# VUV AND EUV IRRADIATION OF $CH_4$ + $NH_3$ ICE MIXTURES

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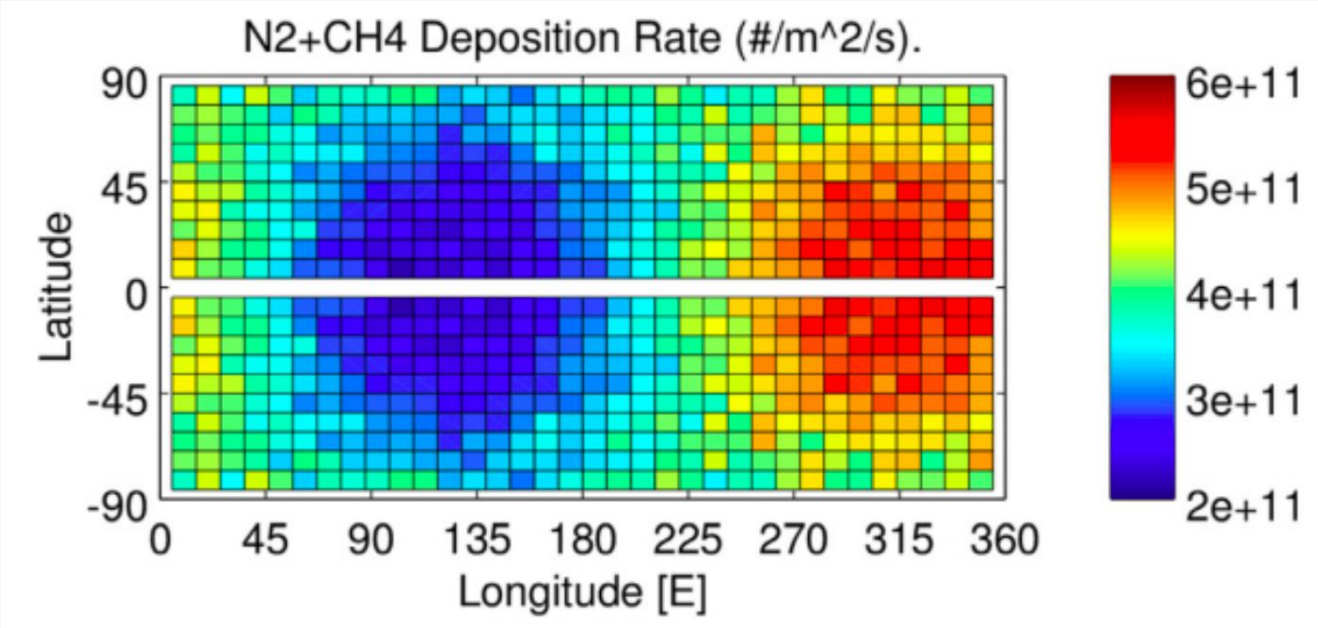
# Introduction

# Deposition rate of methane on Charon

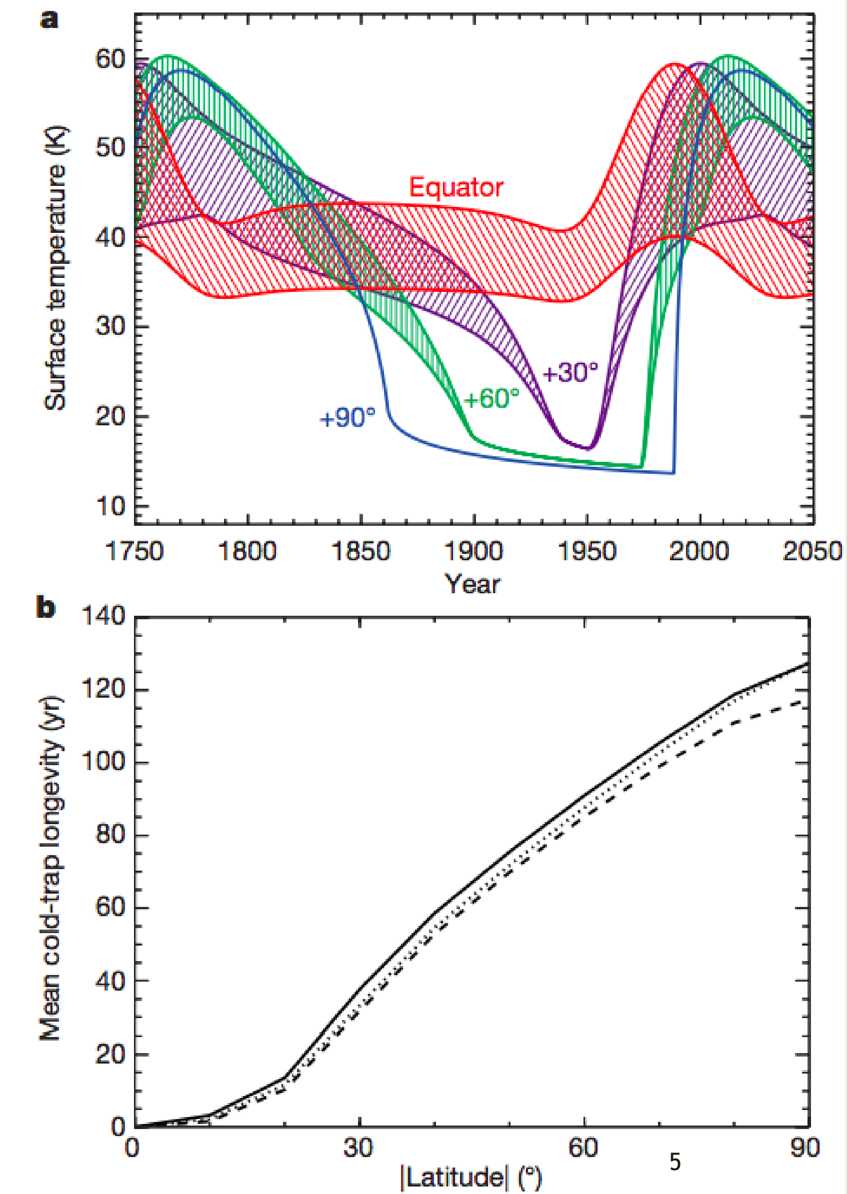



quoted from Hoey et al. (2017)

# Surface temperatures at different latitudes

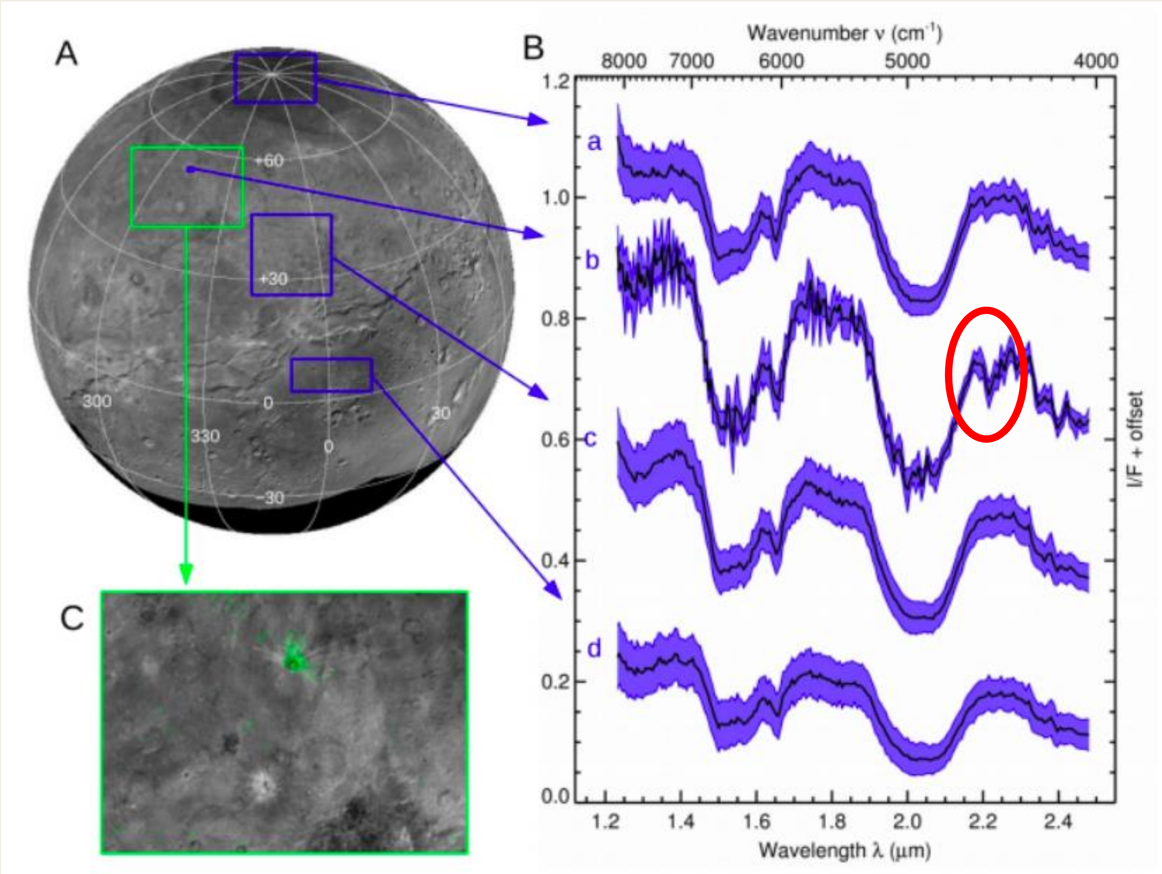
- Thermal model from Grundy et al. (2016) shows the pole position is below 25 K for 130 years
- Methane can condense on those positions where the temperature is below 25 K.

Quoted from Grundy et al. (2016)



# Ammonia on Organa Crater

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



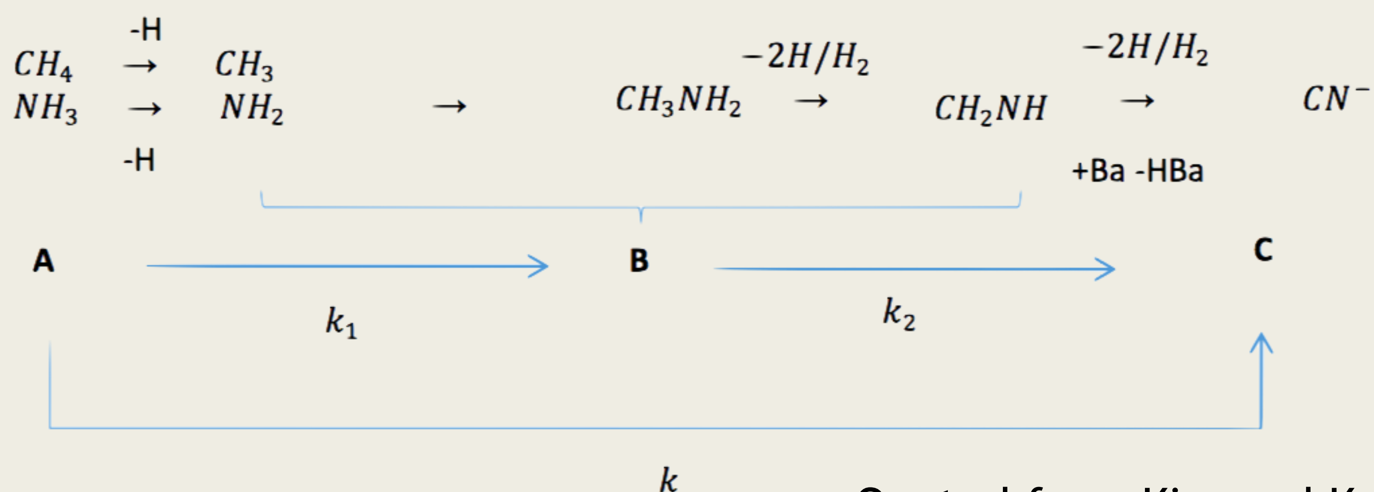

from Grundy et al. (2016)

# 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 $CN^-$

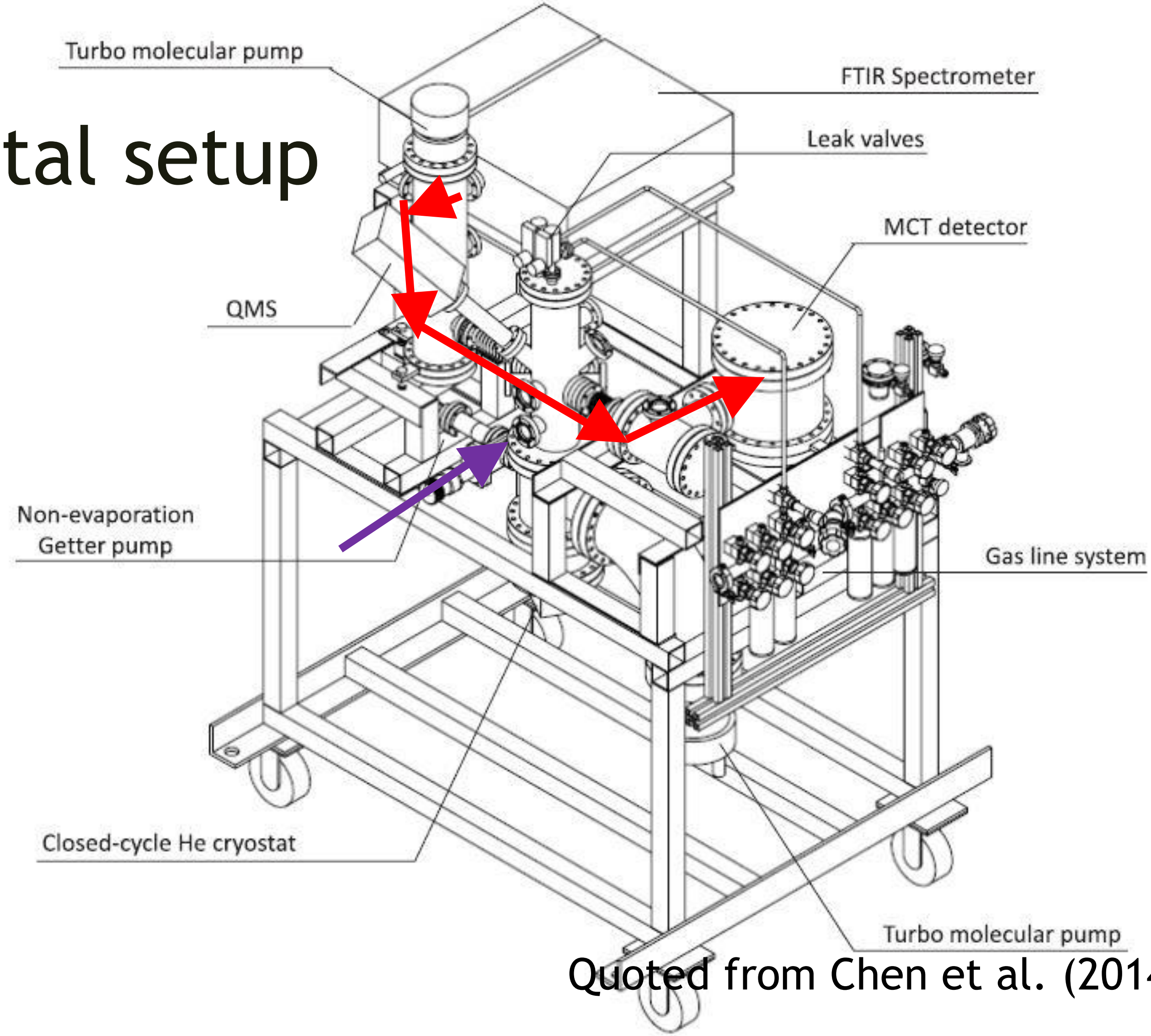
Attempts to detect $CH_3NH_2$:

- 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?

# Methodology

# Experimental setup




IR path

VUV/EUV path

Quoted from Chen et al. (2014)

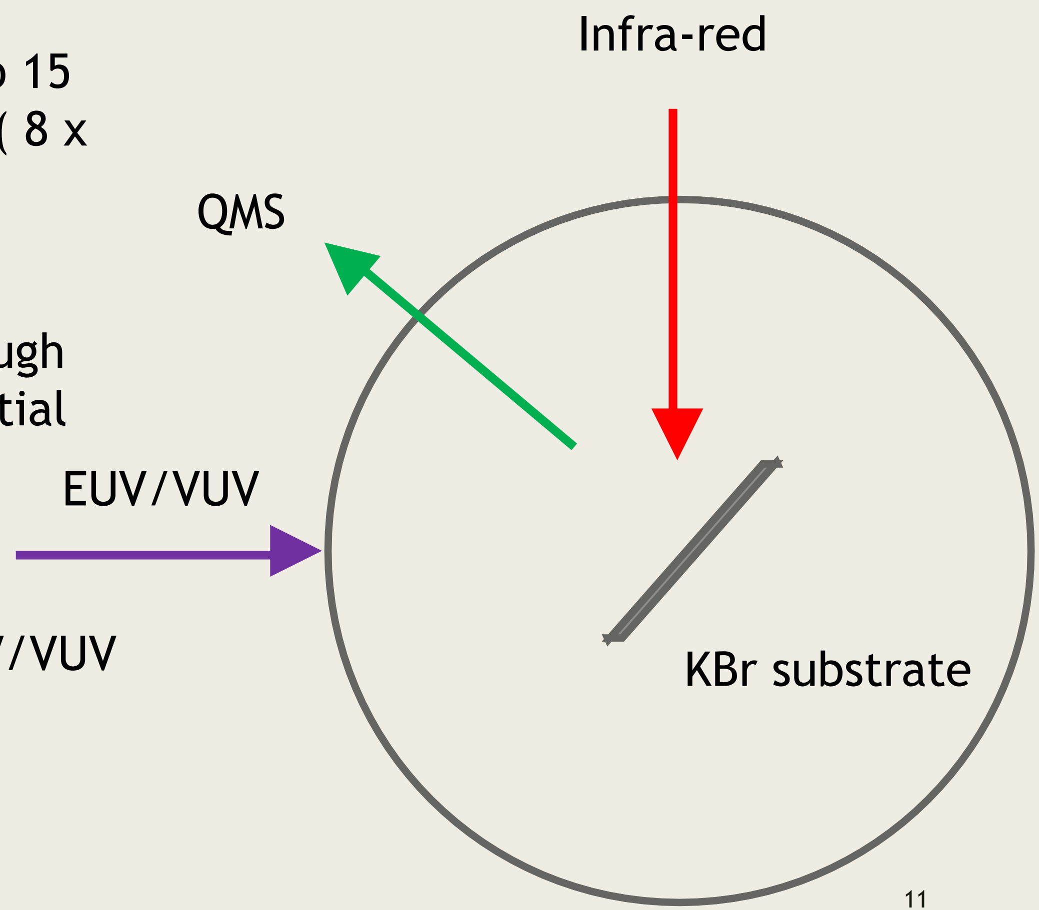
# Experimental Protocol

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

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

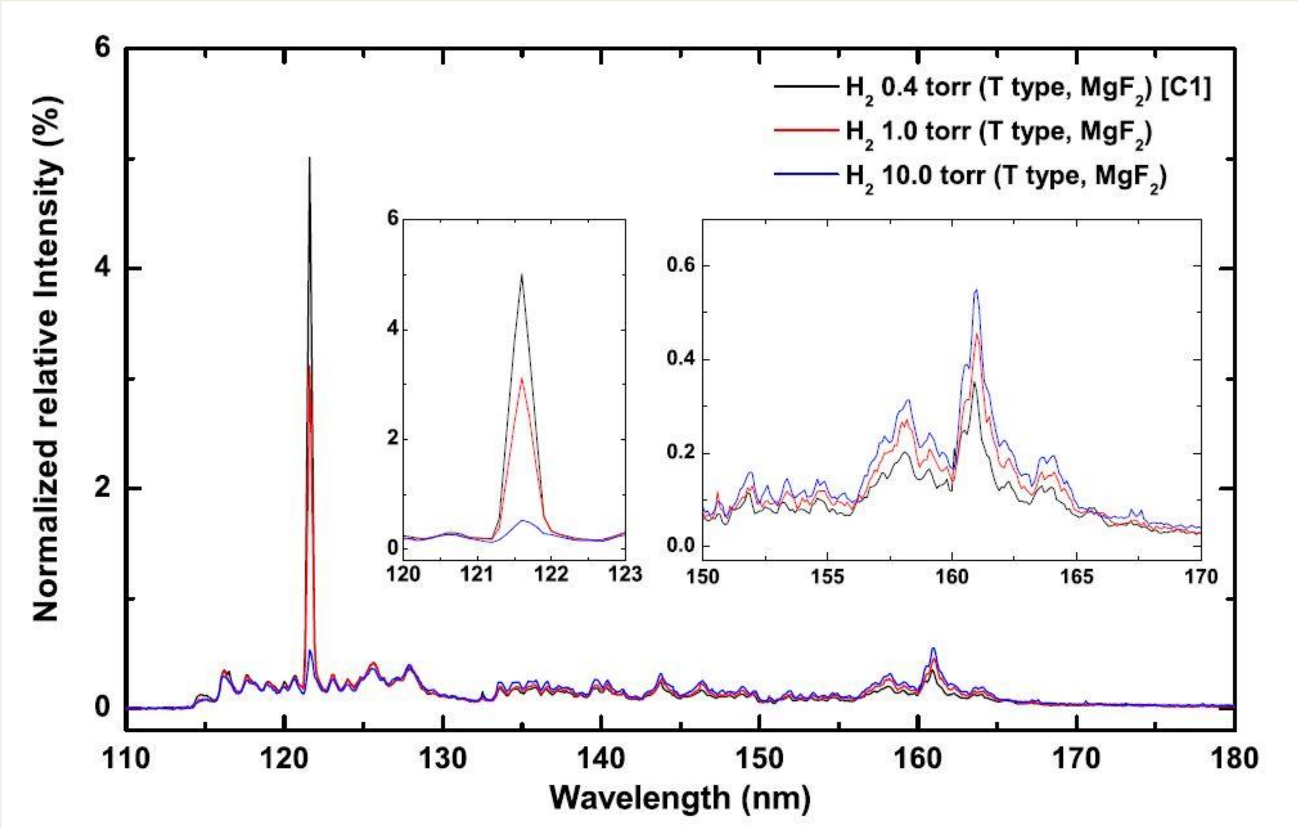
Irradiate the samples by EUV/VUV

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 9.27 eV




Quoted from Chen et al. (2014)

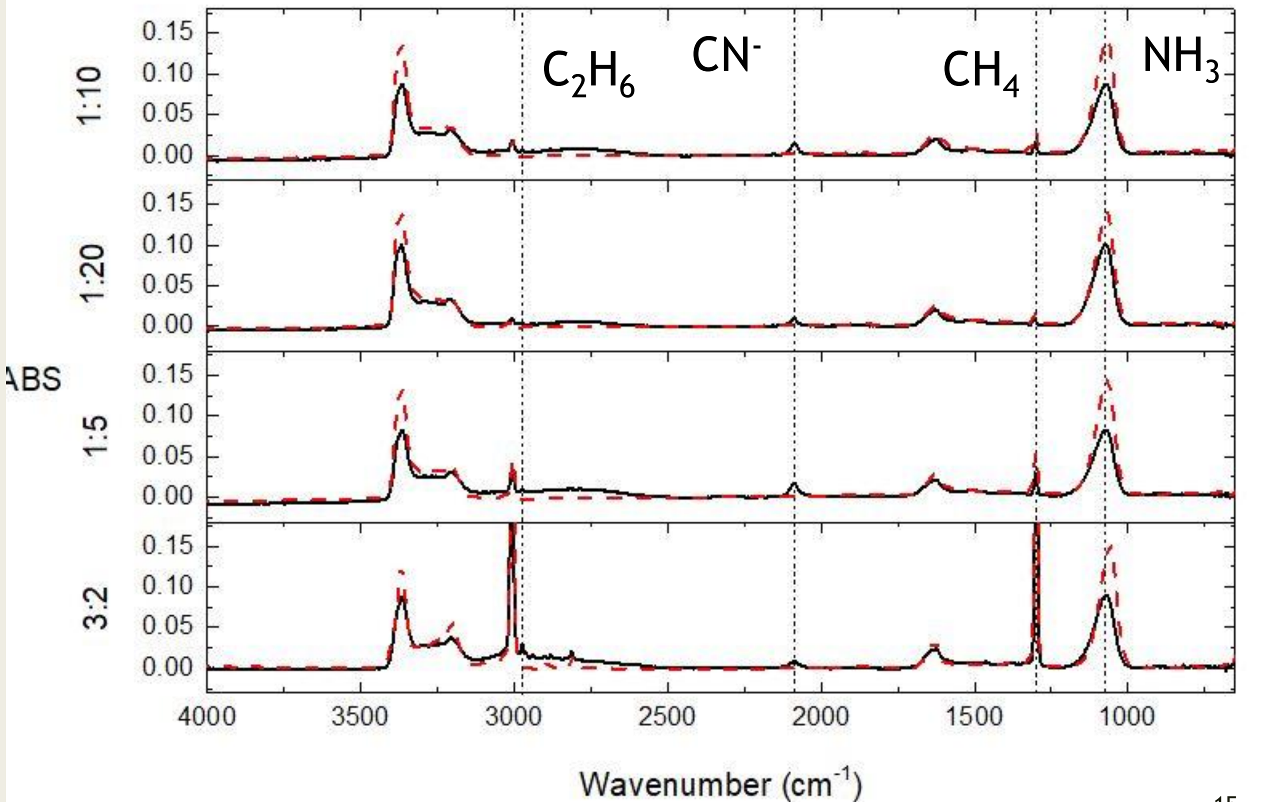
# Experimental Configurations

| Energetic Source | constituent | Column Density of $CH_4$+$NH_3$ ice mixtures (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:*

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

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

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

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 $A(v)$ is the absorption strength (A-value) (cm molecule-1) from litertures

# 1. Production of CN⁻

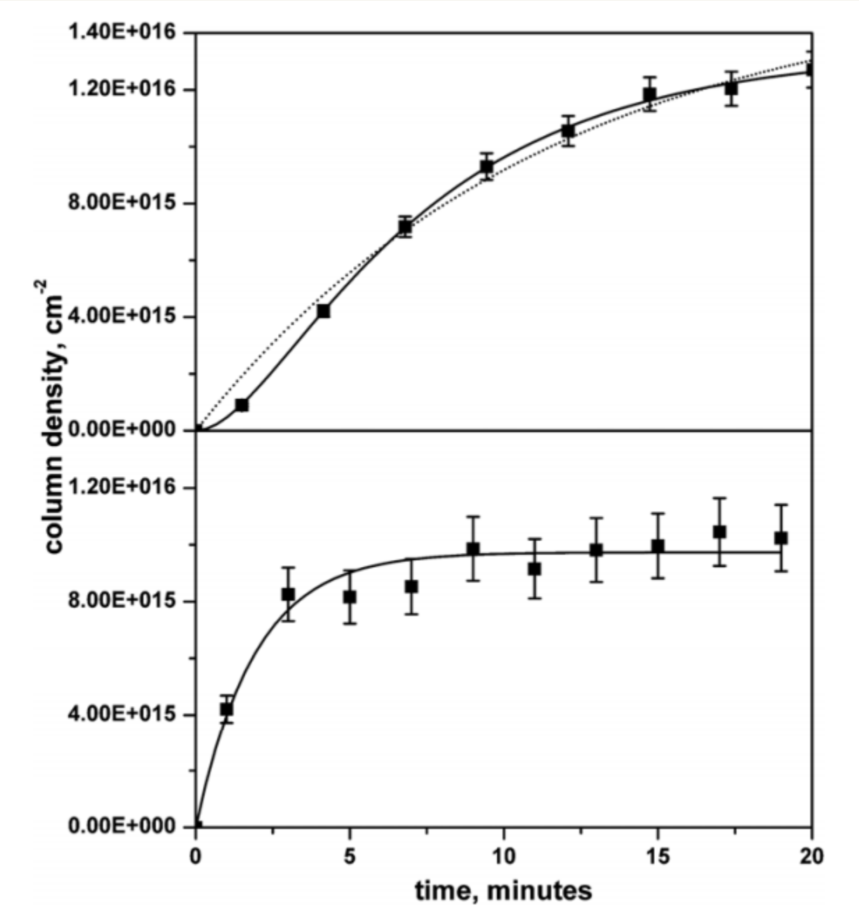
- 2 step/1 step?

2 step 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:

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

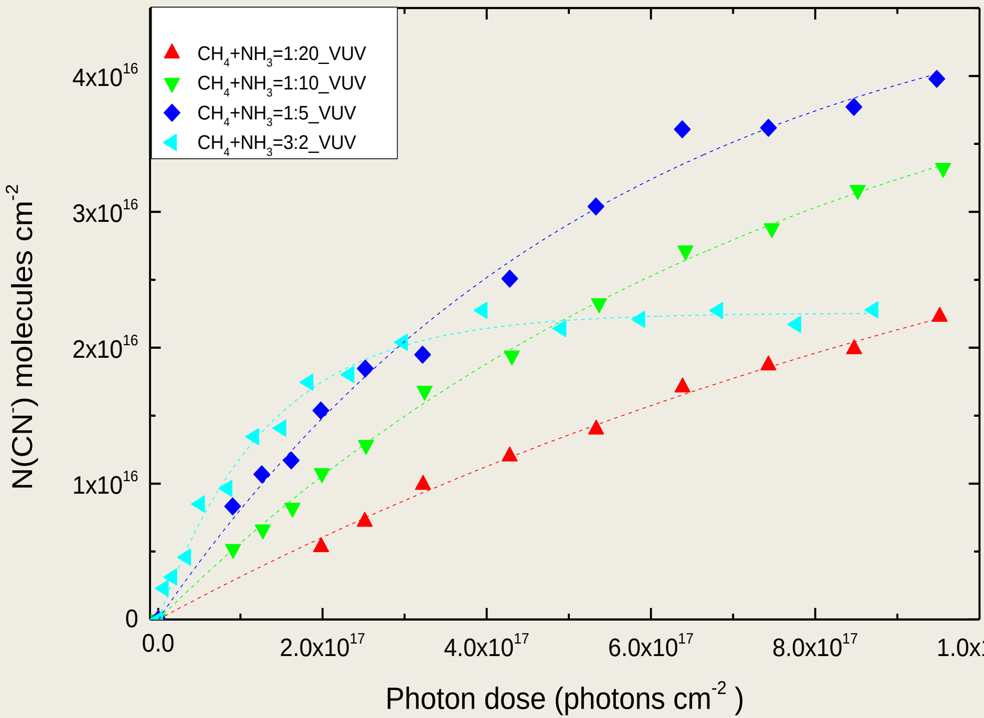



Quoted from Kim and Kaiser (2011)

# 1. Production of $CN^-$

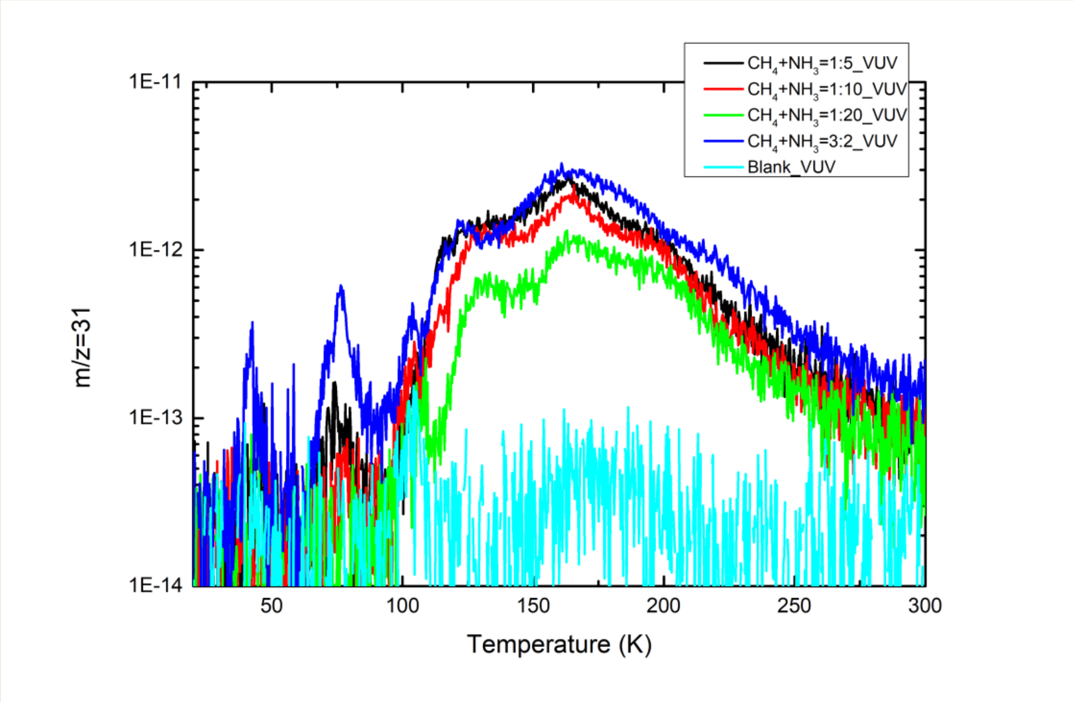
- 2 step/1 step?

| light source | Ratio of $CH_4$+$NH_3$ | A ($\times 10^{16}$ molecules $cm^{-2}$) | k ($\times 10^{-18}$ $photon^{-1}$) |
|---|---|---|---|
| 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 |



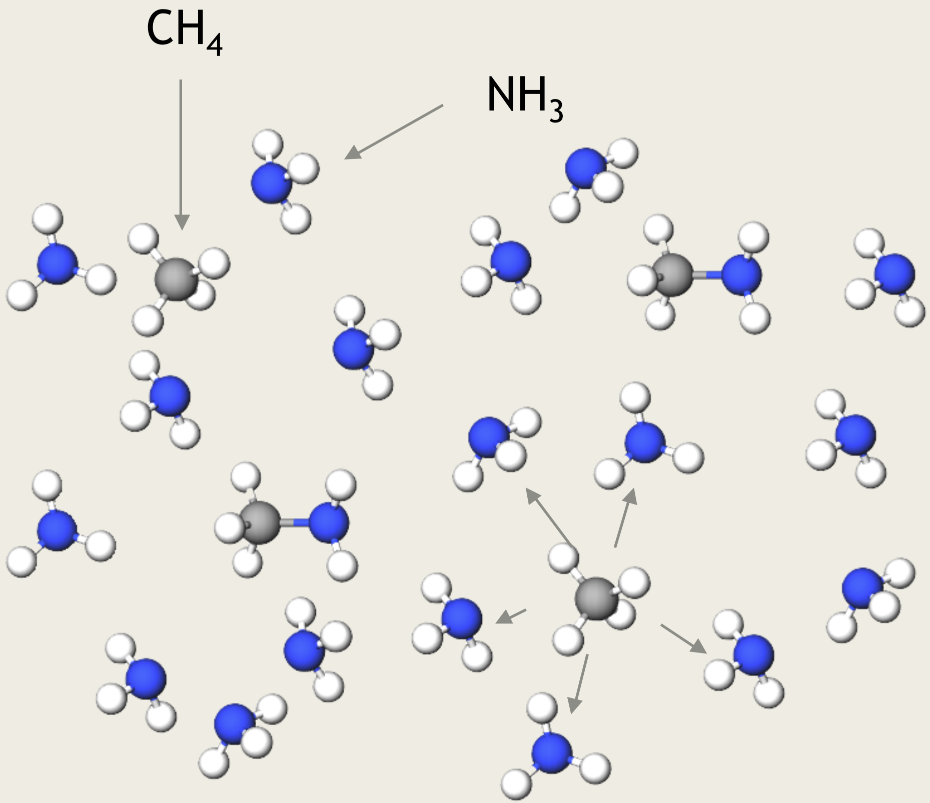
# 1. Production of $CN^-$

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

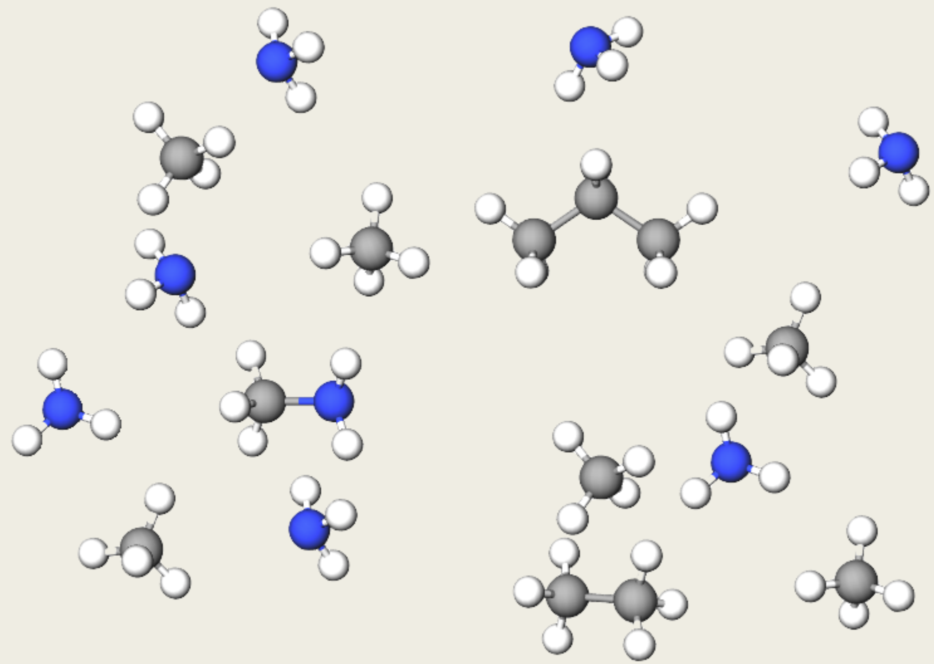
- $NH_2$ (forming $CH_3NH_2$) has a competing relationship with $CH_2$ $CH_3$ and $C_2H_4$ (forming $C_2H_6$ and $C_3H_8$)
- Once $CH_4$ becomes $CH_3$ radical, it can easily forms methylamine and hence become $CN^-$.




A diagram of $CH_4$+$NH_3$ = 1:5

# 2. The scenario for $CH_4$ dominating ice mixtures

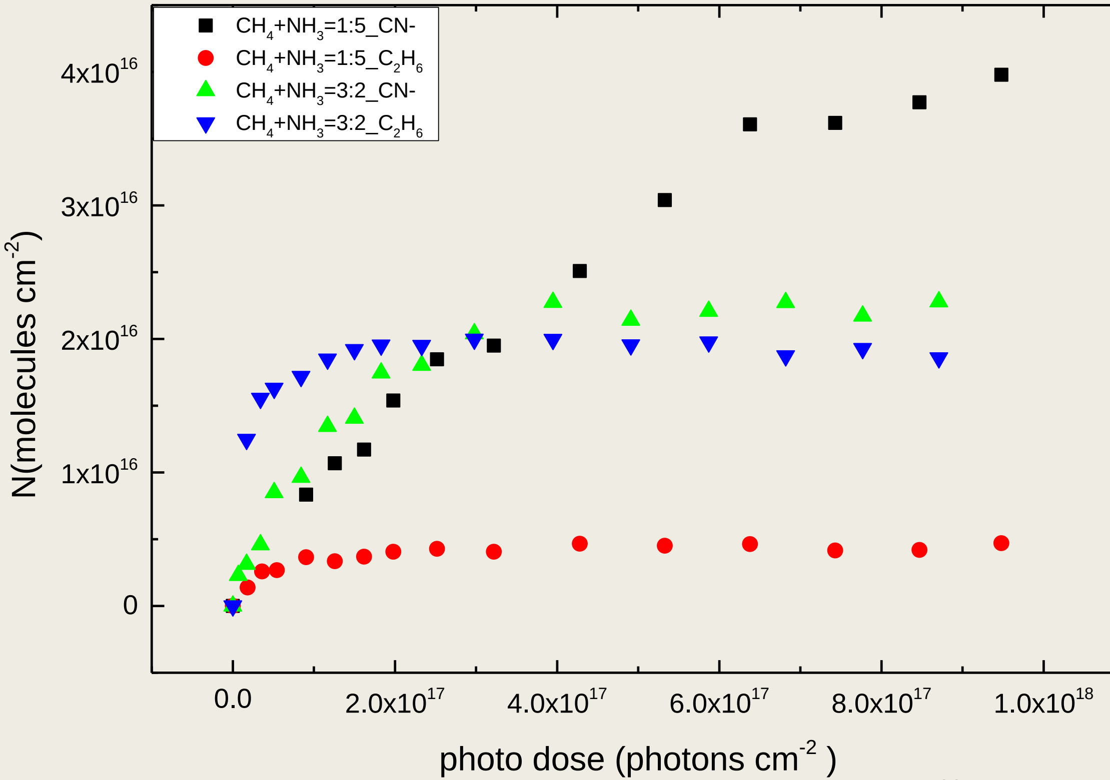
- $NH_2$ (forming $CH_3NH_2$) has a competing relationship with $CH_2$ $CH_3$ and $C_2H_4$ (forming $C_2H_6$ and $C_3H_8$)
- Once $CH_4$ becomes $CH_3$ radical, it reacts with either $NH_2$ or $CH_3$ radicals, forming $CH_3NH_2$, $C_2H_6$ and $C_3H_8$



A diagram of $CH_4$+$NH_3$ = 3:2

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

| Ratio of $CH_4+NH_3$ | $C_2H_6$ (ML) | $CN^-$ (ML) |
|---|---|---|
| 3:2 | 19.1 | 23 |
| 1:5 | 4.3 | 49 |



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

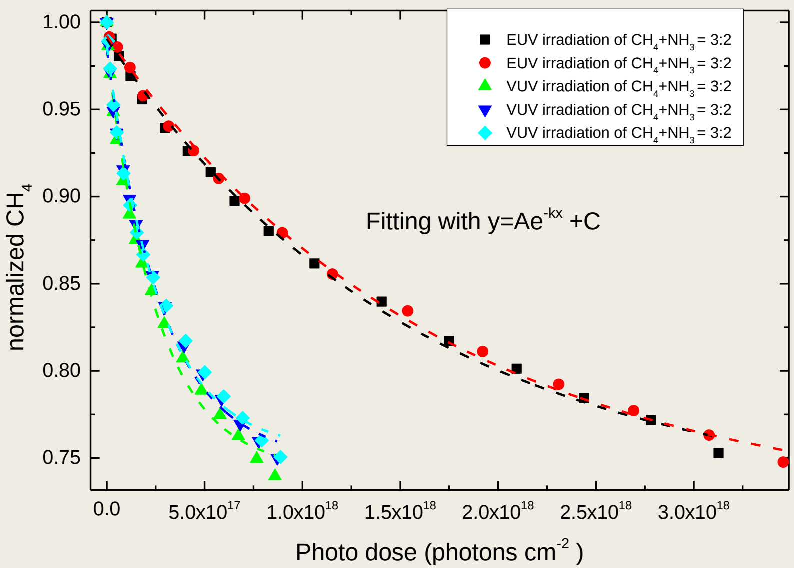
| Radicals \ species | $CH_4$ | $NH_3$ |
|---|---|---|
| - 1 H | 4.55 eV | 4.67 eV |
| -2 H | 4.78 eV | 4.38 eV |
| -3 H | 9.19 eV | 7.63 eV |

(quoted from Kundu et al. (2017))

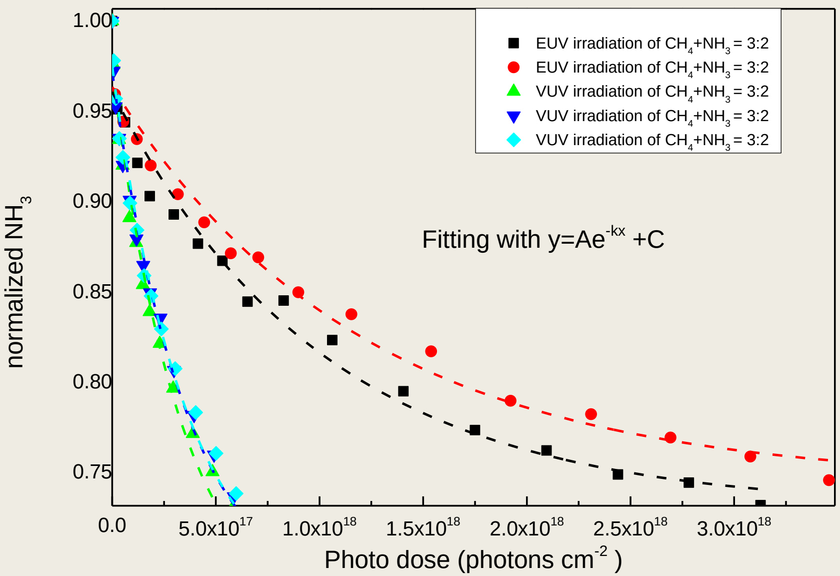
# 3. $CN^-$ formation efficiency of EUV (40.1 eV) and VUV (9.27 eV)

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

$CH_4$

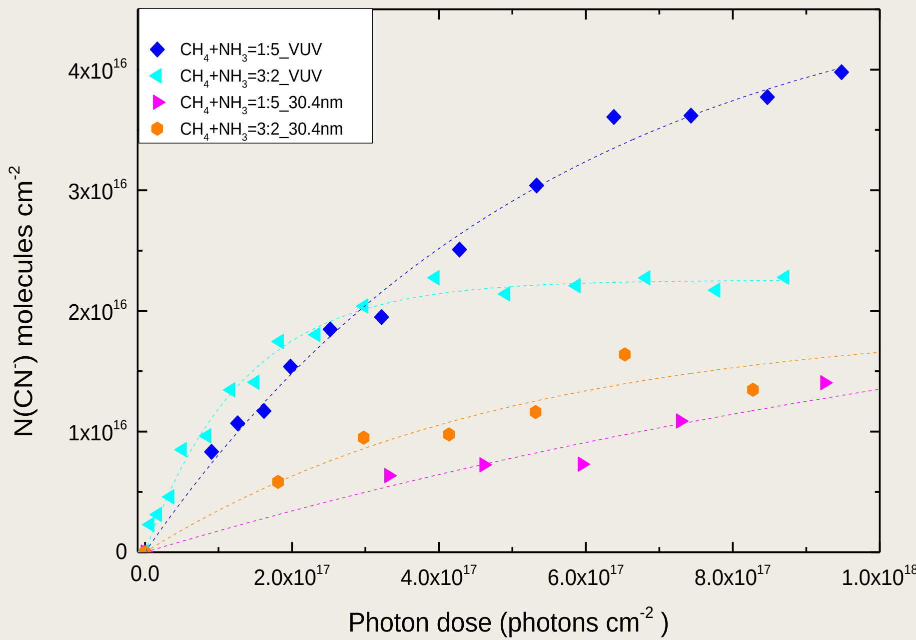



$NH_3$



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

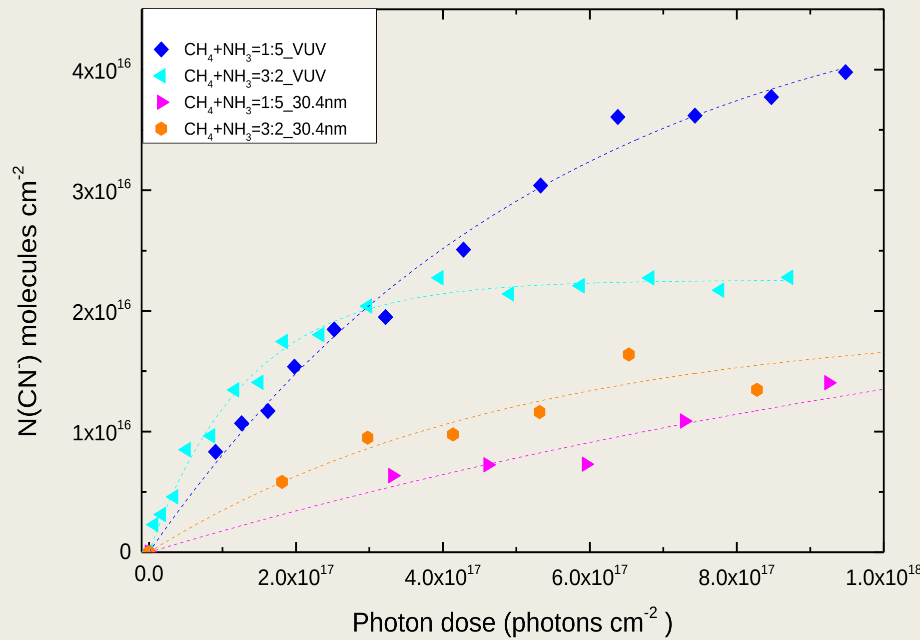
| k (photons $^{-1}$) | $CH_4$(x $10^{-18}$) | $NH_3$ (x$10^{-18}$) |
|---|---|---|
| VUV (MDHL) | 3.70±0.18 | 2.89±0.10 |
| EUV (30.4nm) | 0.61±0.03 | 0.91±0.11 |
| Destruction cross-section ratio | 6.06±0.07 | 3.18±0.12 |
| k (photon $^{-1}$) | $CH_4$ to $NH_3$ 3:2 (x $10^{-18}$) | $CH_4$ to $NH_3$ 1:5 (x$10^{-18}$) |
| 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: $1.9 \times 10^9$ eV $cm^{-2}$ $s^{-1}$*
    - *EUV exposure: $8.7 \times 10^7$ eV $cm^{-2}$ $s^{-1}$*



# Understand CN- formation after winter on surface of Charon

*Surface composition after 1 Pluto winter:*

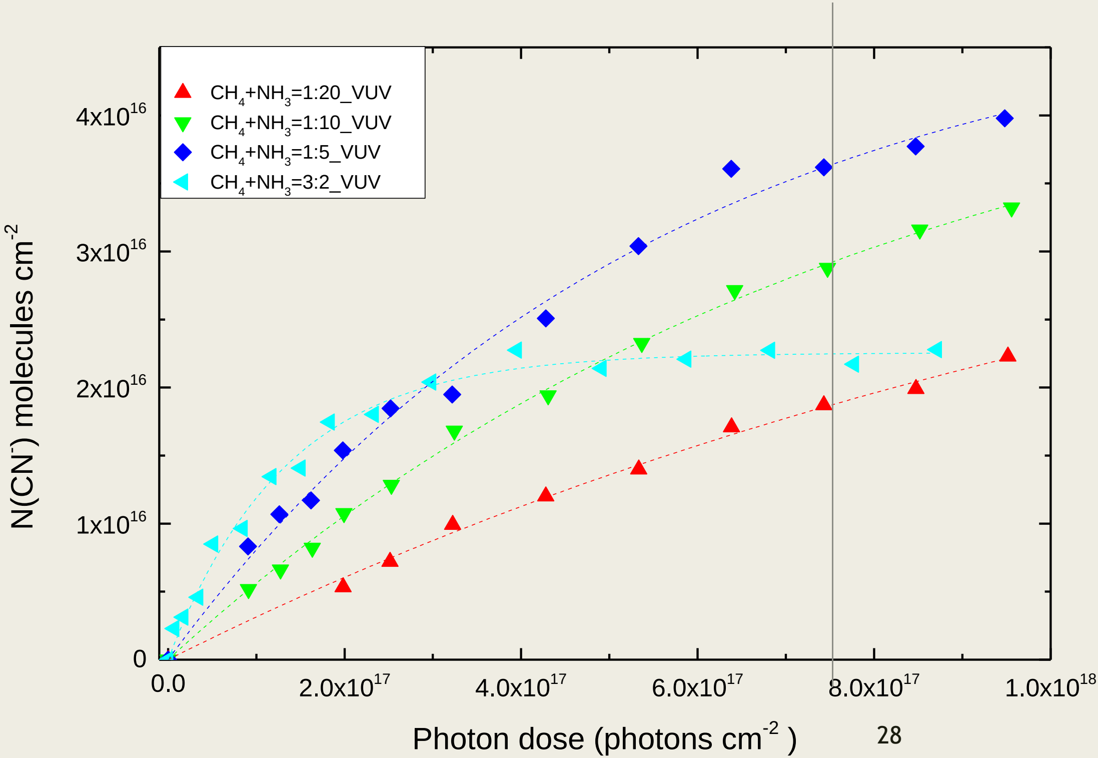
- Ly α exposure: $1.9 \times 10^{9}$ eV $cm^{-2}$ $s^{-1}$ (Grundy et al. 2016)

= photon dose $7.64 \times 10^{17}$ 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.