VUV AND EUV IRRADIATION OF CH_4 + NH_3 ICE MIXTURES

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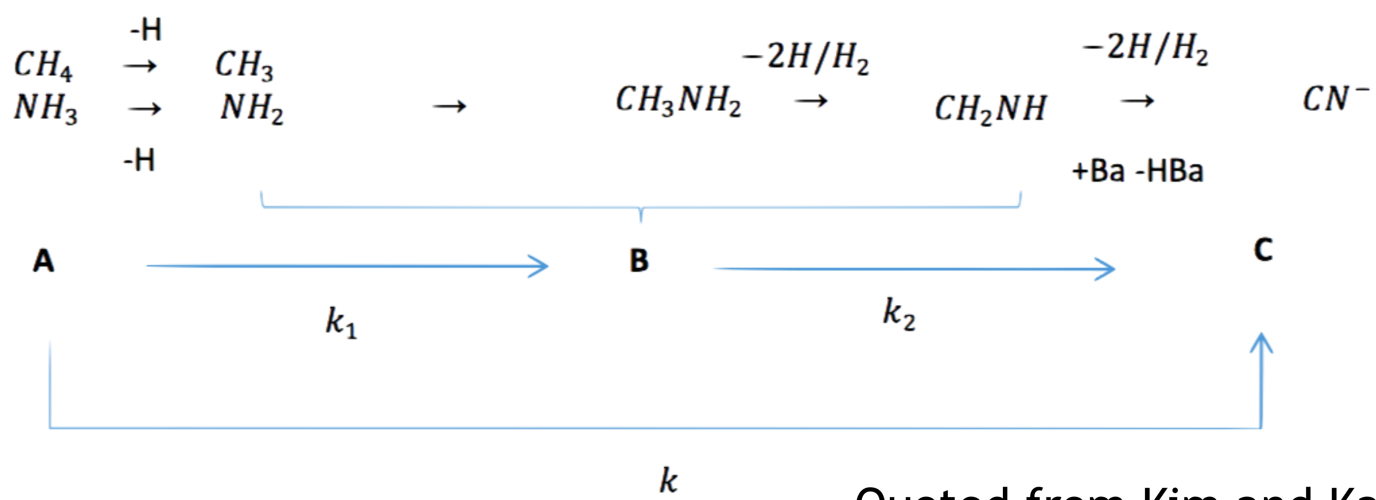
Introduction

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^-

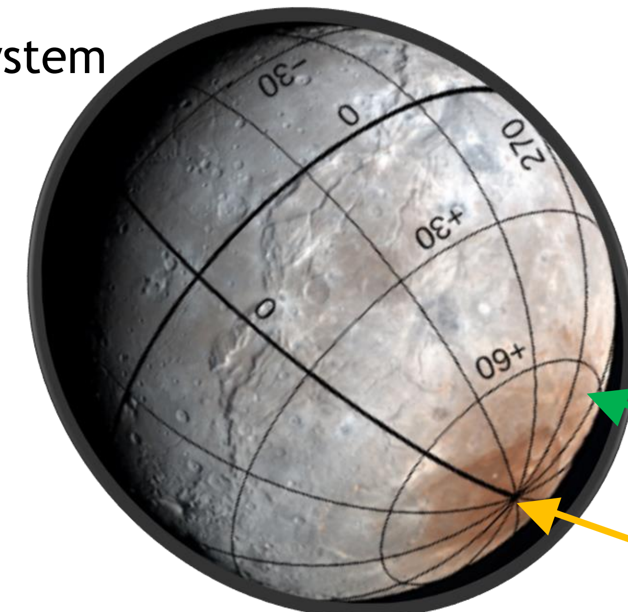
Attempts to detect CH_3NH_2:

- 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 EUV and VUV photons?

What astrophysical environments are we demonstrating?

Charon in Pluto system



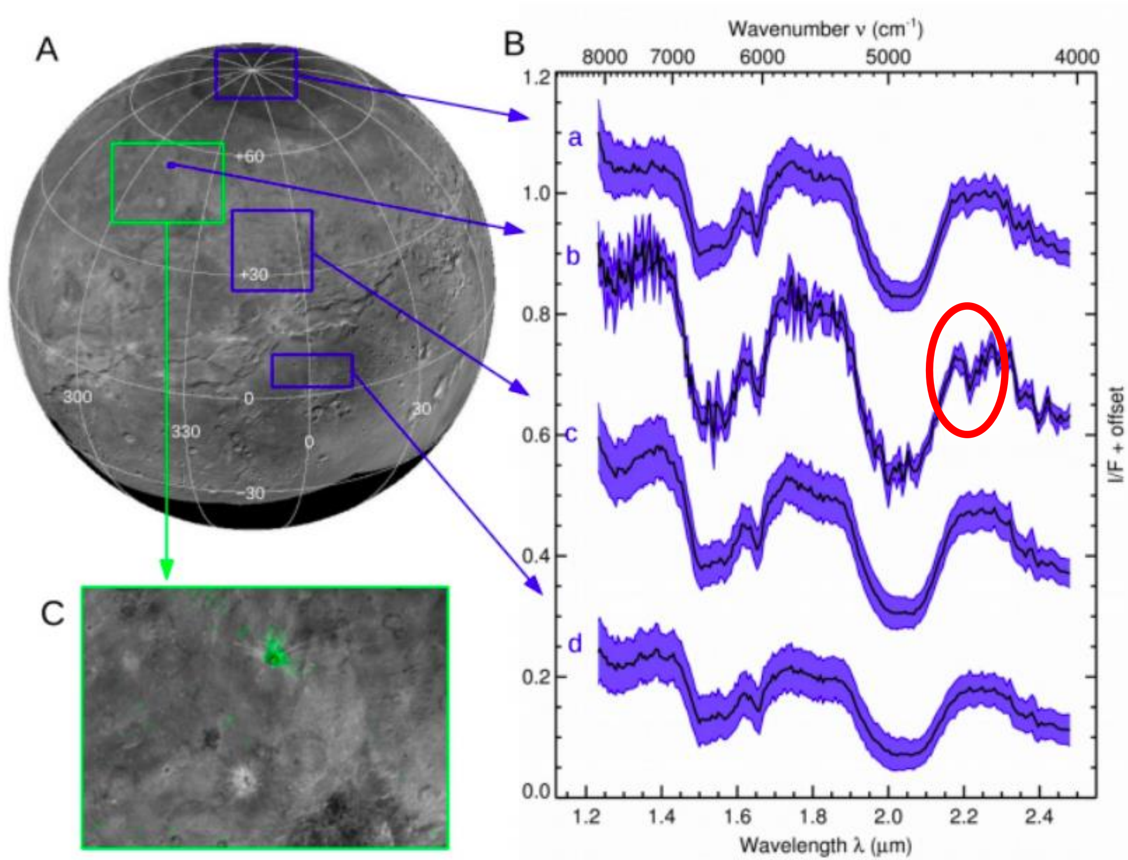
VUV and EUV irradiation

NH_3 + CH_4 $\longrightarrow$ CN^-

Quoted from Grundy et al. (2017)

Ammonia on Organa Crater

- *Ammonia hydrate (2.21μm) was detected all over the surfaces, especially on Organa Crater*

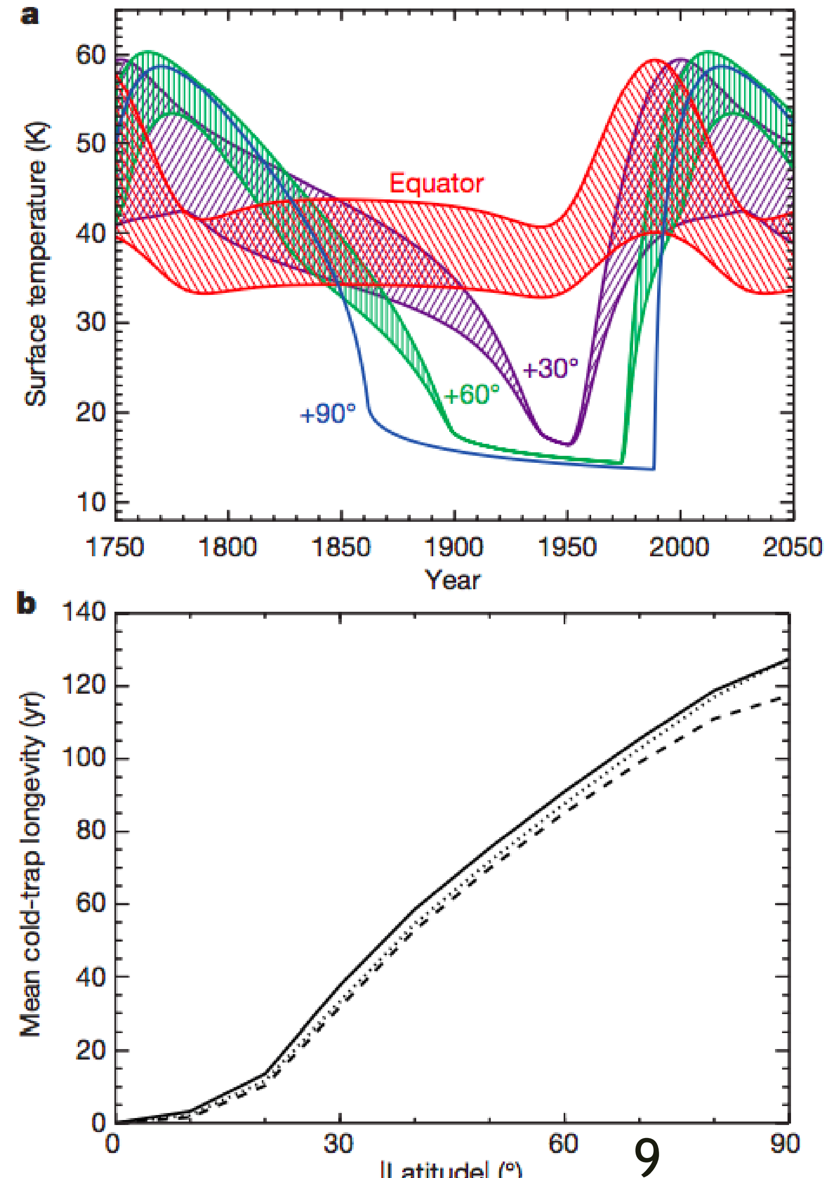


from Grundy et al. (2016)

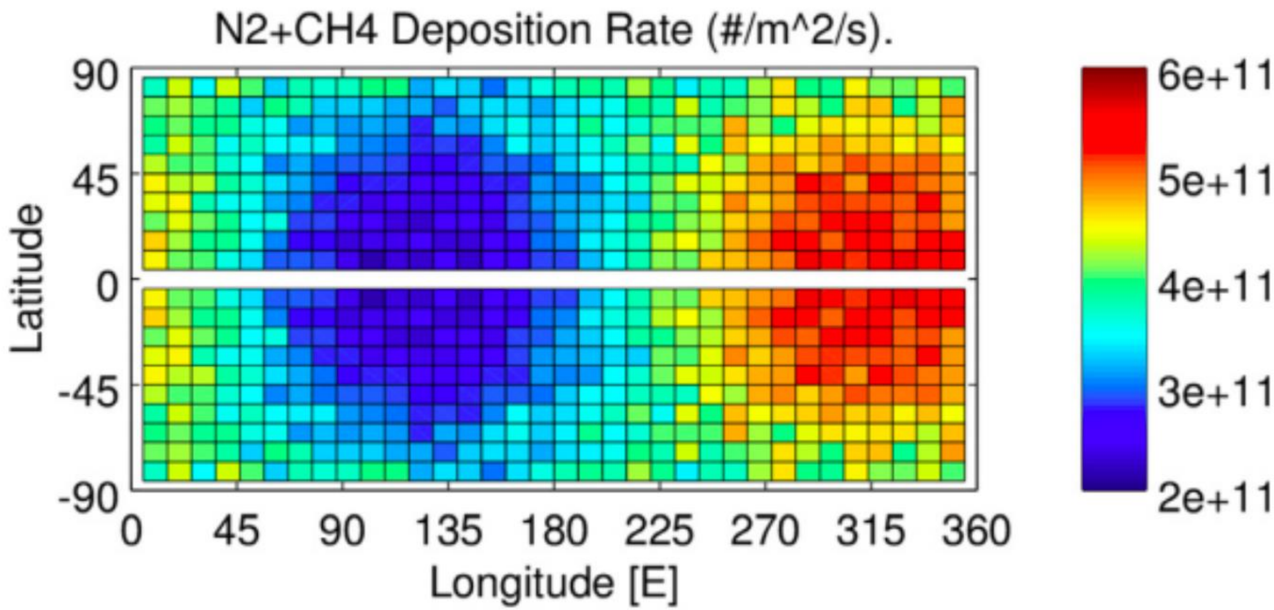
Surface temperatures at different latitudes

- 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)



Deposition rate of methane on Charon



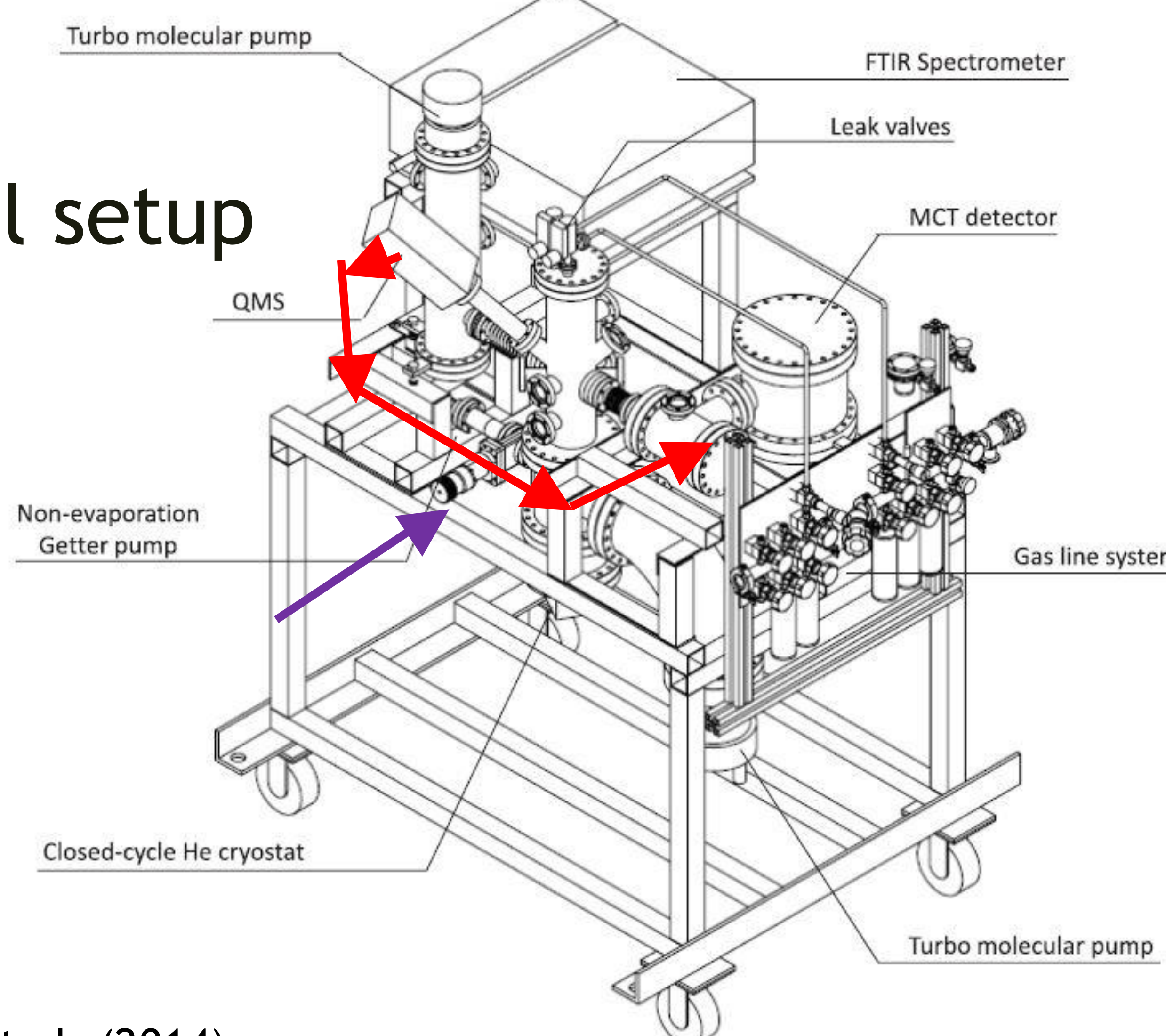
quoted from Hoey et al. (2017)

Motivation

- 1. To compare with previous studies
  - *Kim and Kaiser (CH_4+NH_3 3:1) and Kundy et al. (2017) (CH_4+NH_3 3:2)*
  - *We perform experiment of CH_4+NH_3 = 3:2*
  - *Confirm the 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 (1×10^{-10} torr) from 300 K (8×10^{-10} torr)

↓

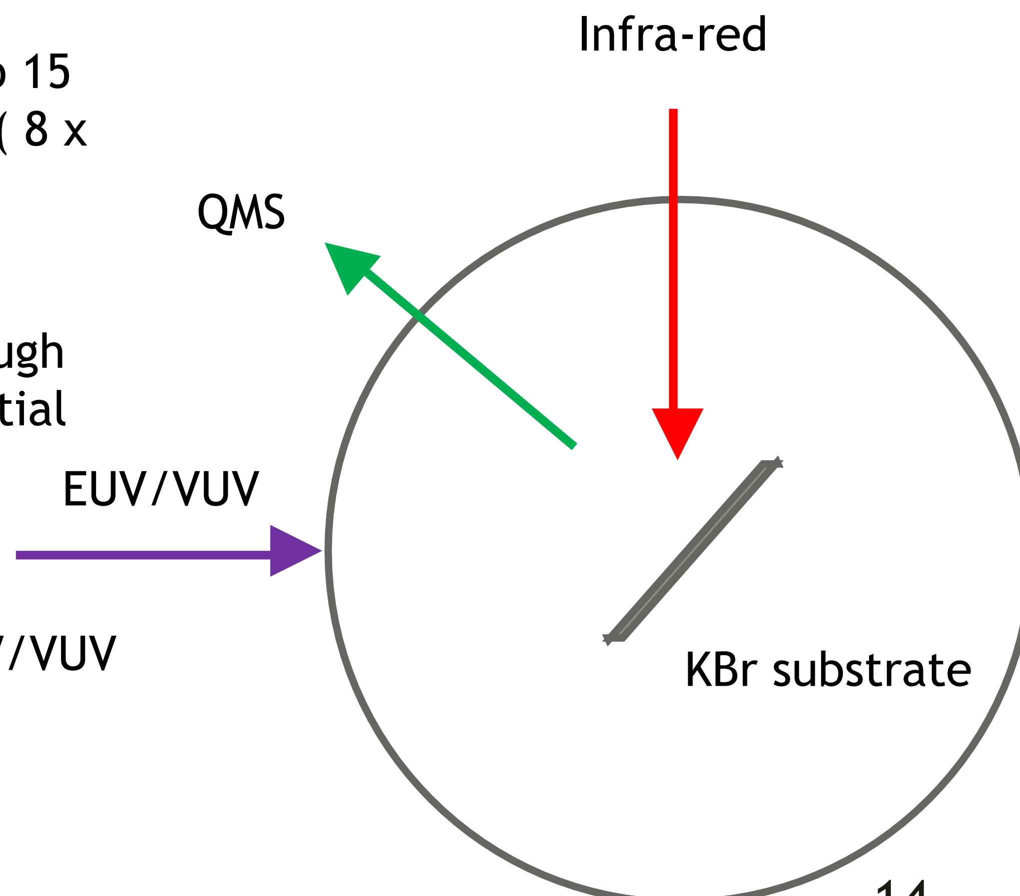
Deposit the ice mixtures through leak valve, with different partial pressures of CH_4 and NH_3

↓

Irradiate the samples by EUV/VUV

↓

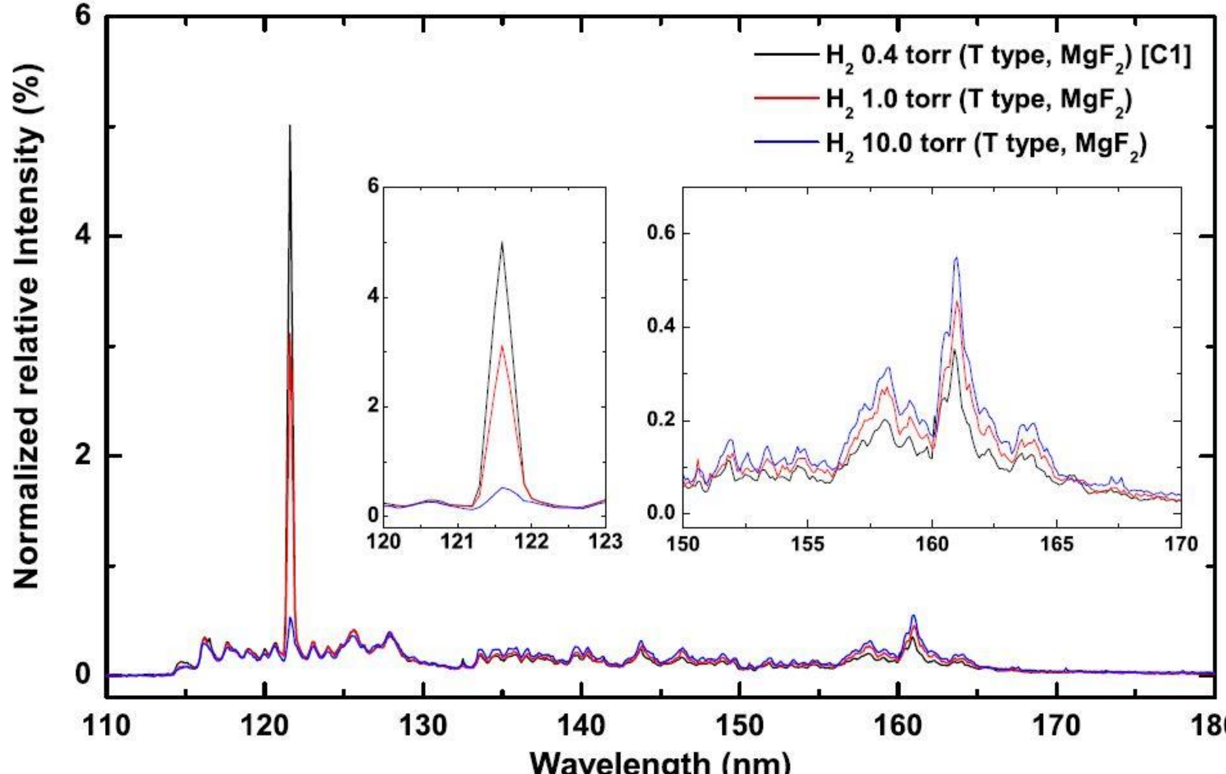
Warm-up with 1 K/min



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

- EUV is 40.8 eV (30.4nm)



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

Beer's Law

Transmittance $T(v)$ is defined by:

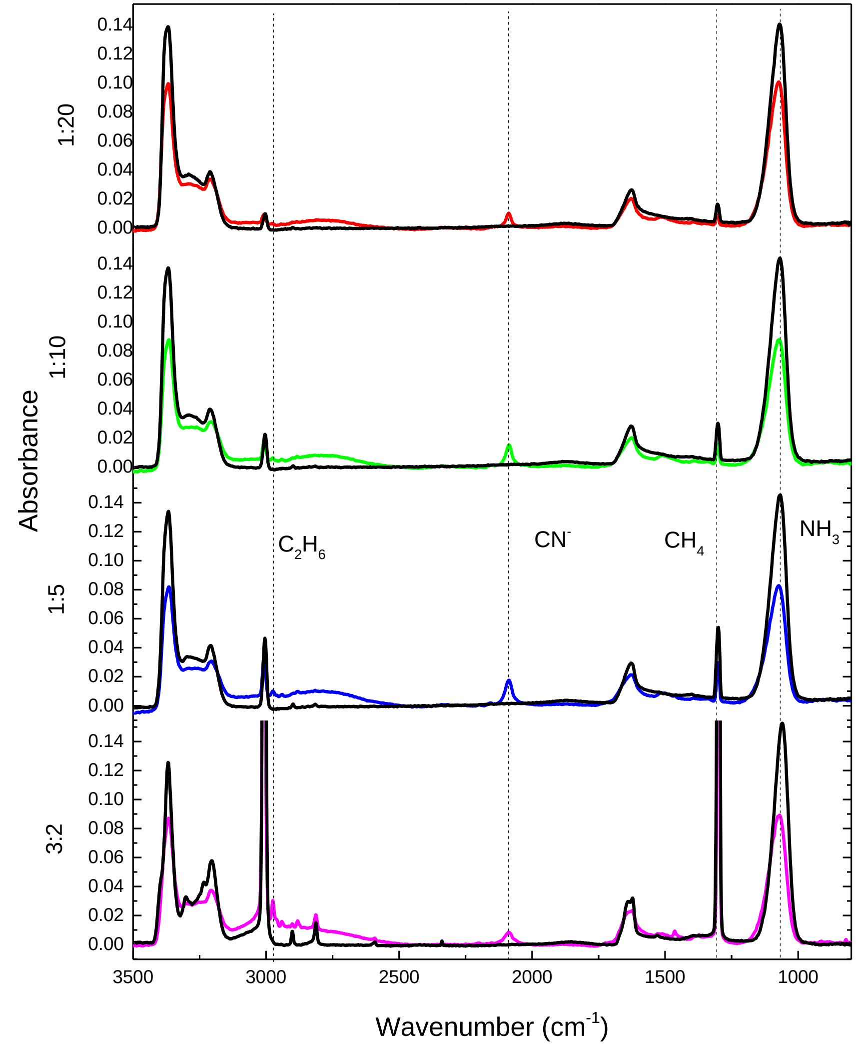
- $T(v) = \frac{I(v)}{I_o(v)}$

Absorbance $\tau(v)$ *is defined by:*

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

- $N = \frac{\int \tau(v)dv}{A(v)}$
  - *where N is column density (molecules cm^{-2}), $A(v)$ is the absorption strength (A-value) (cm molecule^{-1}) from literatures*



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

1. Production of CN^-

- 2 steps/1 step?

2 steps rate equation:

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

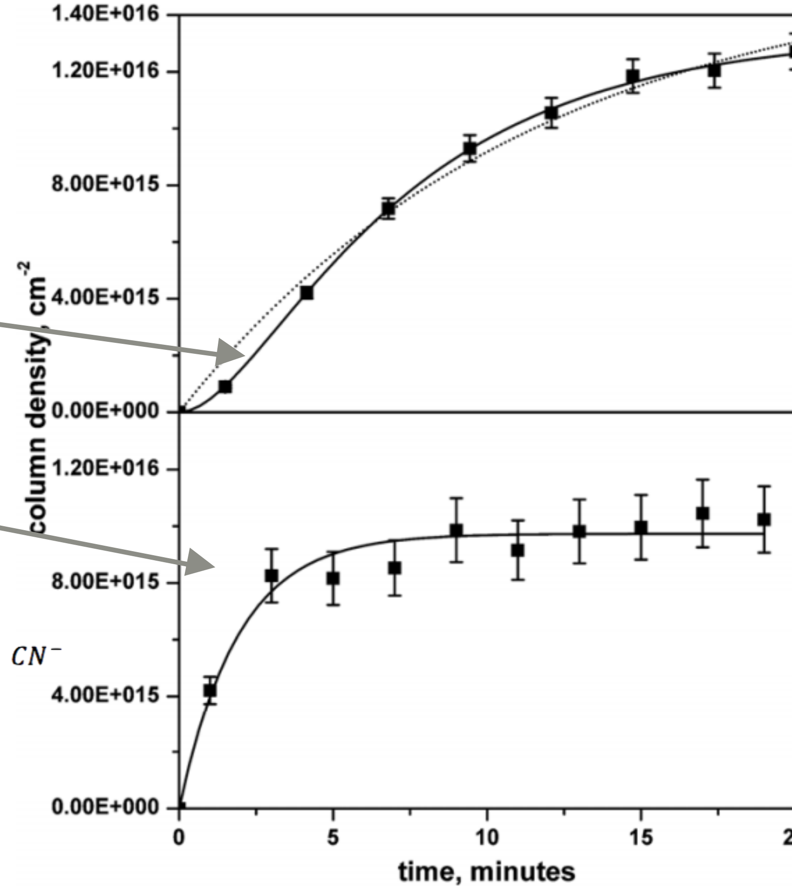
1 step rate equation:

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

$$\begin{array}{ccccccccc} CH_4 & \xrightarrow{-H} & CH_3 & & & & & & \\ NH_3 & \xrightarrow[-H]{} & NH_2 & \rightarrow & CH_3NH_2 & \xrightarrow{-2H/H_2} & CH_2NH & \xrightarrow[+Ba\ -HBa]{-2H/H_2} & CN^- \end{array}$$

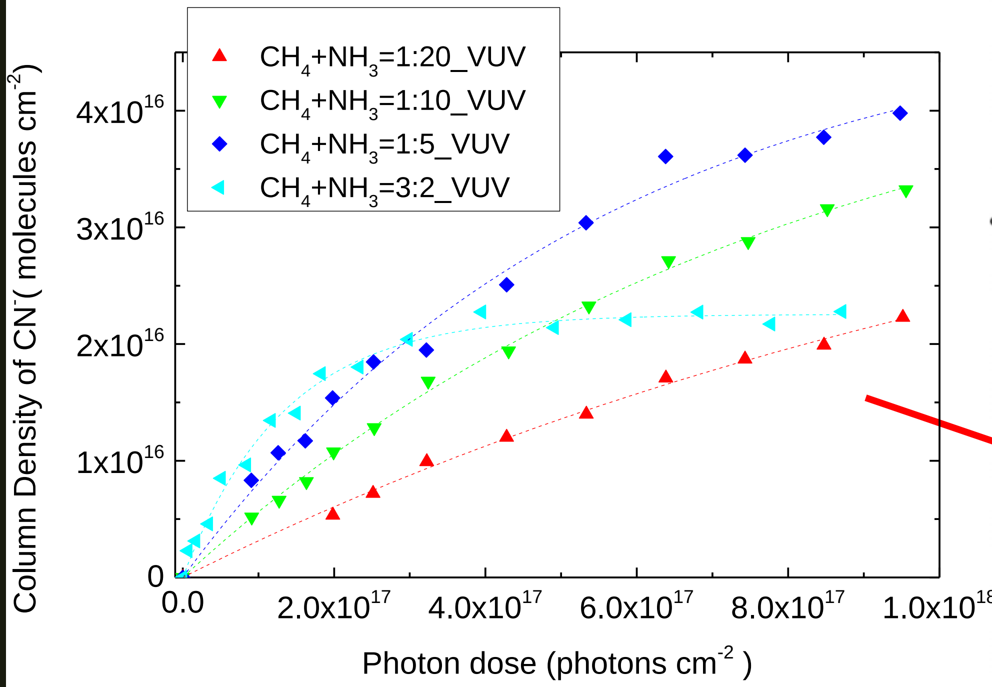
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

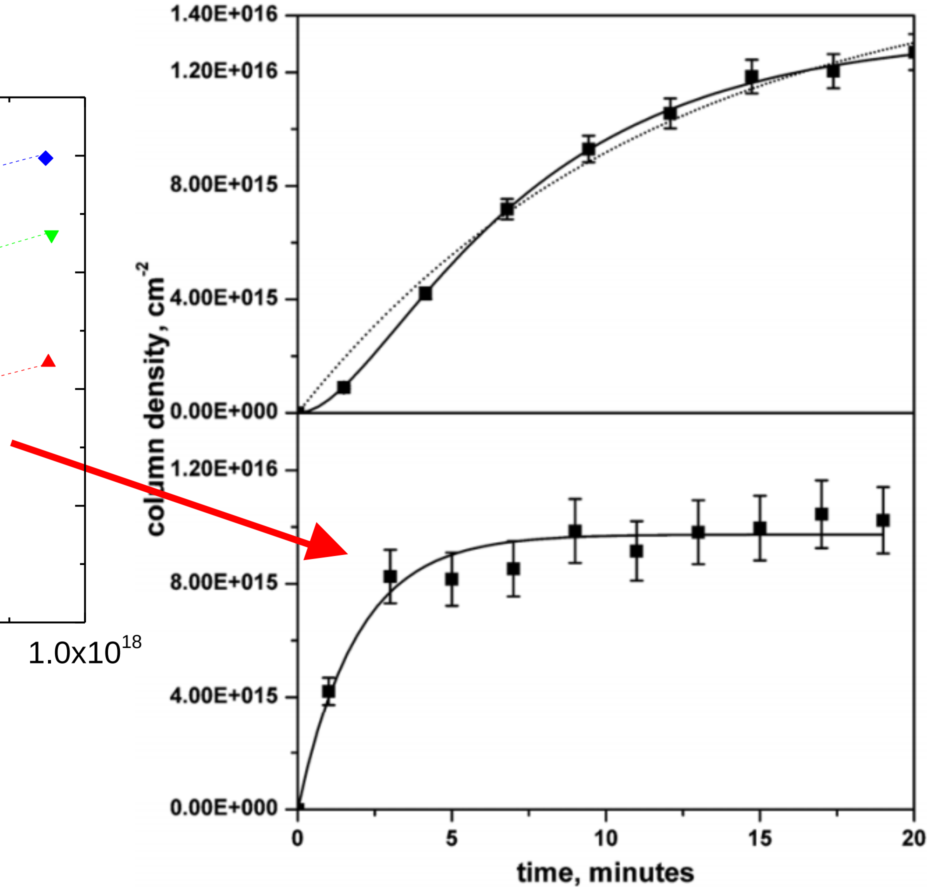
$$A \xrightarrow{k} C$$



Quoted from Kim and Kaiser (2011)

1. Production of CN^-





1. Production of CN⁻

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1 step rate equation:

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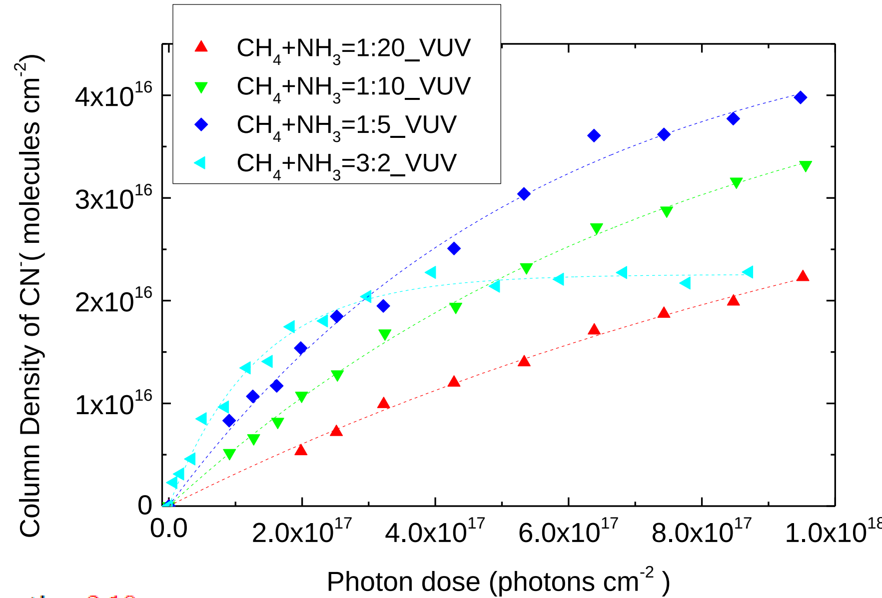


Table 3.5: The fitting results of CN^- by equation 2.10

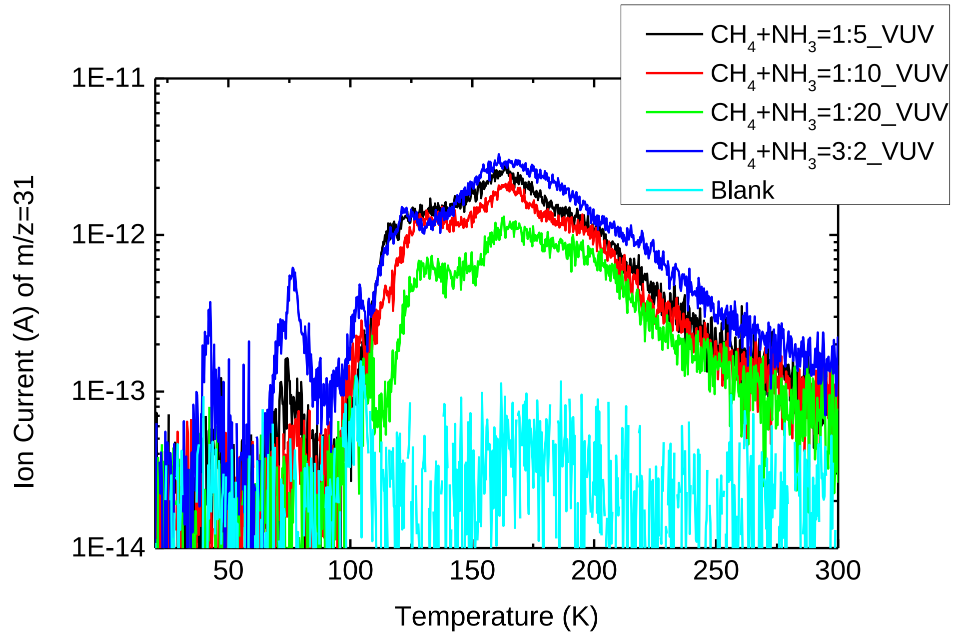
Ratio	A ($x10^{16}$ molecules cm^{-2})	k_1 ($x10^{-18}$ $photon^{-1}$)	k_2 ($photon^{-1}$)
VUV experiments with CH_4+NH_3 ice mixtures			
1:20	4.75 ± 0.40	0.70 ± 0.09	>1
1:10	4.51 ± 0.18	1.33 ± 0.13	>1
1:5	4.61 ± 0.18	1.93 ± 0.19	>1
3:2	2.24 ± 0.03	8.21 ± 0.70	>1

Ratio	A($x10^{16}$ molecules cm^{-2})	k_1 ($\times 10^{-3}$ s^{-1})	k_2 ($\times 10^{-3}$ s^{-1})
Quotated from Kim and Kaiser[2]			
0.1 μA e^- with CH_4+NH_3 ice mixtures			
3:1	1.3 ± 0.0	2.7 ± 0.3	8.9 ± 1.6
1 μA e^- with C_nH_{2n+2} (n=1-6)+NH_3 ice mixtures			
2:5	1.0 ± 0.0	8.7 ± 1.3	»1

A represents the amount of CN^- we may obtain when irradiated the ice for infinitely long.

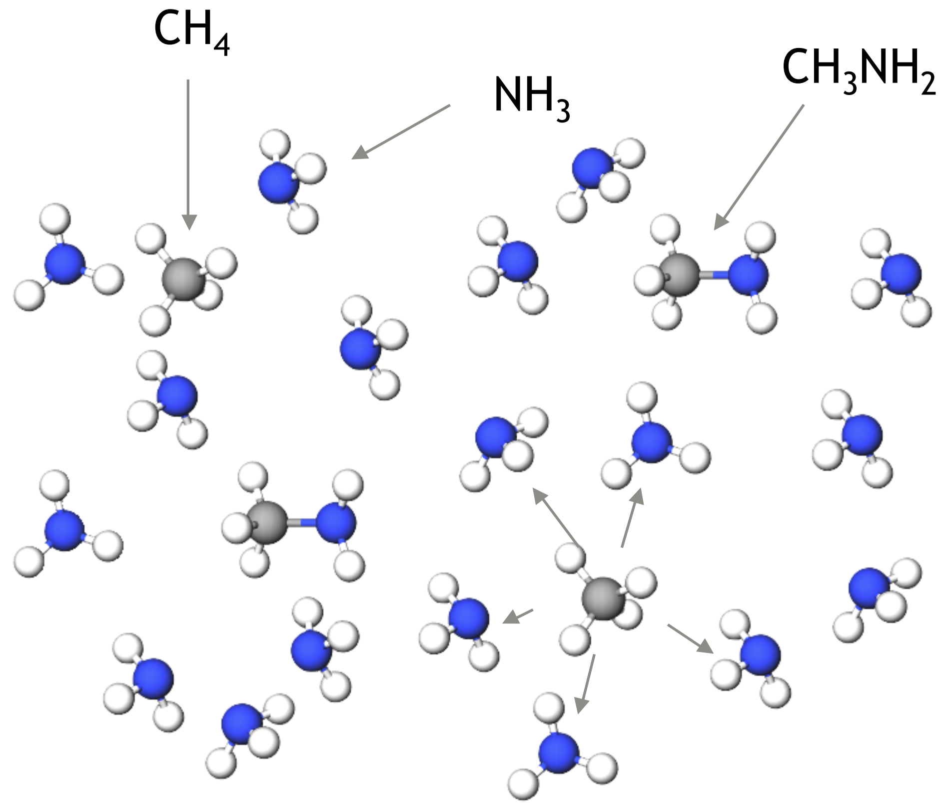
1. Production of CN^-

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

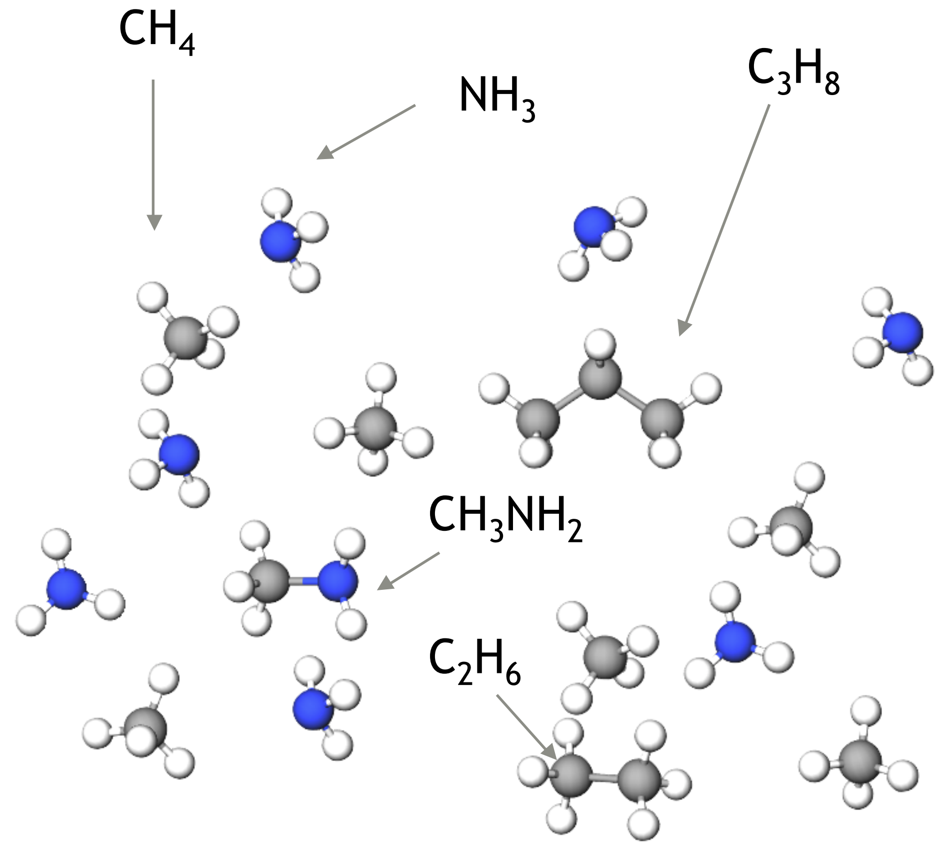
- Once CH_4 becomes CH_3 radical, it can easily forms methylamine and hence become CN^-.



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

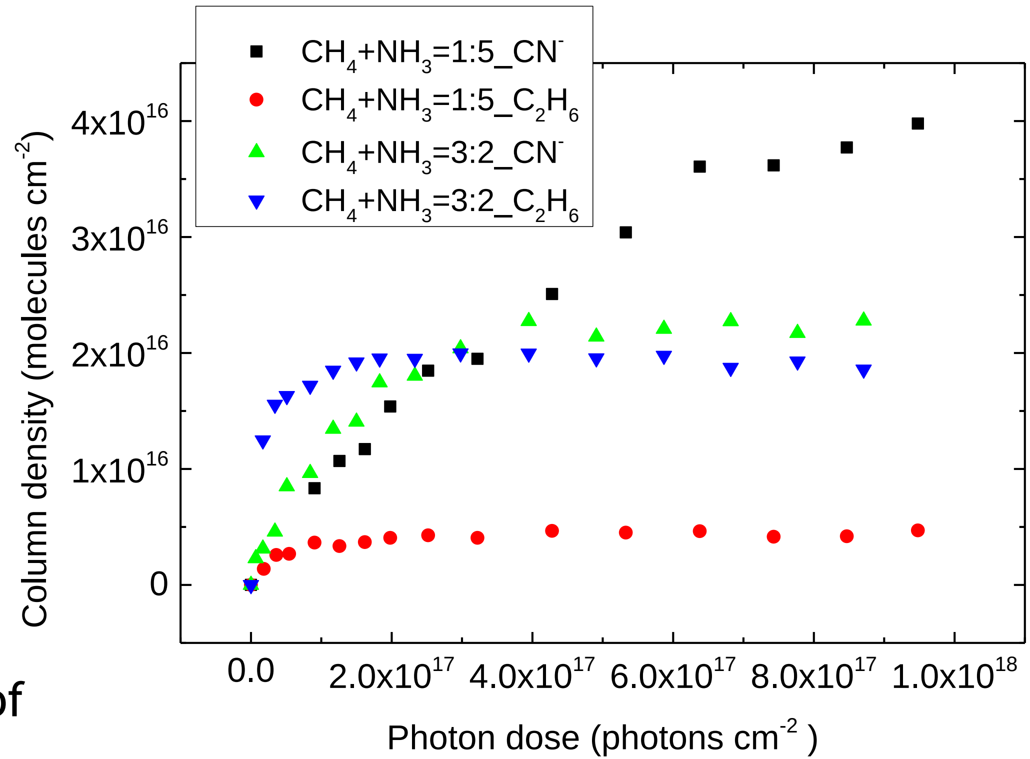


A diagram of CH_4+NH_3 = 3:2

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

CH_4:NH_3	C_2H_6 (ML)	CN^- (ML)	Ratio of CN^- to C_2H_6
3:2 (CH_4 dominant)	19.1	23	1.2
1:5 (NH_3 dominant)	4.3	49	11.3

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



3. Energy needed for forming radicals by EUV (40.1 eV) and VUV (9.27 eV)

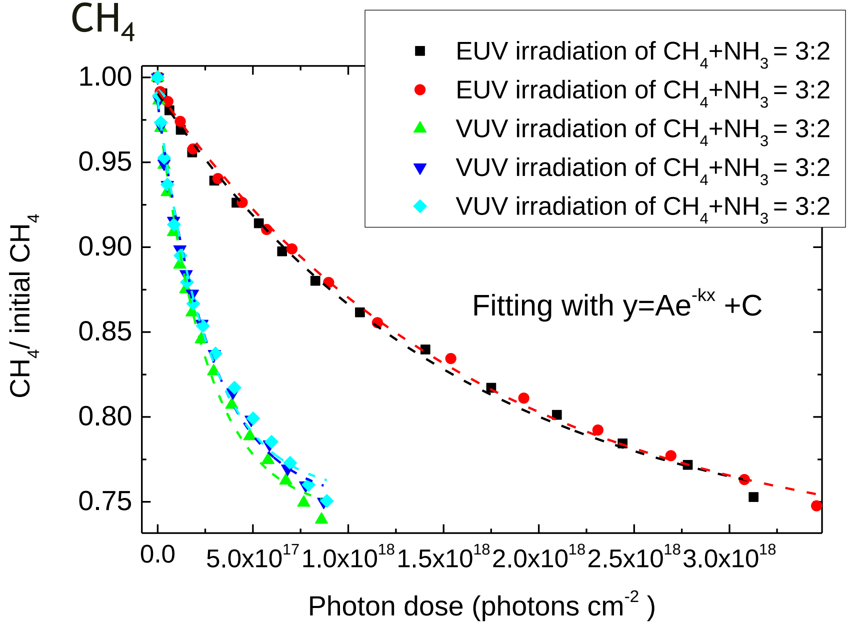
Radicals species	CH_4	NH_3
- 1 H	4.55 eV	4.67 eV
-2 H	4.78 eV	4.38 eV
-3 H	9.19 eV	7.63 eV

(quoted from Kundu et al. (2017))

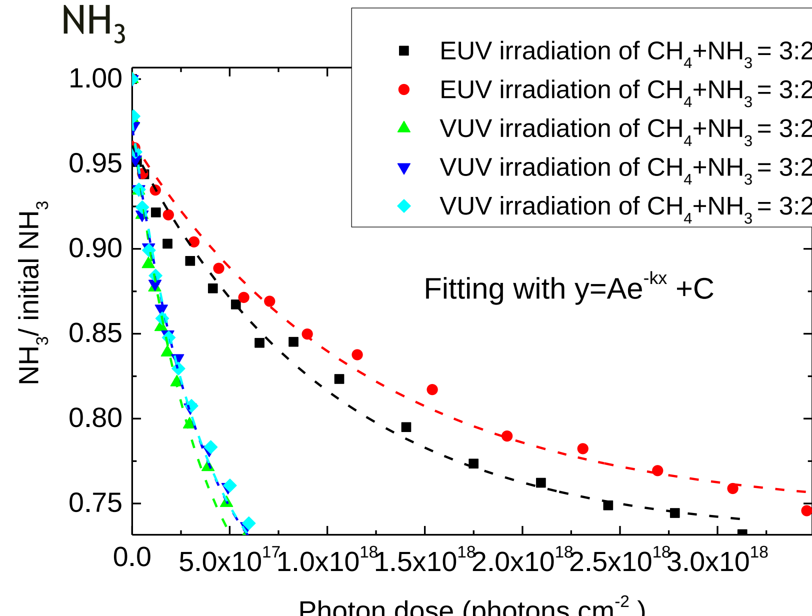
3. Destruction cross-section of EUV (40.1 eV) and VUV (9.27 eV)

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

CH_4

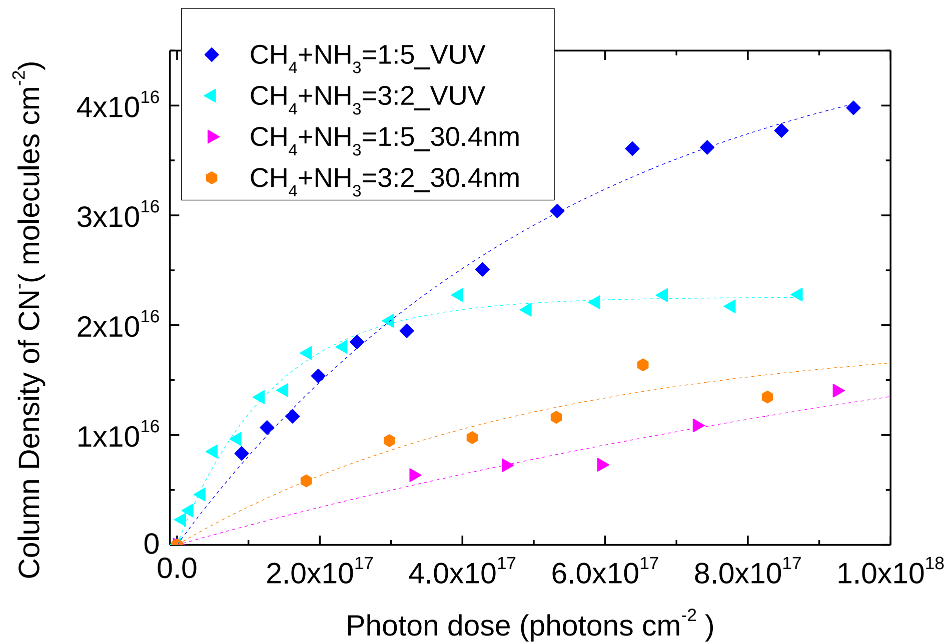


NH_3



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

k ($photons^{-1}cm^2$)	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 ($photon^{-1}cm^2$)	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

Understand CN^- formation after winter on surface of Charon

Surface composition after 1 Pluto winter:

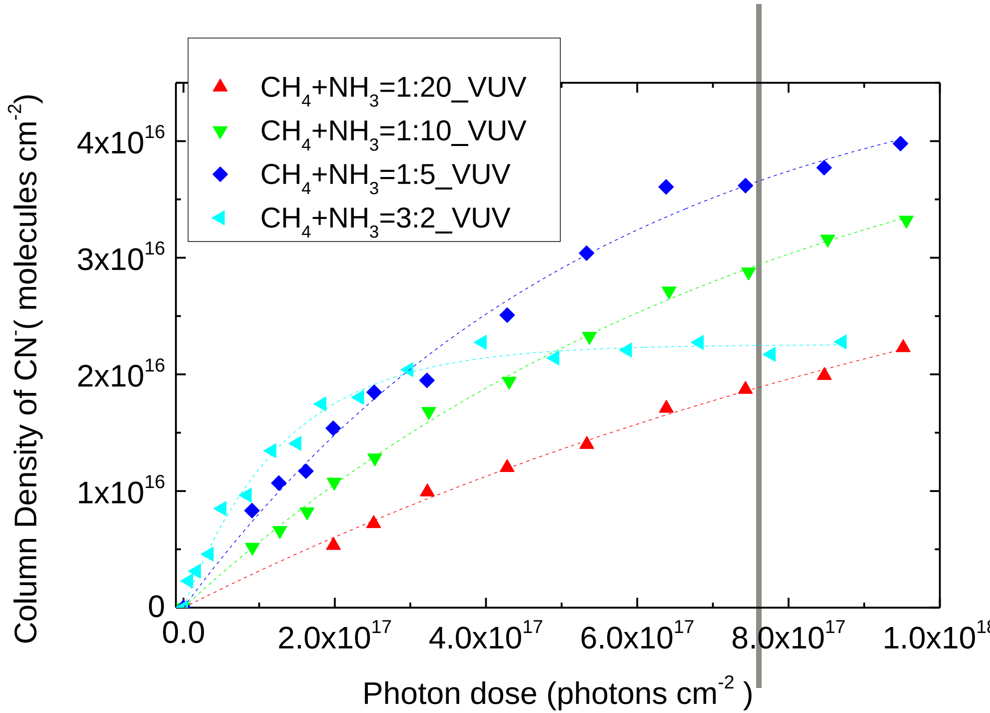
- Ly α exposure: 1.9 x 10^9 eV cm^{-2} s^{-1} (Grundy et al. 2016)

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

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

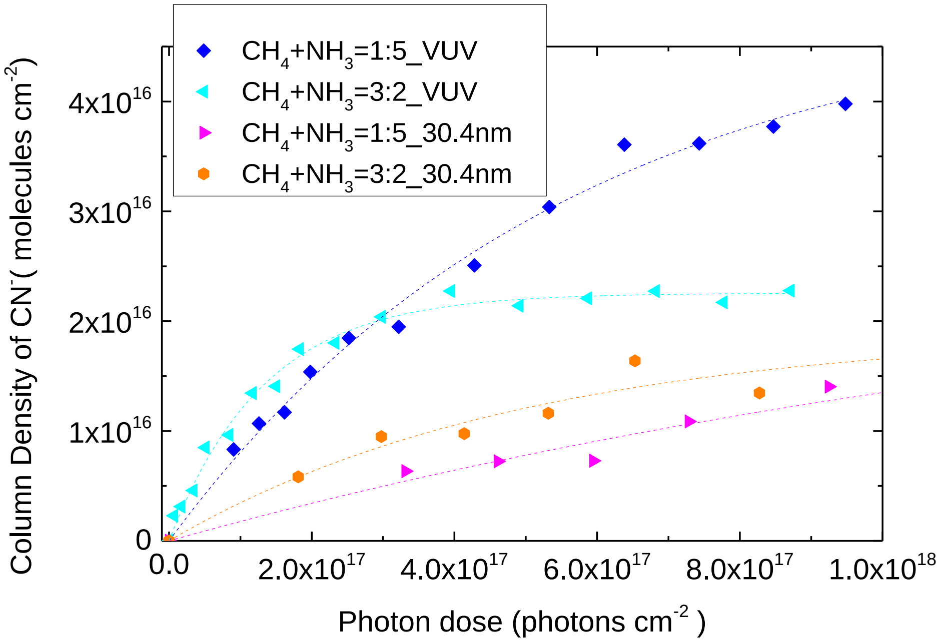
→ 82-246 ML in 130 earth years

CH_4+NH_3	CH_4 (ML)	CN^- (ML)
1:5	110	36.6
1:10	60	29.5
1:20	30	18.9
3:2	900	22.5



Astrophysical implications

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



Conclusion

- 1. Detection of methylamine implies that CN^- is formed via a 2 step mechanism.

- 2. Concentration of CN^- is not proportional to the initial amount of CH_4 when CH_4 is in excess.
  - *This implies that we have to experimentally simulate the amount of CN^- after Charon winter for further investigations.*

- 3. The reduced destruction cross-section of EUV 30.4nm irradiation is the main factor of slowing the rate of formations.
  - *This implies that Ly-a is the main energy source to produce CN^- on Charon.*

Q & A

Reason of changing from Sgr B2 to Charon

- Temperatures of Sgr B2 is not 15 K
- There exists 3 hot cores with very high temperatures
- Hence, we prefer to refer our study to Charon rather than Sgr B2.

Ammonia concentrations

- From a recent manuscript (Morea Dalle Ore et al. (2018))
  - *ammonia hydrate with band 2.21 µm is mainly presents at the northern parts of Charon, associated with crater positions.*

Production yield and production rates

- The yields should be correlated with initial limiting substances
- Fitting rates are the same