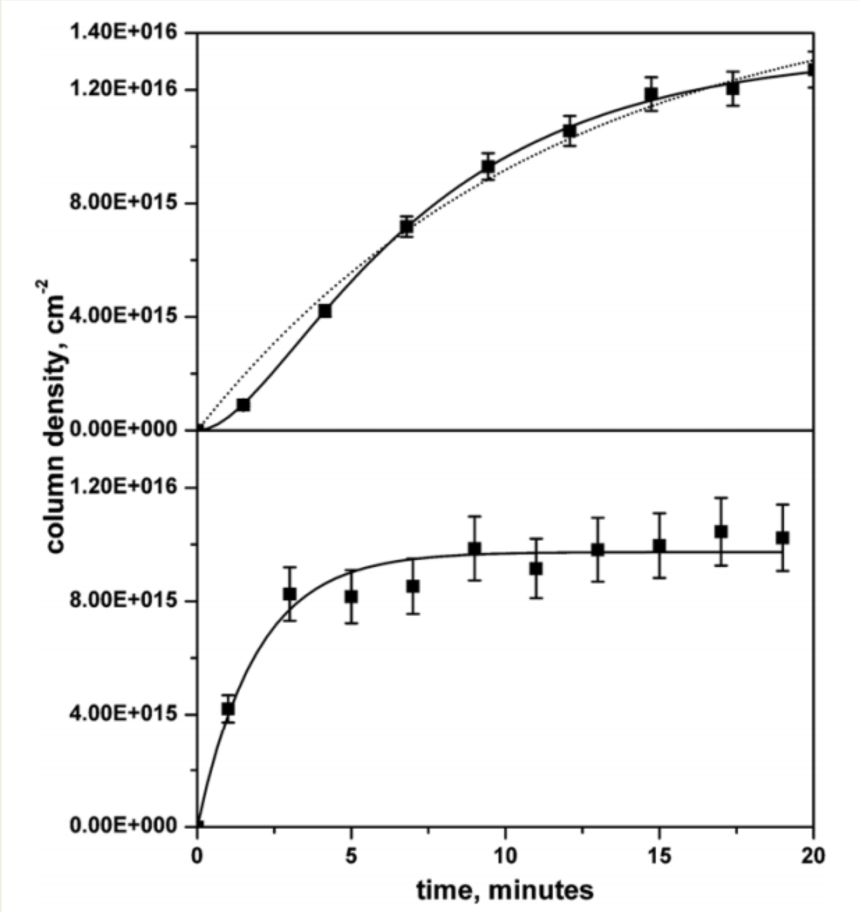
- 2 steps/1 step?

2 steps rate equation:

- $[CN^-] = \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right)[A]_o$

1 step rate equation:

- $[CN^-] = \left(1 + e^{-kt}\right)[A]_o$

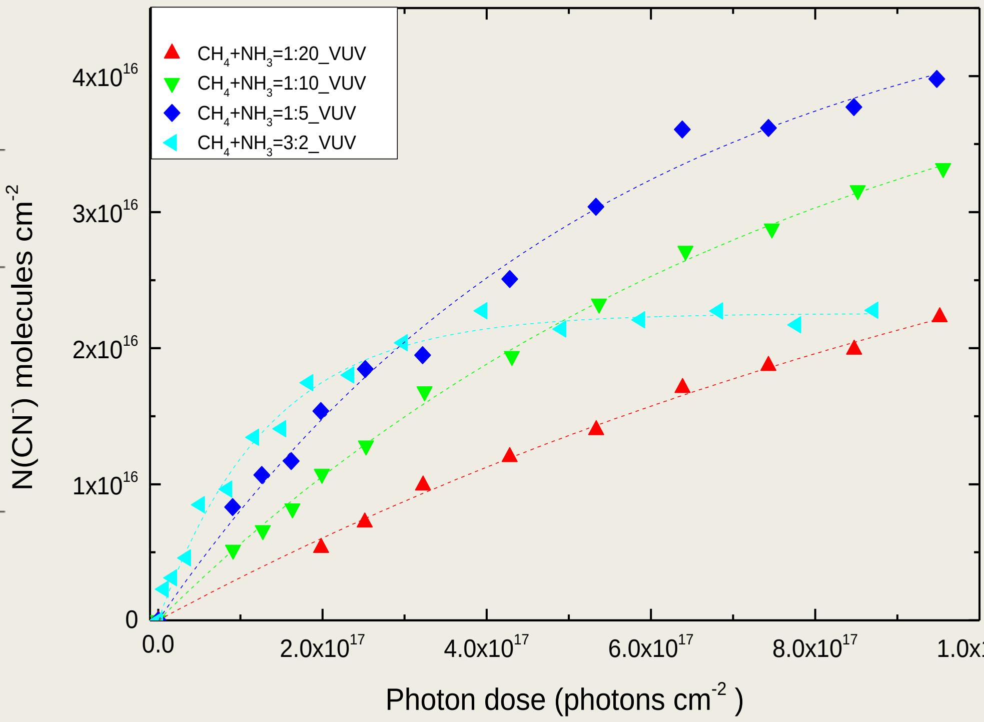


Quoted from Kim and Kaiser (2011)

1. Production of CN^-

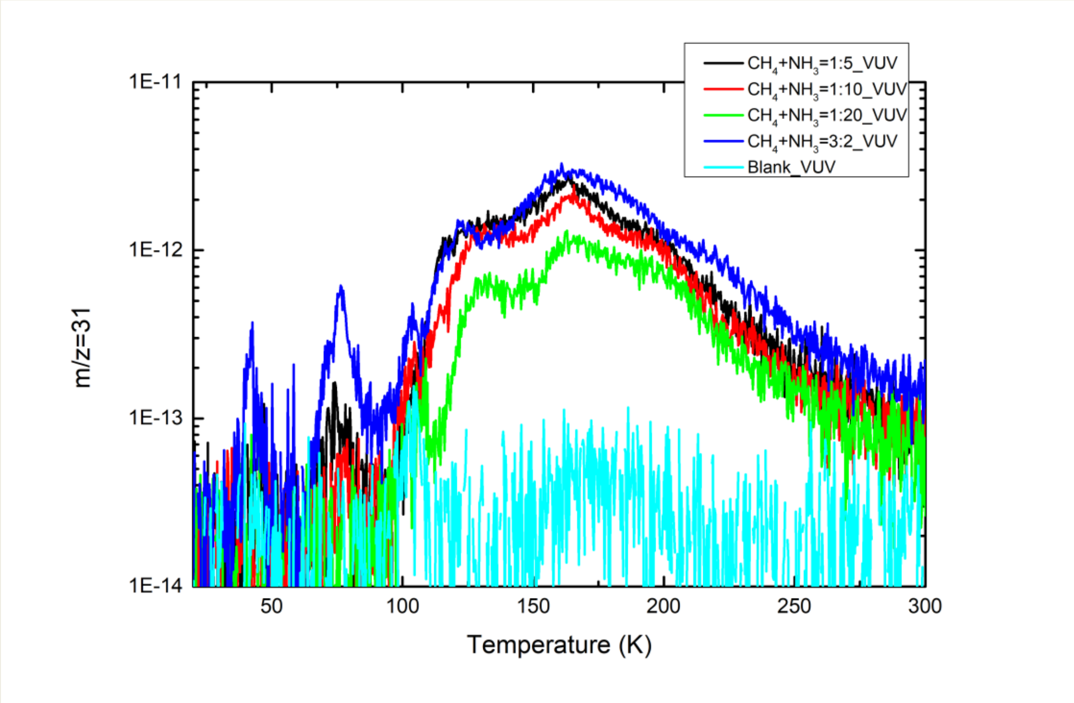
- 2 steps/1 step?

light source	Ratio of CH_4+NH_3	A ($x10^{16}$ molecules cm^{-2})	k ($x10^{-18}$ $photon^{-1}$)
MDHL	1:5	4.61±0.18	1.93±0.19
	1:10	4.51±0.18	1.33±0.13
	1:20	4.75±0.40	0.70±0.09
	3:2	2.24±0.03	8.21±0.70



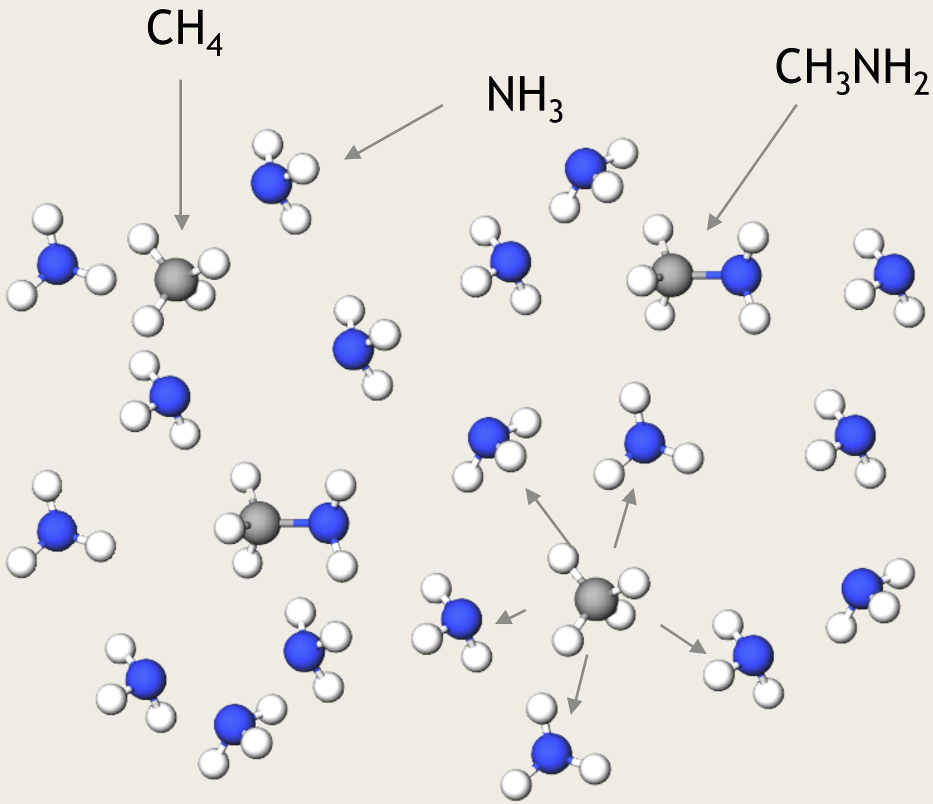
1. Production of CN^-

Methylamine (CH_3NH_2) with m/z=31 is detected by QMS after isothermal VUV irradiation during warm-up which is the intermediate of the CN^-



2. The scenario for NH_3 dominating ice mixtures

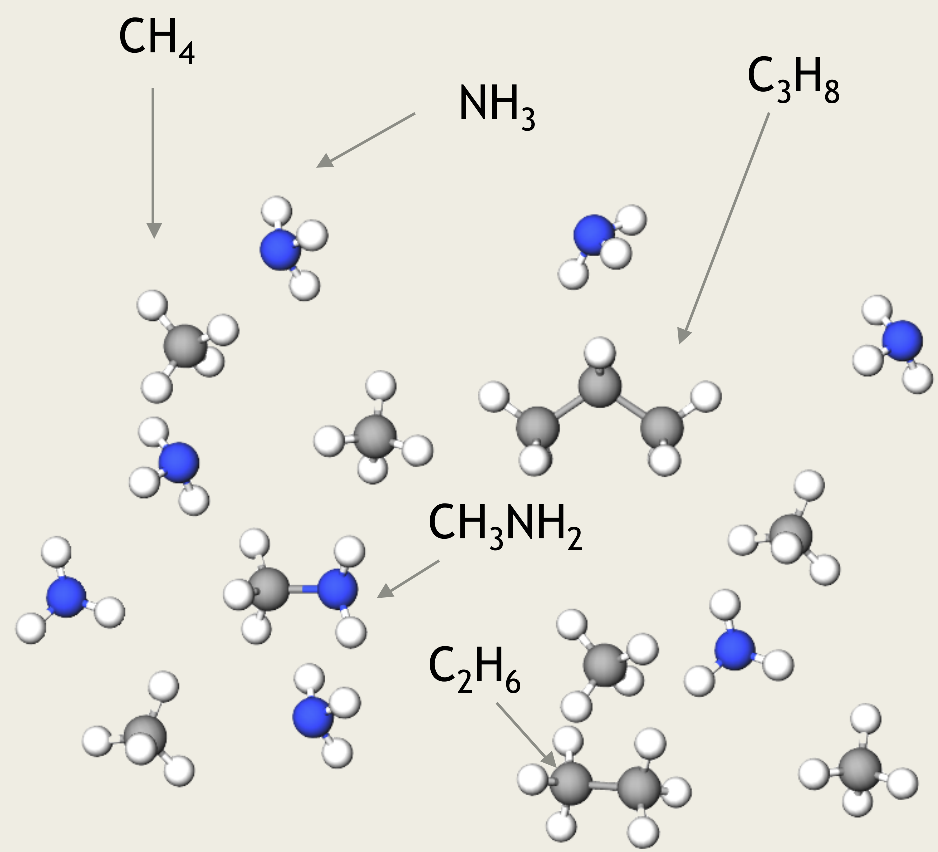
- Once CH_4 becomes CH_3 radical, it can easily forms methylamine and hence become CN^-.



A diagram of CH_4:NH_3 = 1:5

2. The scenario for CH_4 dominating ice mixtures

- CH_2NH_3 (formed by CH_3 + NH_2) has a competing relationship with C_2H_6 (formed by 2 CH_3) and C_3H_8 (formed by CH_2 + C_2H_6 or C_2H_4 + CH_4)
- Once CH_4 becomes CH_3 radical, it reacts with either NH_2 or CH_3 radicals, forming CH_3NH_2 or C_2H_6 respectively

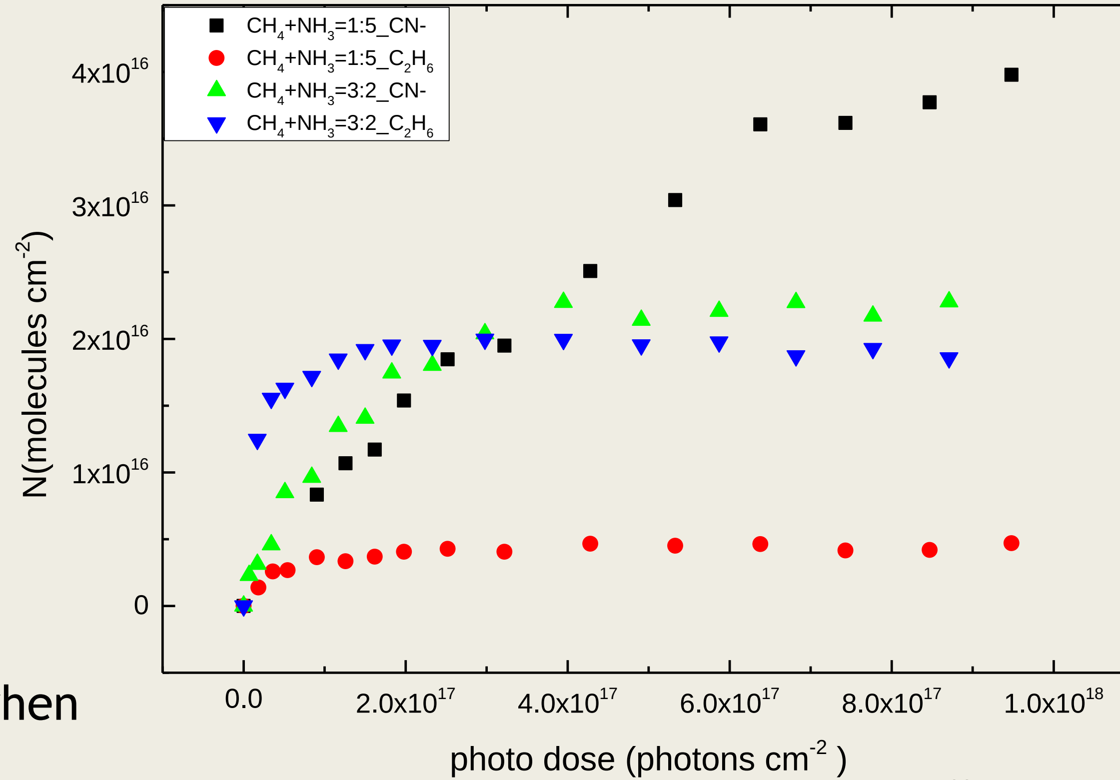


A diagram of CH_4+NH_3 = 3:2

2. The relations between CN^- and C_2H_6 during VUV irradiations

CH_4:NH_3	C_2H_6 (ML)	CN^- (ML)
3:2 (CH_4 dominant)	19.1	23
1:5 (NH_3 dominant)	4.3	49

Concentration of CN^- is not proportional to initial CH_4 when CH_4 is in excess.



3. Efficiency of EUV (40.1 eV) and VUV (9.27 eV)

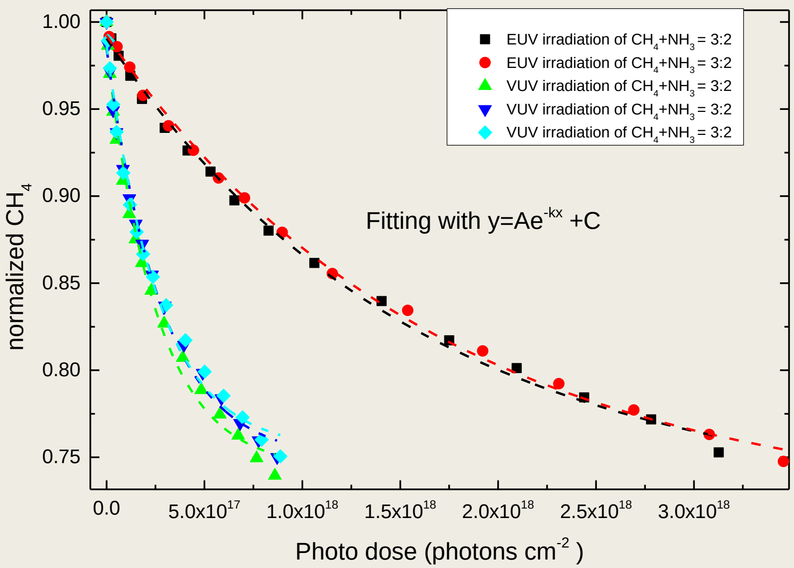
Radicals \ species	CH_4	NH_3
- 1 H	4.55 eV	4.67 eV
-2 H	4.78 eV	4.38 eV
-3 H	9.19 eV	7.63 eV

(quoted from Kundu et al. (2017))

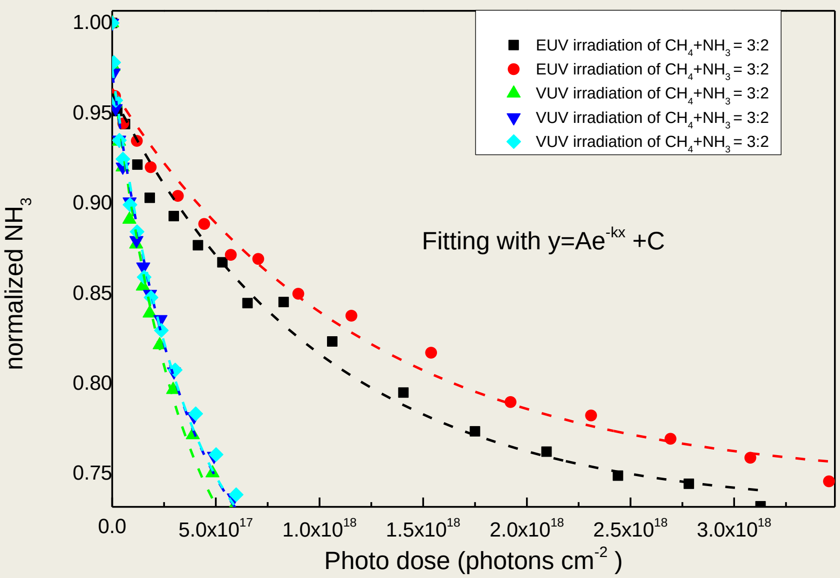
3. CN^- formation efficiency of EUV (40.1 eV) and VUV (9.27 eV)

- Fitting with $y = Ae^{-kx} + C$ (pseudo first order kinetics)

CH_4

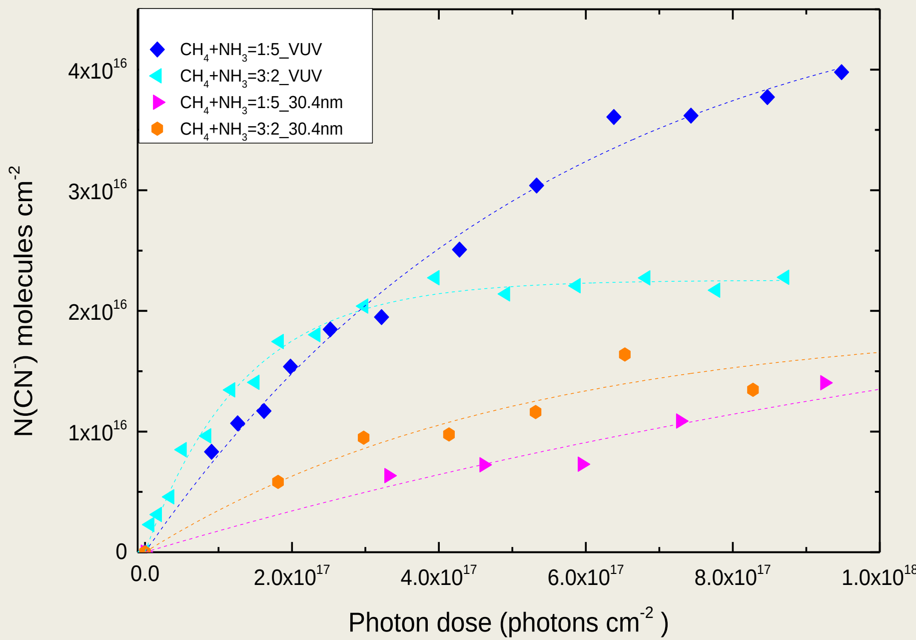


NH_3



3. CN^- formation efficiency of EUV (40.1 eV) and VUV (9.27 eV)

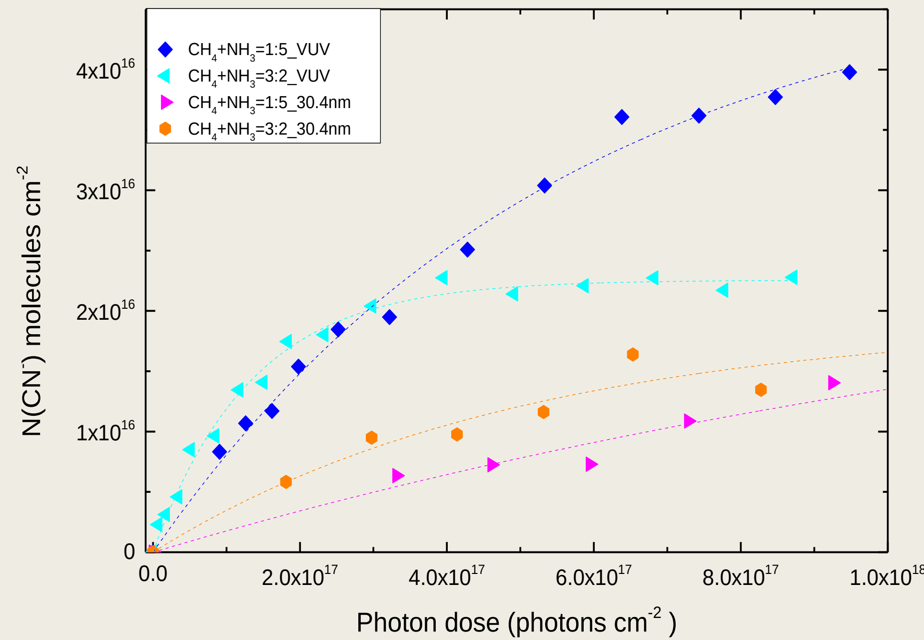
k (photons $^{-1}$)	CH_4(x 10^{-18})	NH_3 (x10^{-18})
VUV (MDHL)	3.70±0.18	2.89±0.10
EUV (30.4nm)	0.61±0.03	0.91±0.11
Destruction cross-section ratio	6.06±0.07	3.18±0.12
k (photon $^{-1}$)	CH_4 to NH_3 3:2 (x 10^{-18})	CH_4 to NH_3 1:5 (x10^{-18})
VUV (MDHL)	8.21±0.70	1.93±0.19
EUV (30.4nm)	1.92±1.99	0.63±0.37
CN- production ratio	4.28	3.06



Astrophysical implications

Astrophysical implications

- Ly α is the main energy source to produce CN^- on Charon
  - *3.06 to 4.28 times more efficient by VUV then EUV*
  - *VUV flux is 1 order of magnitude more intense than EUV irradiations (Grundy et al. 2016)*
    - *Ly a exposure: 1.9×10^9 eV cm^{-2} s^{-1}*
    - *EUV exposure: 8.7×10^7 eV cm^{-2} s^{-1}*



Understand CN- formation after winter on surface of Charon

Surface composition after 1 Pluto winter:

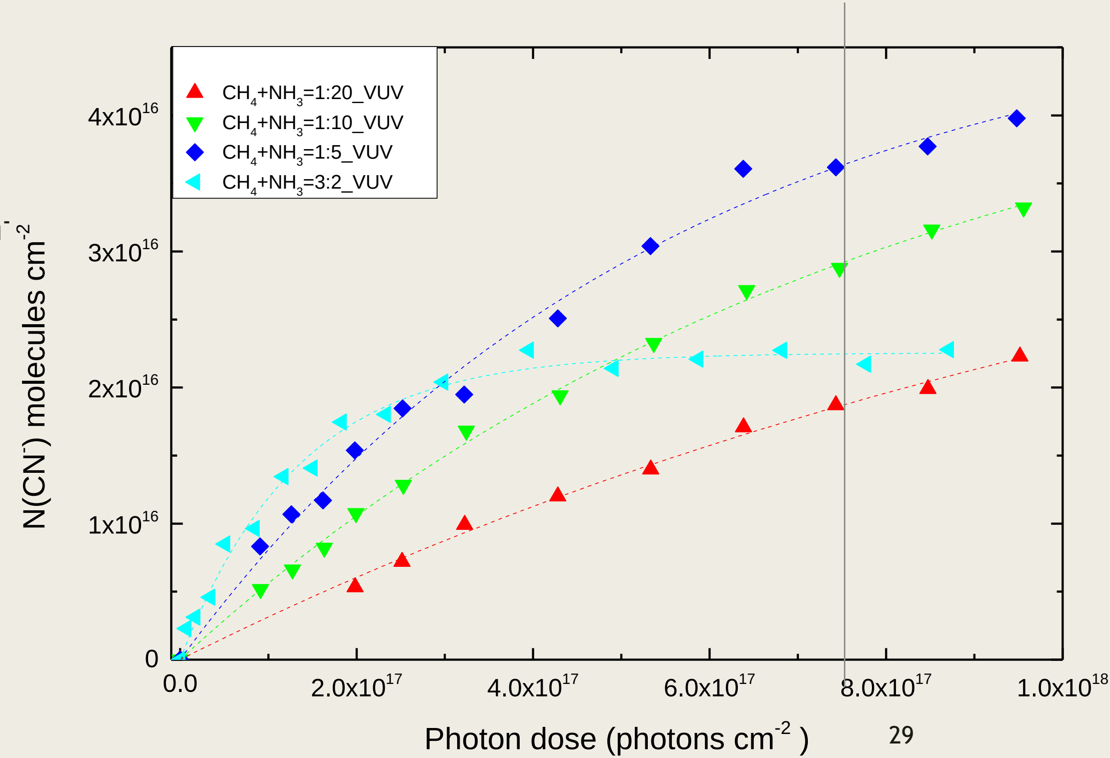
- Ly α exposure: 1.9 x 10^9 eV cm^{-2} s^{-1} (Grundy et al. 2016)

= photon dose 7.64x 10^{17} photons cm^{-2}

- CH_4 deposition rate: 2-6 x 10^7 cm^{-2} s^{-1} (Hoey et al. 2017

= 82-246 ML in 130 earth years

CH_4+NH_3	CN^- (ML)
1:5	36.6
1:10	29.5
1:20	18.9
3:2	22.5



Conclusion

- 1. Detection of methylamine implies that in
- 2. Concentration of CN^- is not proportional to initial CH_4 when CH_4 is in excess.
- 3. The reduced destruction cross-section of EUV 30.4nm irradiation is the main factor of slowing the rate of formations.
- 4. The maximum amount of CN^- after Charon winter is simulated experimentally.