VUV AND EUV IRRADIATION OF CH$_4$ + NH$_3$ ICE MIXTURES

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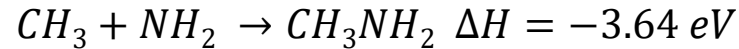
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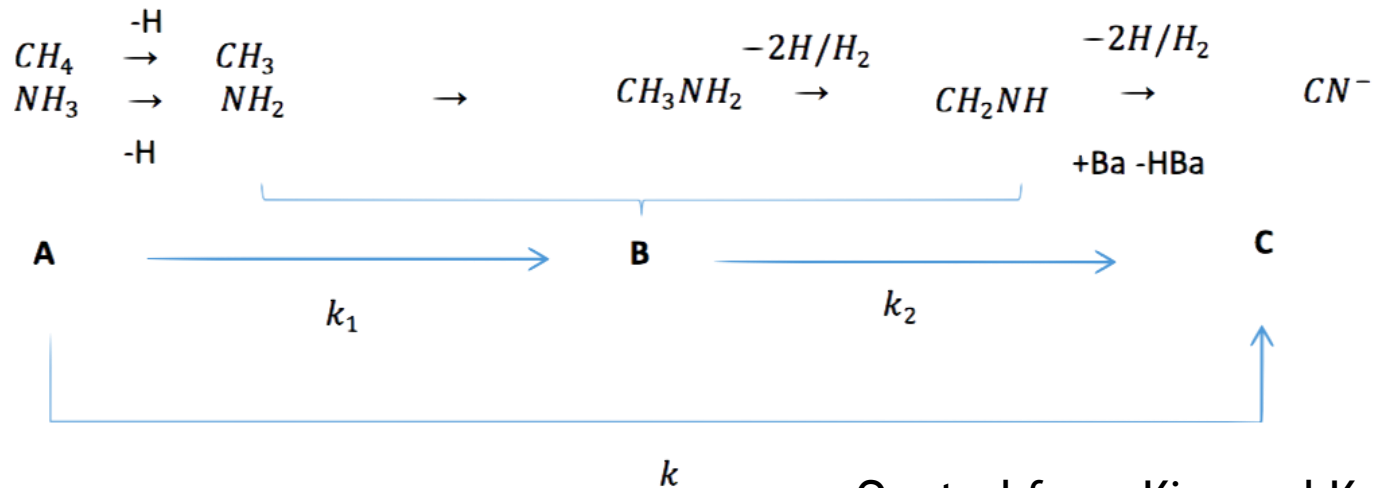 - *Understand CN$^-$ formation after winter on surface of Charon*

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)

$$
\begin{array}{lll}
& \text{-H} & \\
CH_4 & \rightarrow & CH_3 \\
NH_3 & \rightarrow & NH_2 \\
& \text{-H} &
\end{array}
\quad \rightarrow \quad
\begin{array}{l}
-2H/H_2 \\
CH_3NH_2 \quad \rightarrow \quad CH_2NH \\
\end{array}
\quad
\begin{array}{l}
-2H/H_2 \\
\rightarrow \quad CN^- \\
+Ba \ \text{-HBa}
\end{array}
$$

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

k

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?

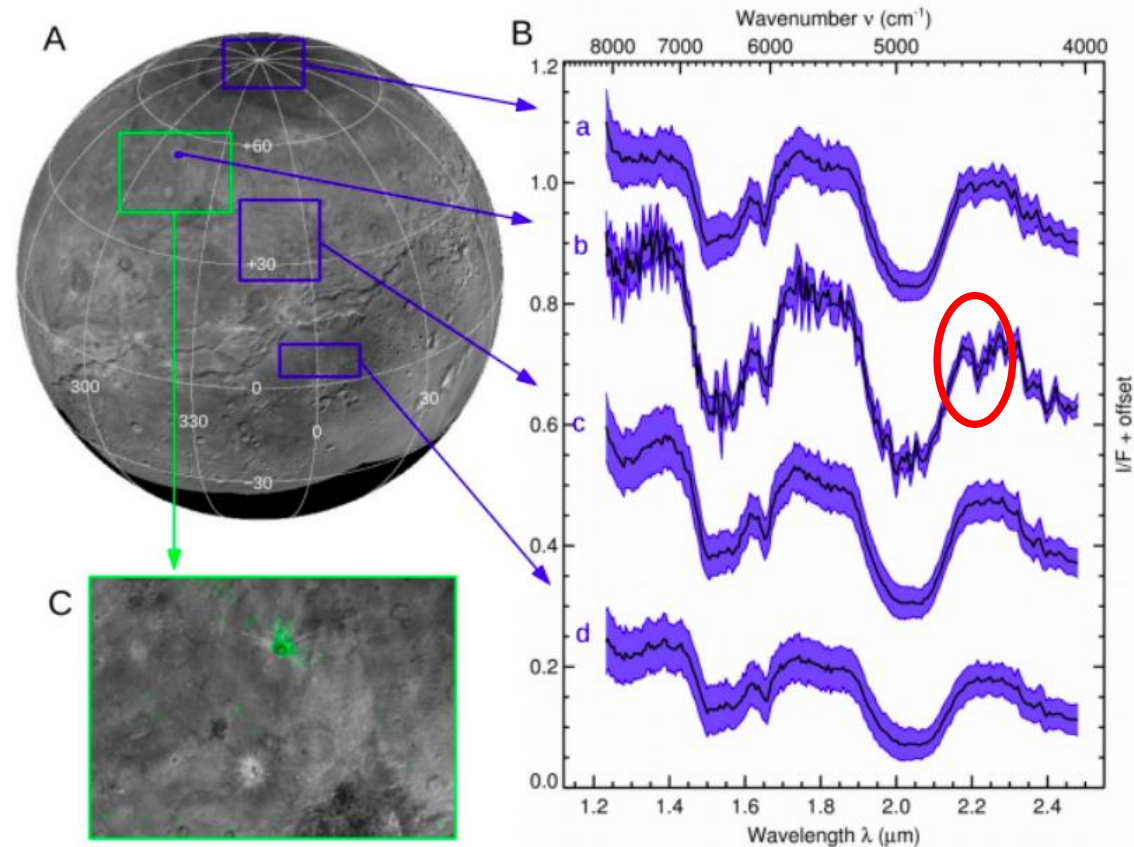# What astrophysical environments are we demonstrating?

Charon in Pluto system

VUV and EUV irradiation

NH_3
$+$ $\longrightarrow$ CN^-
CH_4
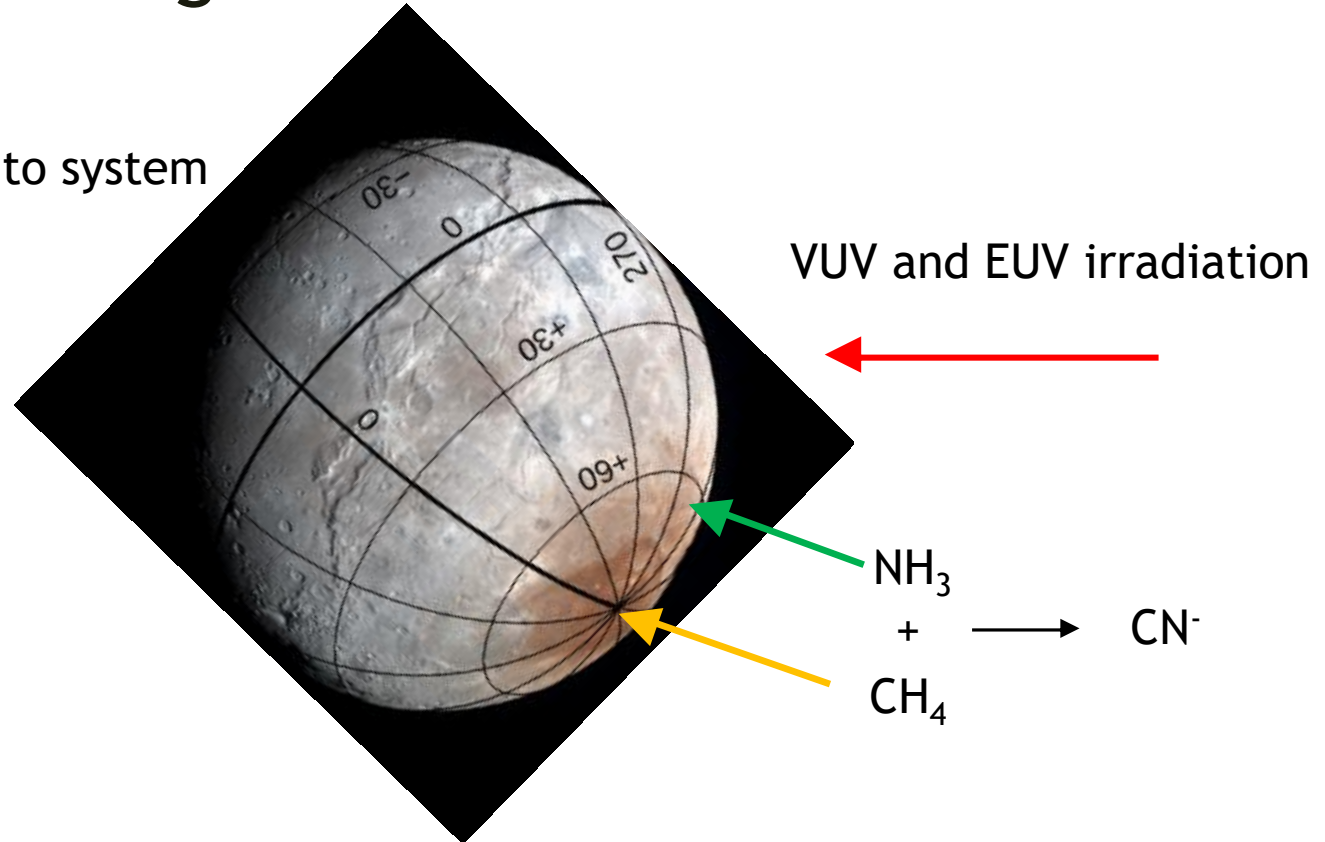
Ammonia on Organa Crater

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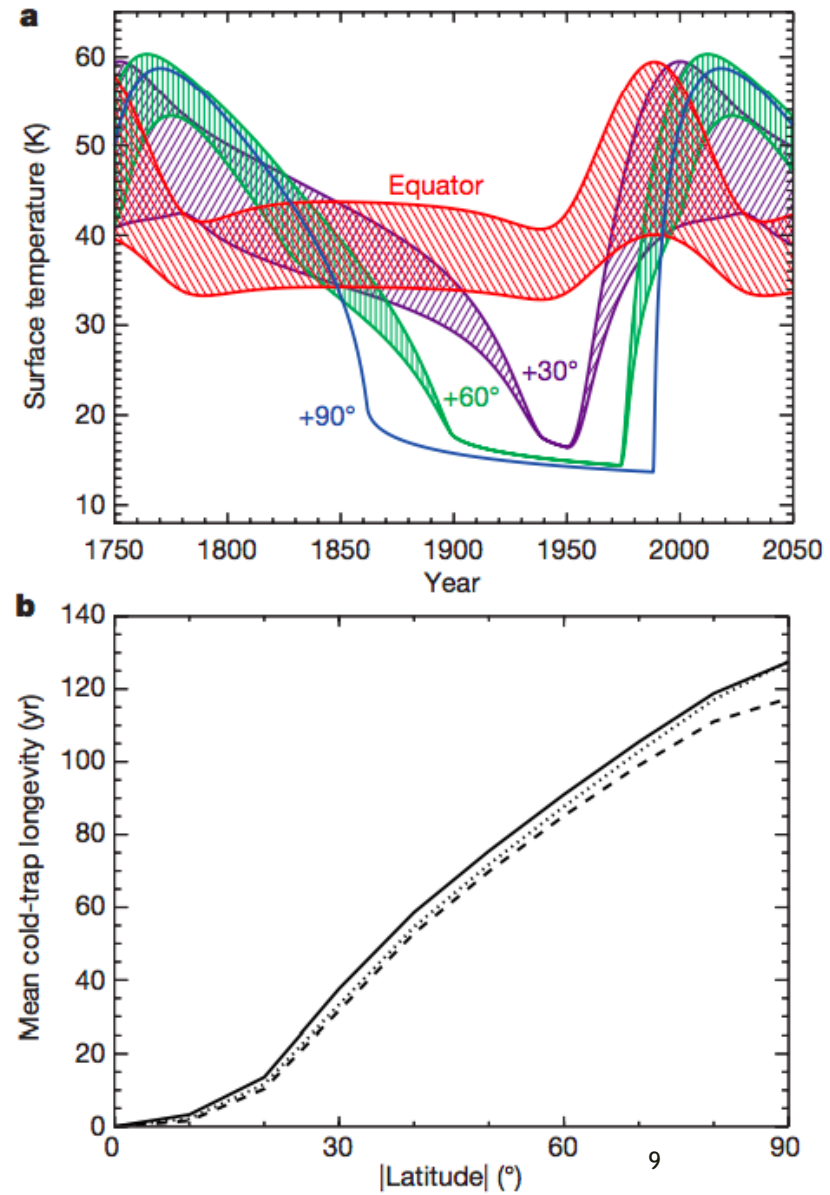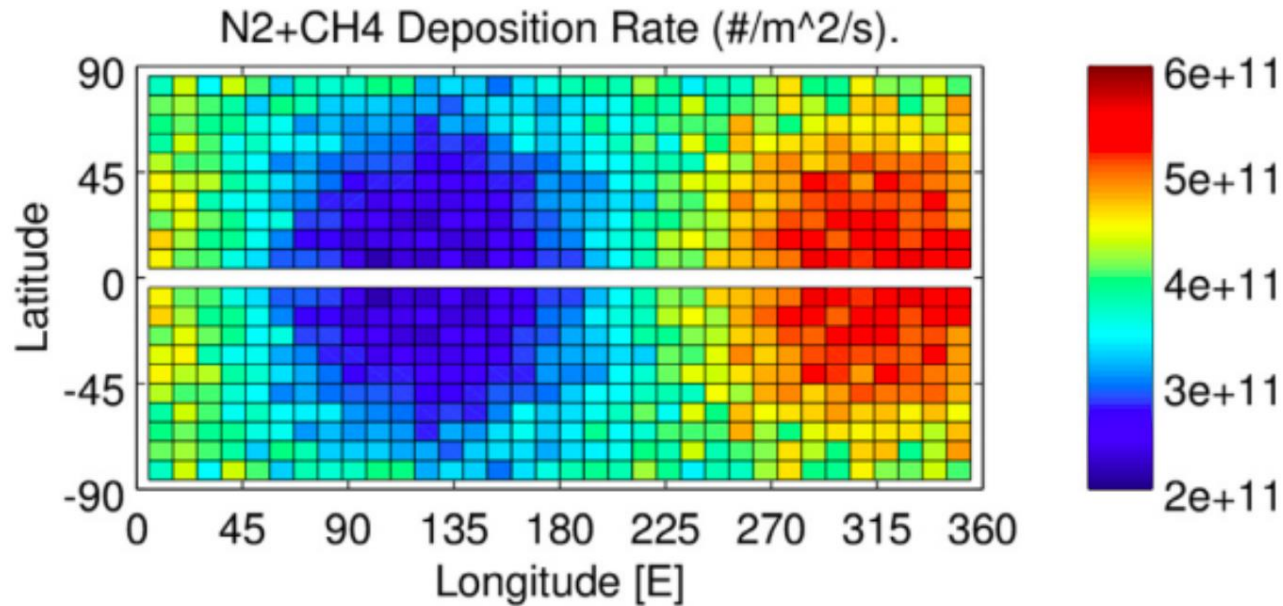

from Grundy et al. (2016)

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.

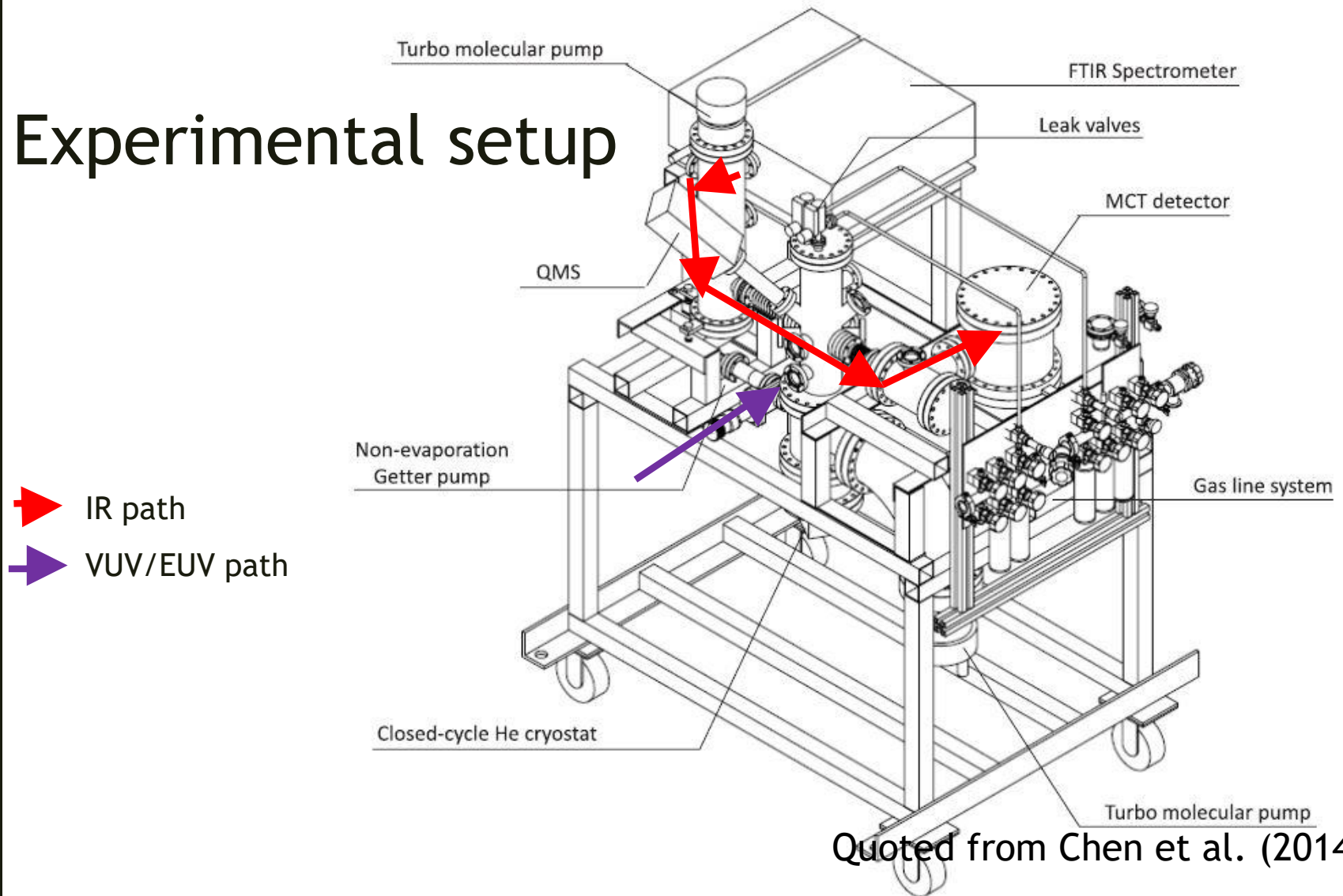Quoted from Grundy et al. (2016)

Deposition rate of methane on Charon

N2+CH4 Deposition Rate (#/m^2/s).

quoted from Hoey et al. (2017)

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

Turbo molecular pump

FTIR Spectrometer

Leak valves

MCT detector

QMS

Non-evaporation Getter pump

Gas line system

IR path

VUV/EUV path

Closed-cycle He cryostat

Turbo molecular pump

Quoted from Chen et al. (2014)

Experimental Protocol

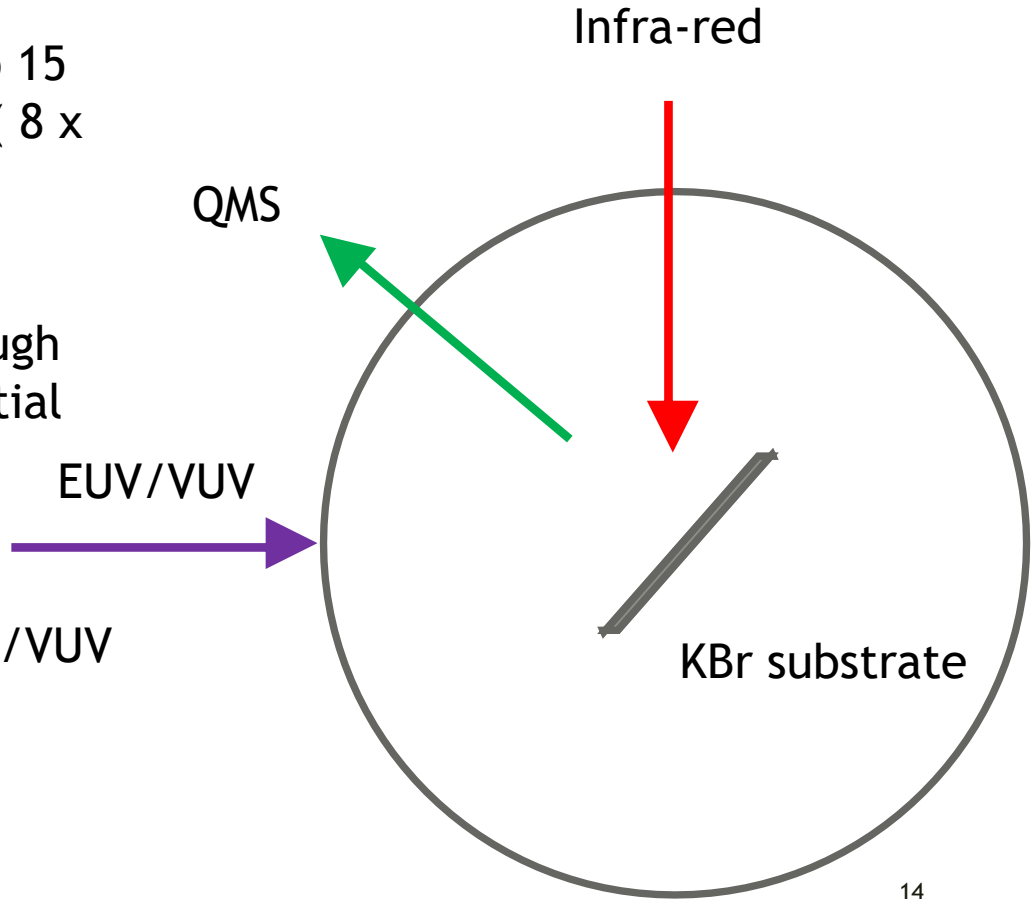KBr substrate is pre-cooled to 15 K (1×10^{-10} torr) from 300 K (8×10^{-10} torr)

⬇

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

⬇

Irradiate the samples by EUV/VUV

⬇

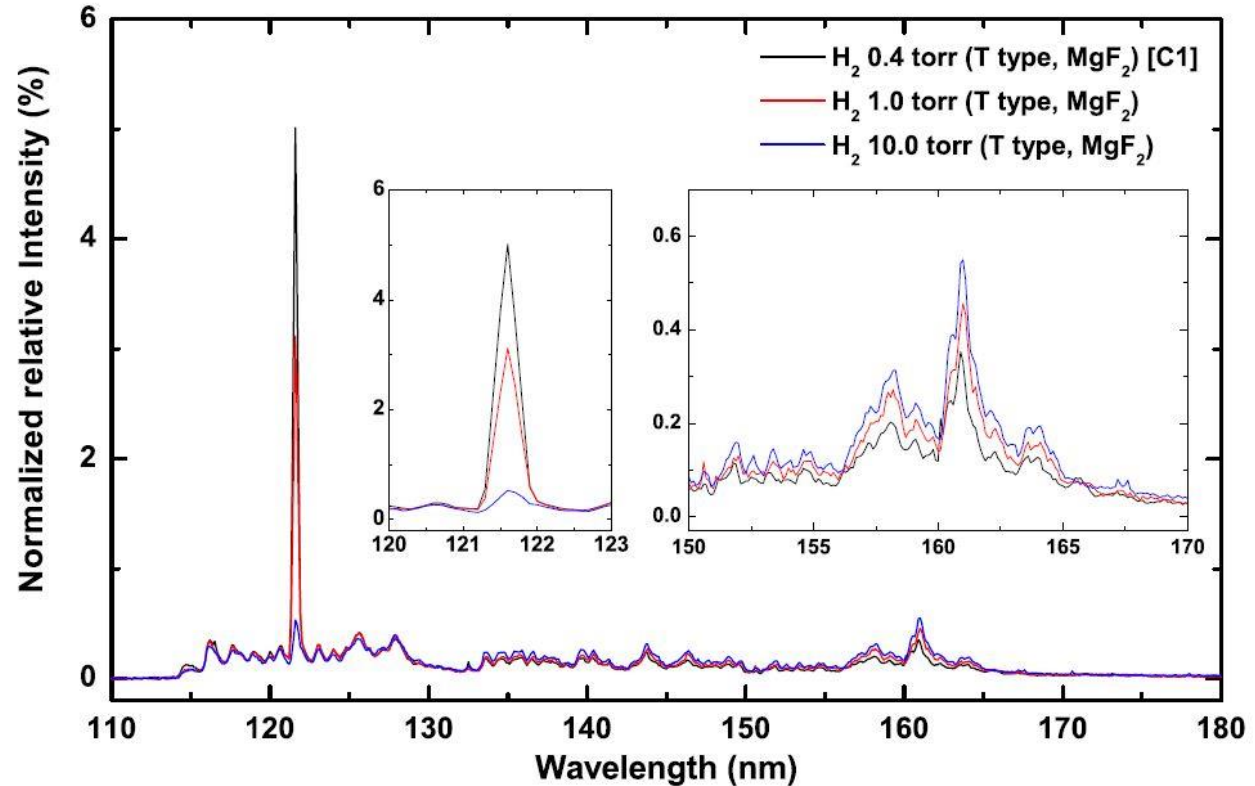Warm-up with 1 K/min

Infra-red

QMS

EUV/VUV

KBr substrate

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 ($\times 10^{15}$ 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 $a(v)$ 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*
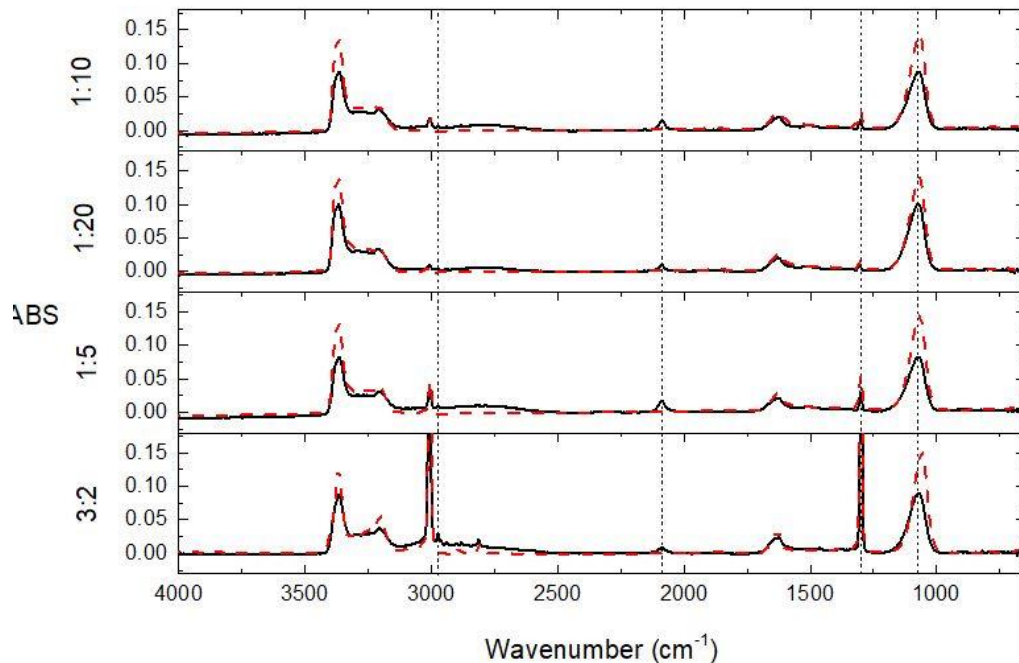
Infra-red spectra before (red dotted lines) and after (black solid lines) VUV irradiation where CN^-, C_2H_6 and C_3H_8 are formed after VUV irradiation.
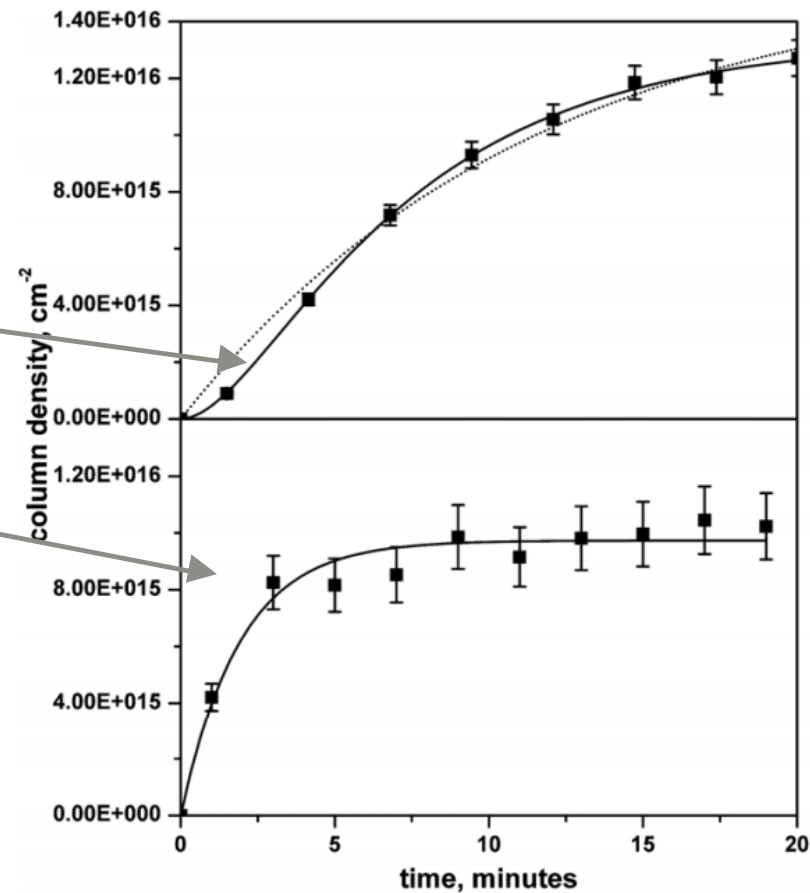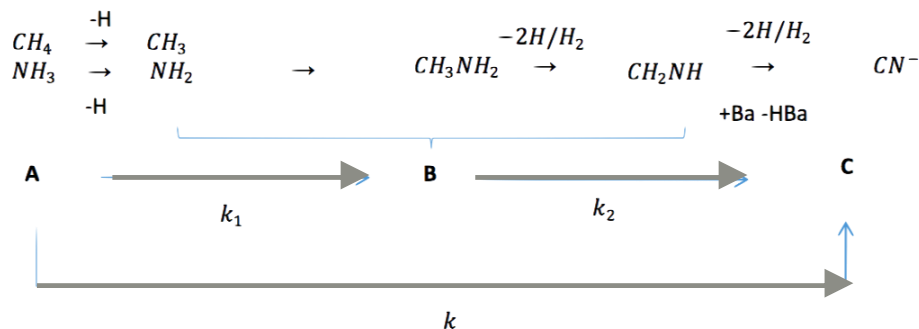
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1. Production of CN⁻

- 2 steps/1 step?

2 steps rate equation:

- $[CN^-] = \left(1 + \dfrac{k_1 e^{-k_2 t}}{k_2 - k_1} - \dfrac{k_2 e^{-k_1 t}}{k_2 - k_1}\right)[A]_o$
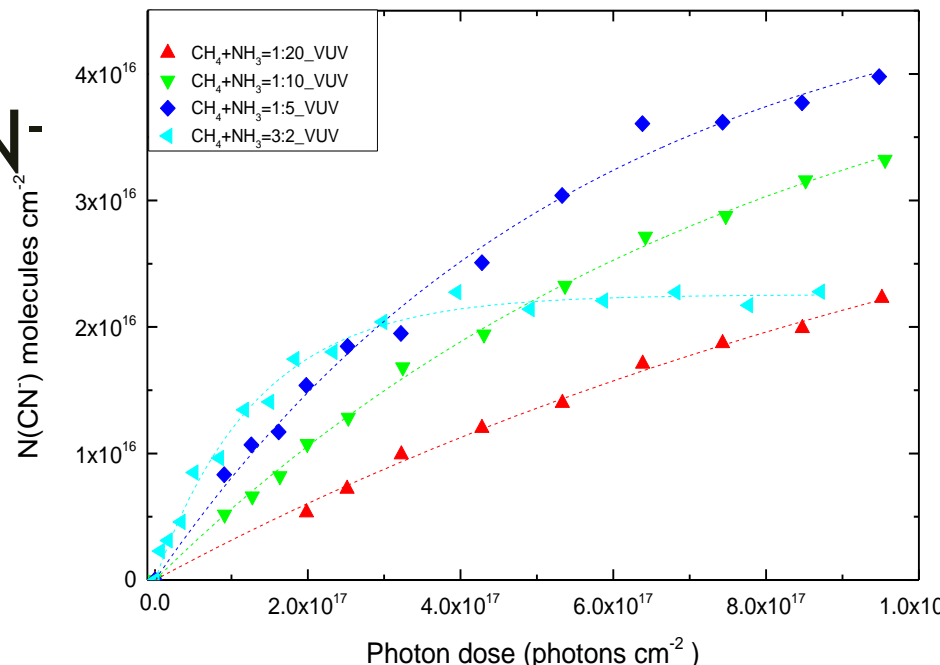
1 step rate equation:

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

$$CH_4 \xrightarrow{-H} CH_3$$
$$NH_3 \xrightarrow{-H} NH_2 \rightarrow CH_3NH_2 \xrightarrow{-2H/H_2} CH_2NH \xrightarrow{-2H/H_2} CN^-$$
$$+Ba\ -HBa$$

A ——→ B ——→ C
k_1 k_2

k

Quoted from Kim and Kaiser (2011)

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1. Production of CN⁻

- 2 steps/1 step?

2 steps rate equation:

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

1 step rate equation:

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

Table 3.5: The fitting results of CN⁻ by equation 2.10

| VUV experiments with $CH_4 + NH_3$ ice mixtures			
Ratio	A ($\times 10^{16}$ molecules cm^{-2})	k_1 ($\times 10^{-18}$ photon^{-1})	k_2 (photon^{-1})
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
Quotated from Kim and Kaiser[2]			
Ratio	A($\times 10^{16}$ molecules cm^{-2})	k_1 ($\times 10^{-3}$ s^{-1})	k_2 ($\times 10^{-3}$ s^{-1})
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 $C_n H_{2n+2}$ (n=1-6)+NH_3 ice mixtures			
2:5	1.0 ± 0.0	8.7 ± 1.3	$\gg 1$

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

1. Production of CN⁻
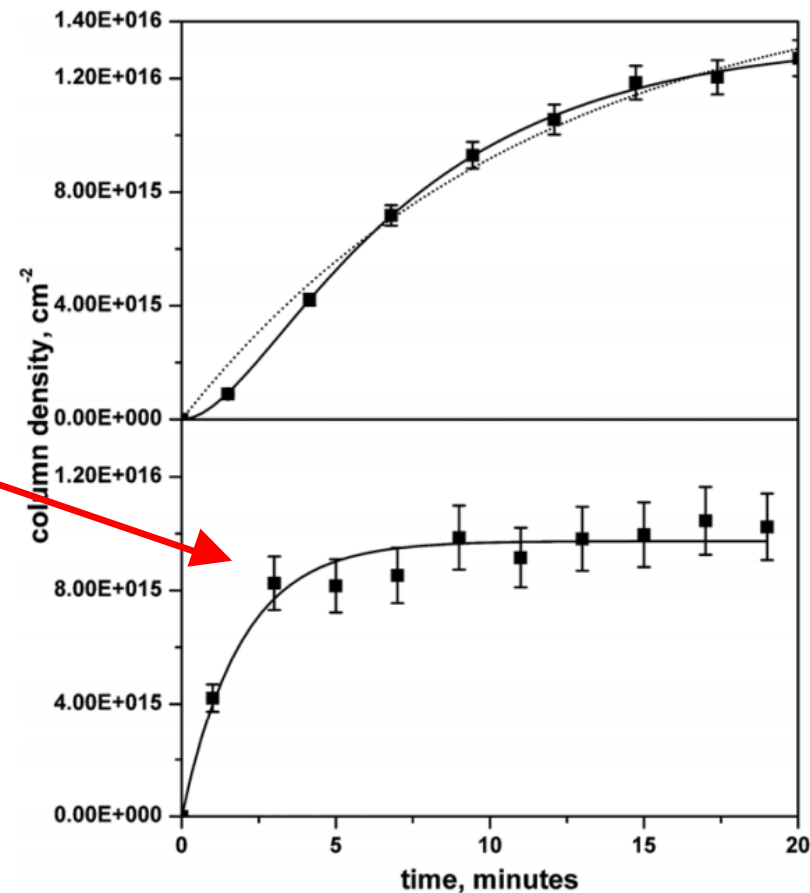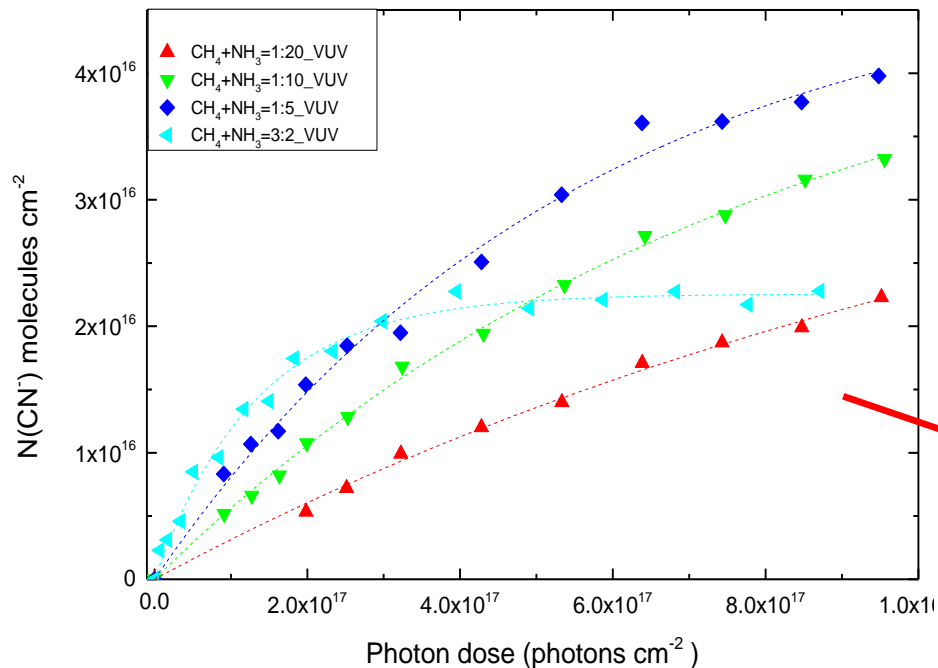
1. Production of CN⁻

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⁻
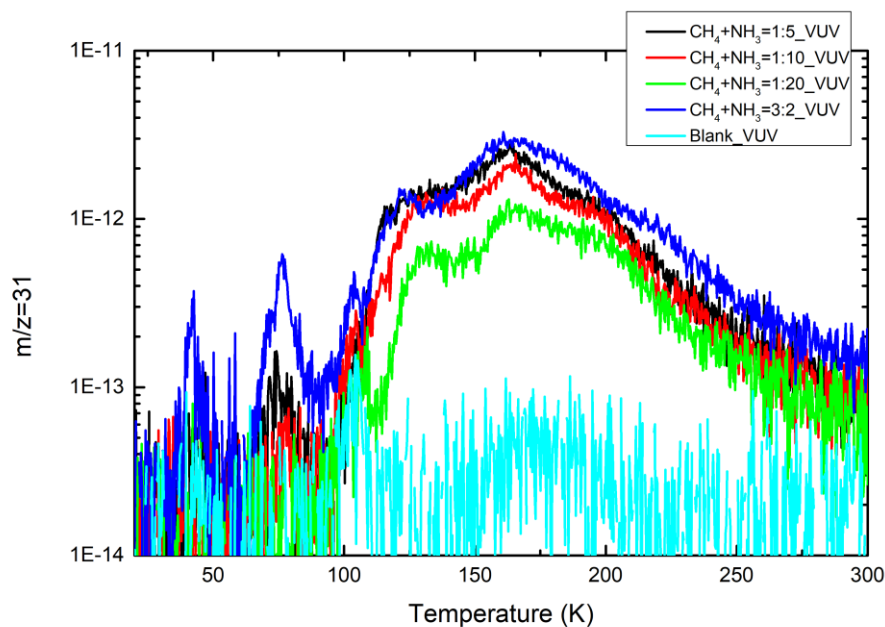
2. The scenario for NH_3 dominating ice mixtures

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

CH_4

NH_3
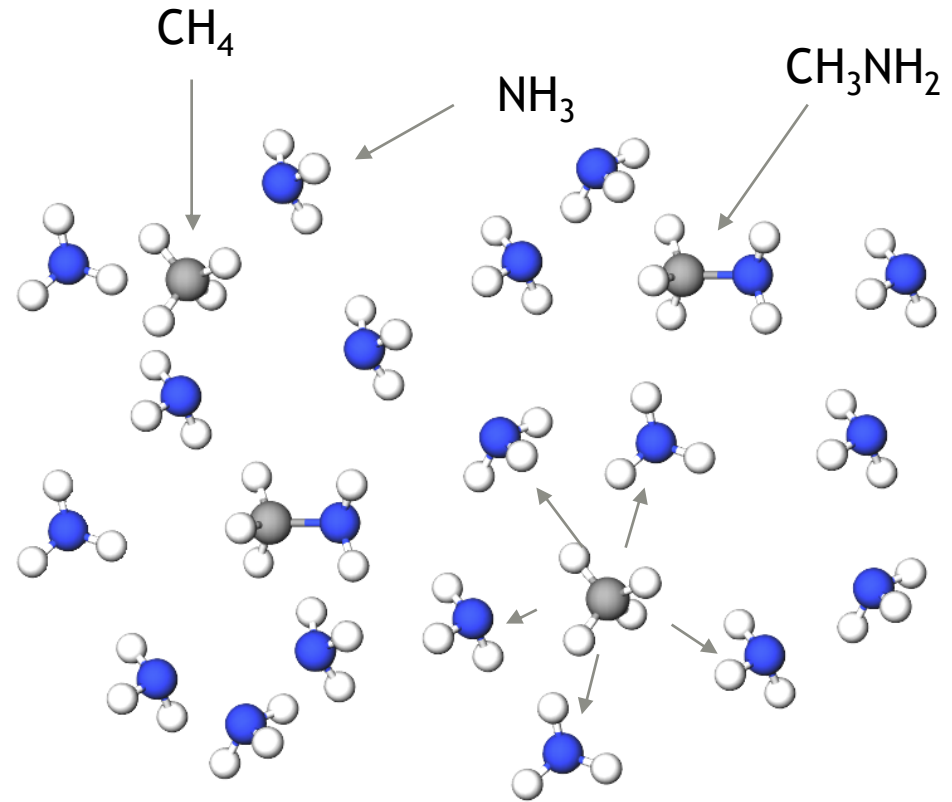
CH_3NH_2

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

CH_4

NH_3

C_3H_8

CH_3NH_2
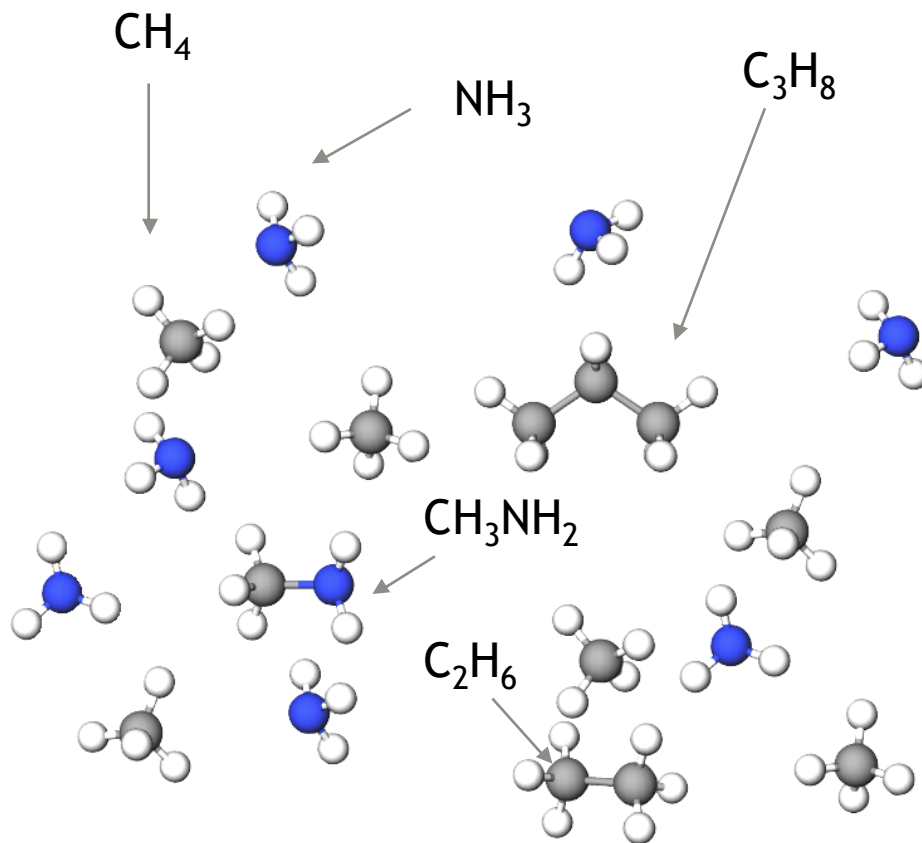
C_2H_6

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.

- $CH_4+NH_3=1:5\_CN-$
- $CH_4+NH_3=1:5\_C_2H_6$
- $CH_4+NH_3=3:2\_CN-$
- $CH_4+NH_3=3:2\_C_2H_6$

N(molecules cm^{-2})

photo dose (photons cm^{-2})
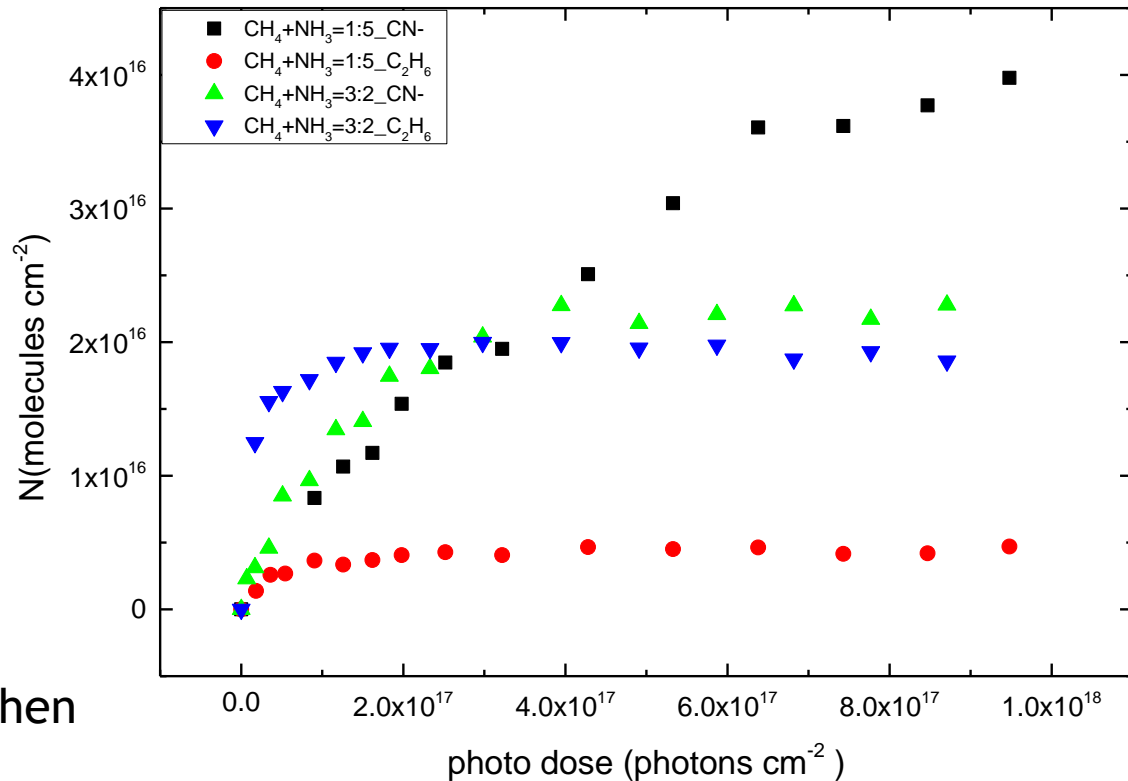
3. Efficiency of EUV (40.1 eV) and VUV (9.27 eV)

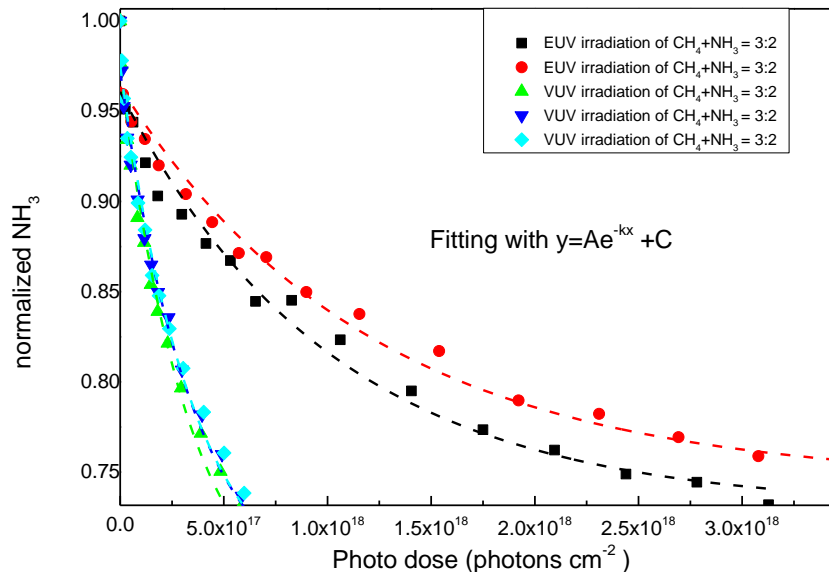| Radicals species	CH_4	NH_3
- 1 H	4.55 eV	4.67 eV
-2 H	4.78 eV	4.38 eV
-3 H	9.19 eV	7.63 eV

(quoted from Kundu et al. (2017))

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

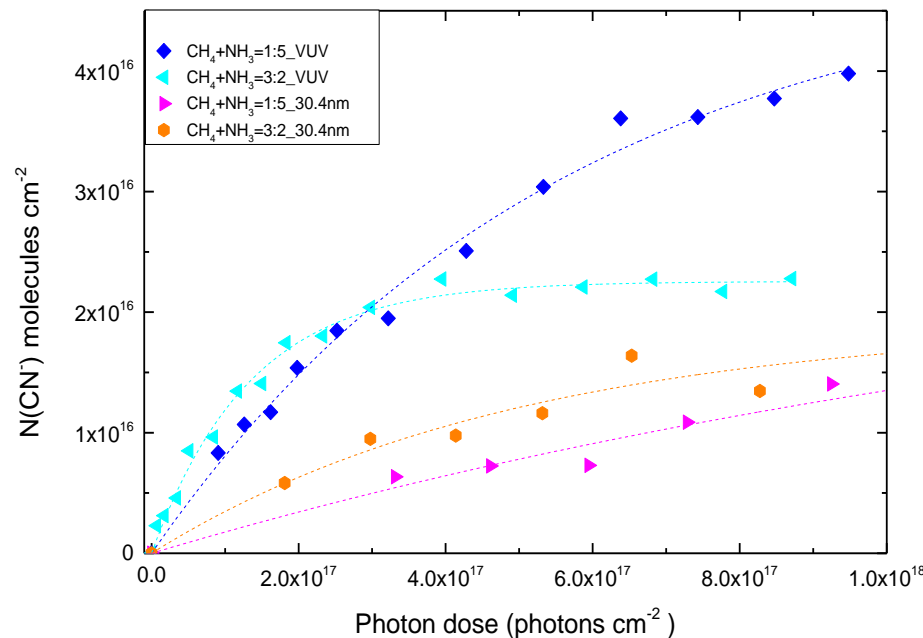■ Fitting with $y = Ae^{-kx} + C$ (pseudo first order kinetics)

CH_4
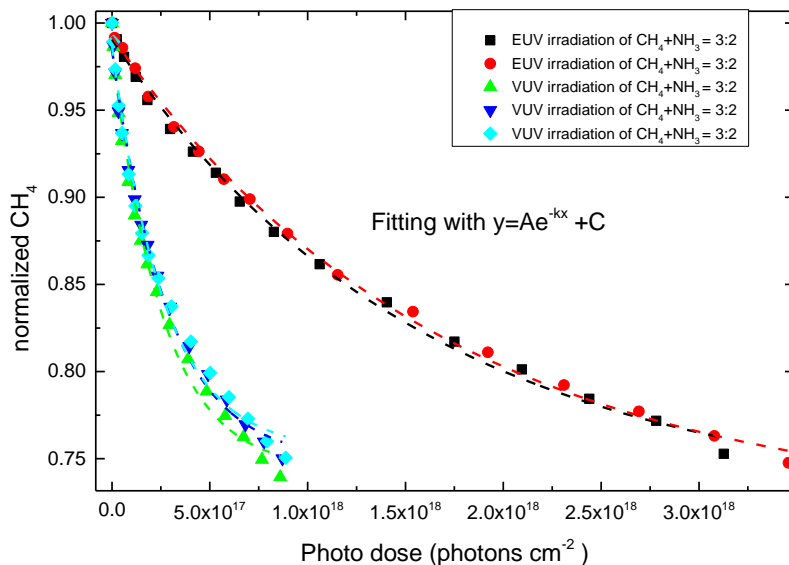
NH_3

# 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}*
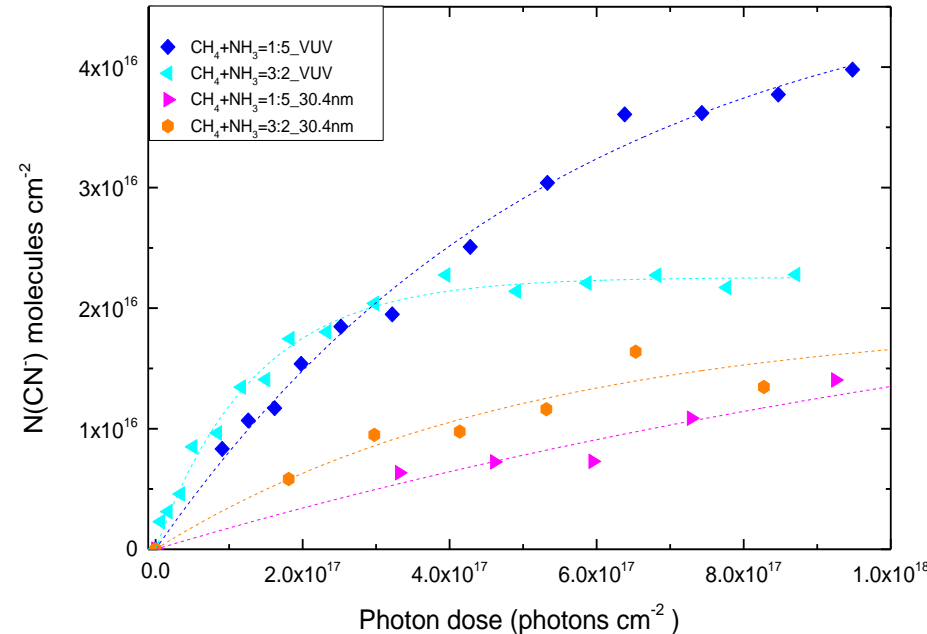
Understand CN- formation after winter on surface of Charon

Surface composition after 1 Pluto winter:

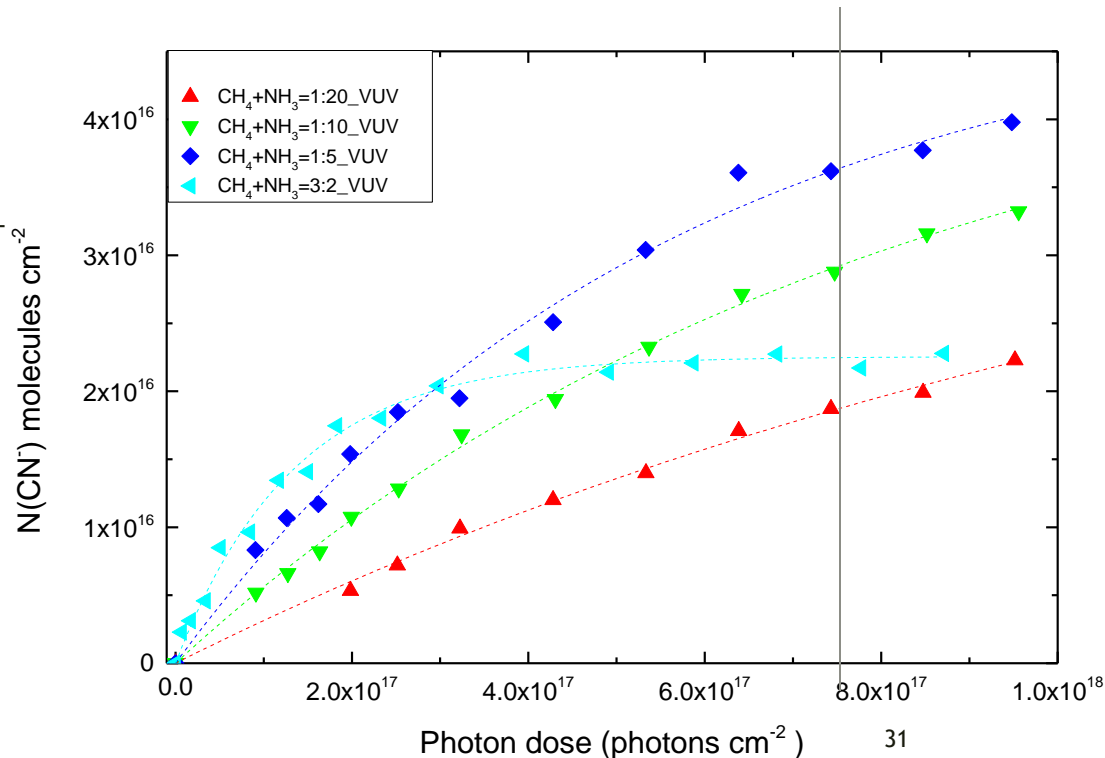- Ly α exposure: 1.9×10^9 eV cm^{-2} s^{-1} (Grundy et al. 2016)

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

- CH_4 deposition rate: $2\text{-}6 \times 10^7$ 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.