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

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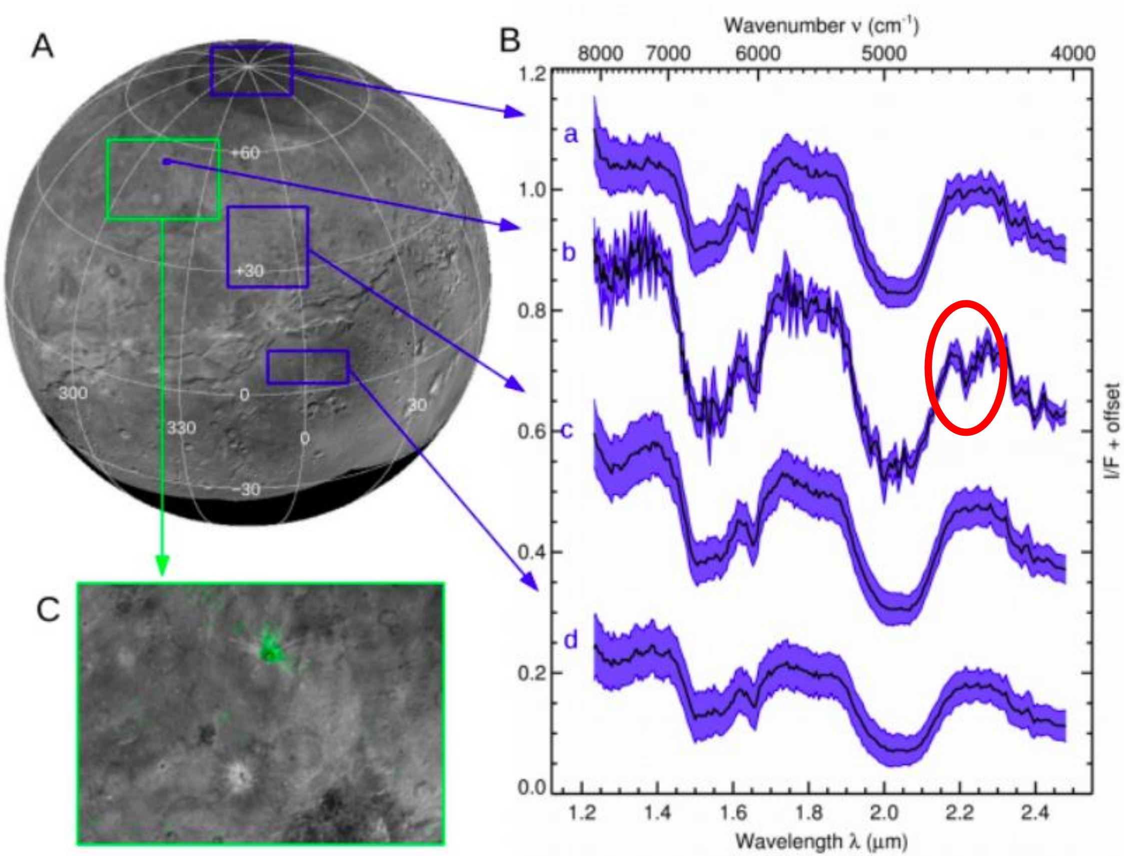
  - Understand $CN^-$ formation after winter on Charon

# Motivation

# Ammonia on Organa Crater

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




90º

50º

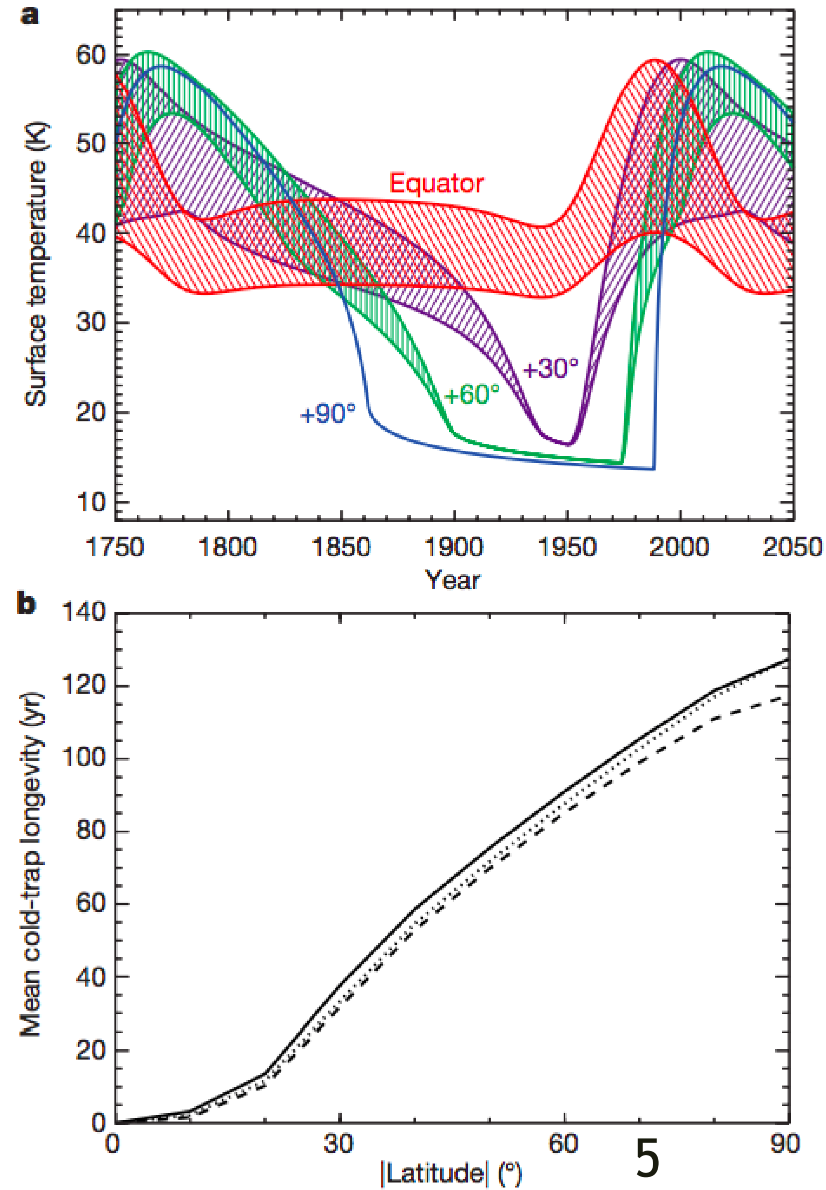
40º

10º

from Grundy et al. (2016)

# Surface temperatures at different latitudes

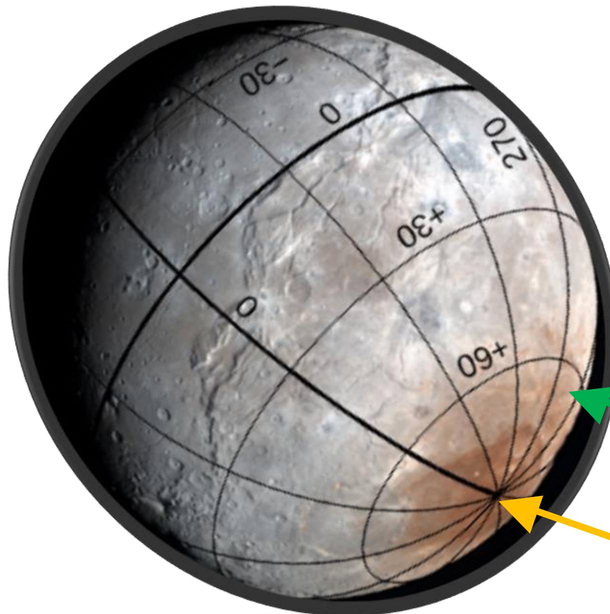
- Thermal model from Grundy et al. (2016) shows the pole position is below 25 K for 130 years
- Methane can condense on those positions where the temperature is below 25 K.




Quoted from Grundy et al. (2016)

# What astrophysical environments are we demonstrating?

Charon in Pluto system



VUV and EUV irradiation

$NH_3 + CH_4 \longrightarrow CN^-$

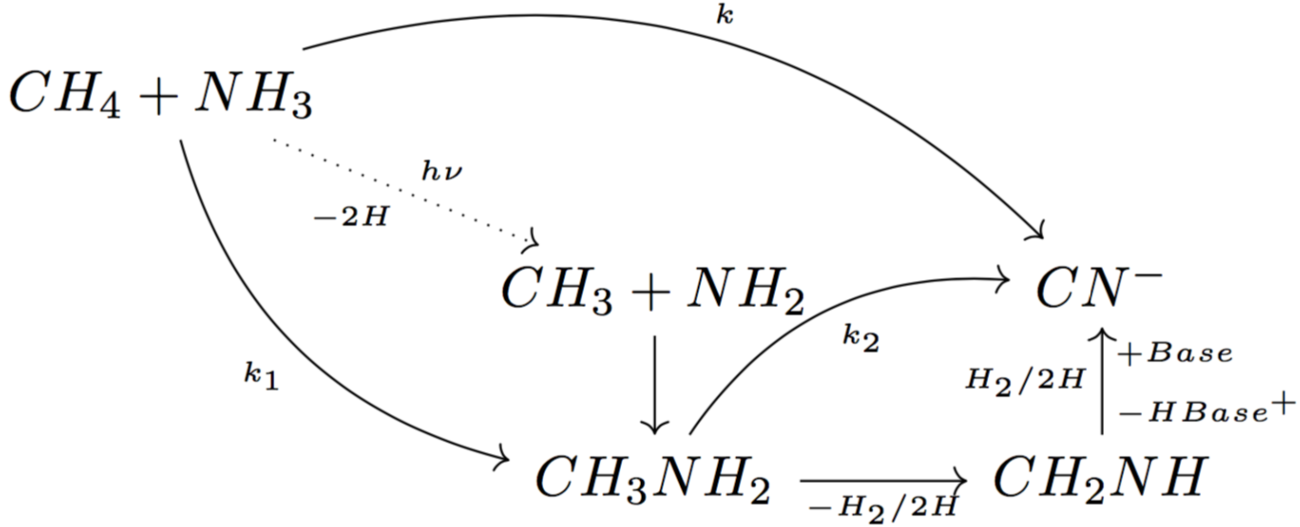
Quoted from Grundy et al. (2017)

# Production mechanism of $CN^-$

Enthalpy of $CH_3NH_2$ formation

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

Quoted from Kundu et al. (2017)




Quoted from Kim and Kaiser (2011)

# Production of CN$^-$

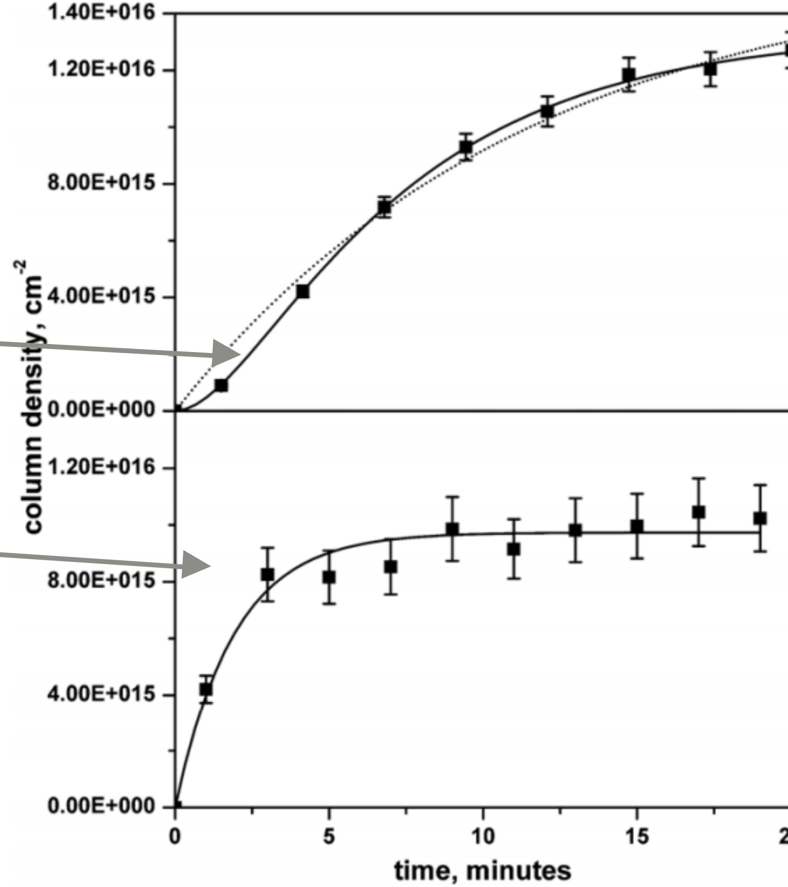
- 2 steps/1 step?

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:

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




Quoted from Kim and Kaiser (2011)

# Production mechanism of $CN^-$

- 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

# Experimental Protocol:

- 1. To compare with previous studies
  - Kim and Kaiser ($CH_4$:$NH_3$ 3:1) (5 keV $e^-$)
  - Kundy et al. ($CH_4$:$NH_3$ 3:2) (1-90 eV $e^-$)
  - We perform ($CH_4$:$NH_3$ 3:2)

  photon sources: VUV (9.27 eV) and EUV (40.8 eV)
- 2. To simulate the surface of Charon
  - Different relative proportion of

  $CH_4$:$NH_3$ 1:5, 1:10, 1:20

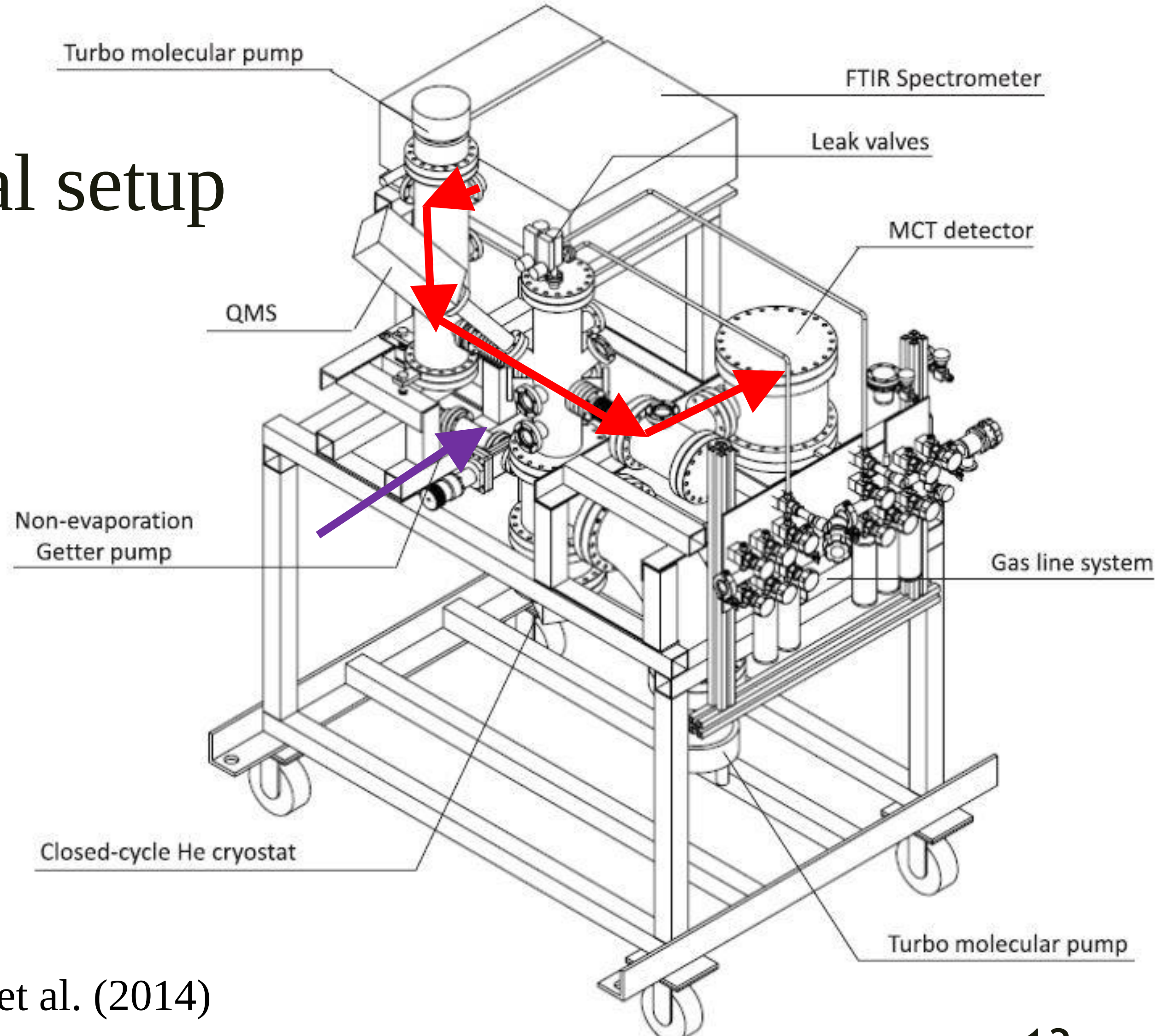
# Methodology

# 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 | -- | -- |

Different initial amount of $CH_4$ correspond to different ratio of $CH_4$:$NH_3$ ice mixtures

# Experimental setup




IR path

VUV/EUV path

Quoted from Chen et al. (2014)

# Experimental Procedure

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

↓

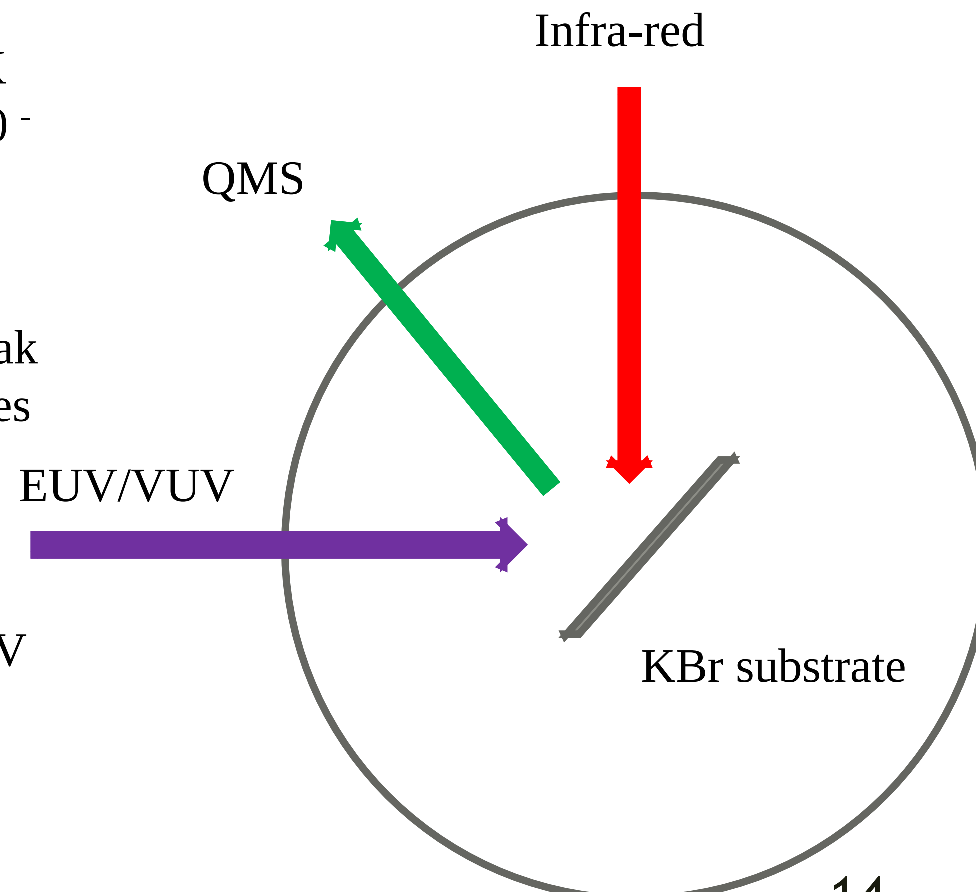
Deposit the ice mixtures through leak valve, with different partial pressures of $CH_4$ and $NH_3$

↓

Irradiate the samples by EUV/VUV

↓

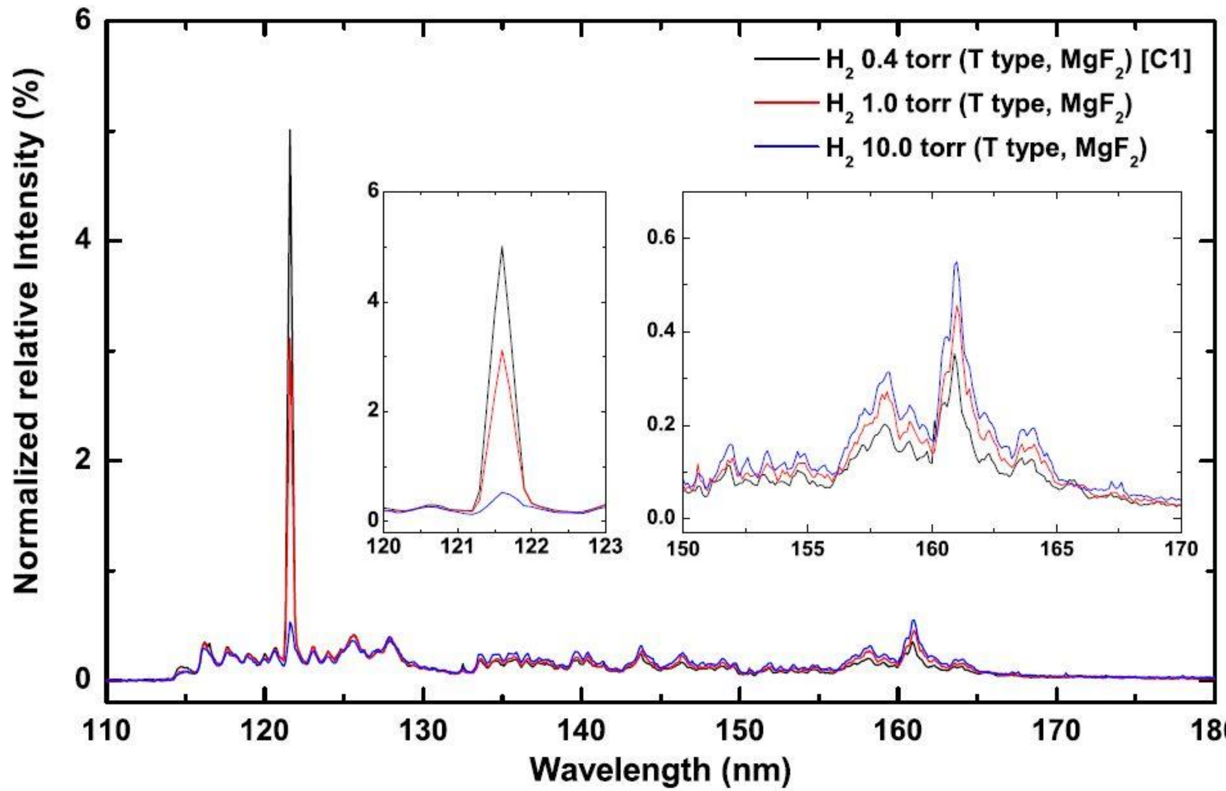
Warm-up with 1 K/min



# The spectrum of VUV (MDHL) energy source

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

- EUV is 40.8 eV (30.4nm) provided by NSRRC




Quoted from Chen et al. (2014)

# Results

# Beer's Law

Absorbance $\tau(v)$ :

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

$n$: number density (molecules cm$^{-3}$)

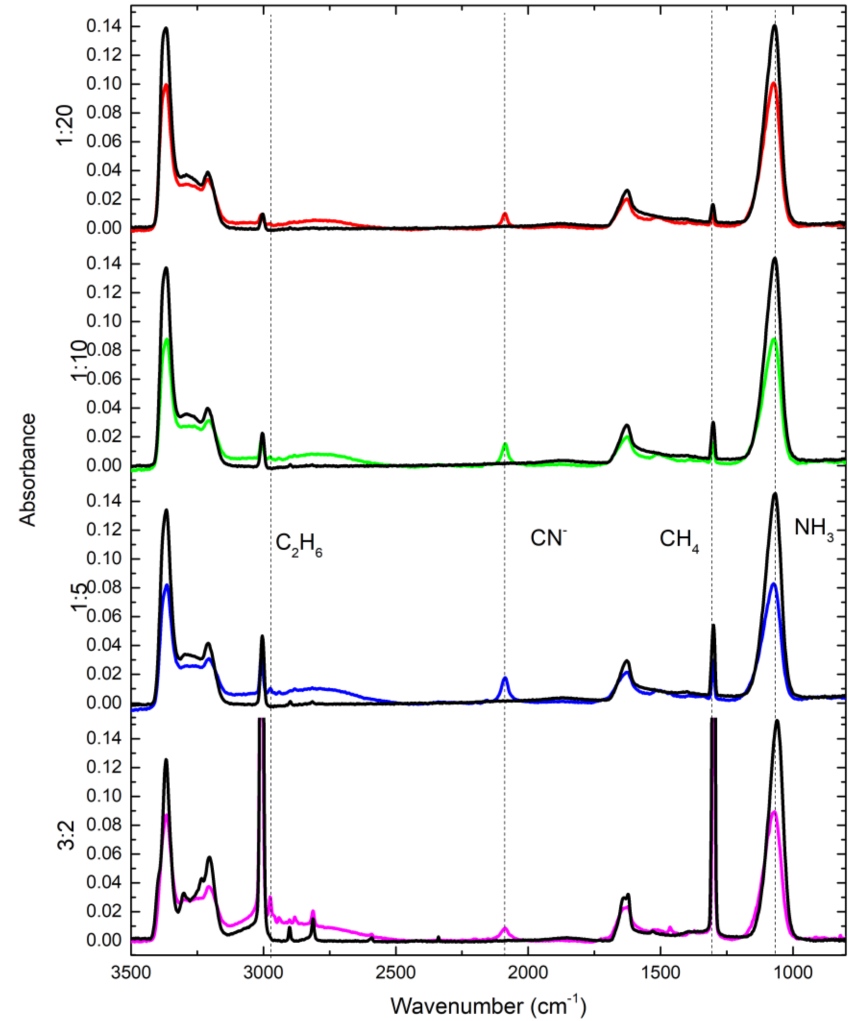
$l$: path length (cm)

$\sigma(v)$: cross-section (cm$^2$ molecules $^{-1}$)

Column density $N$:

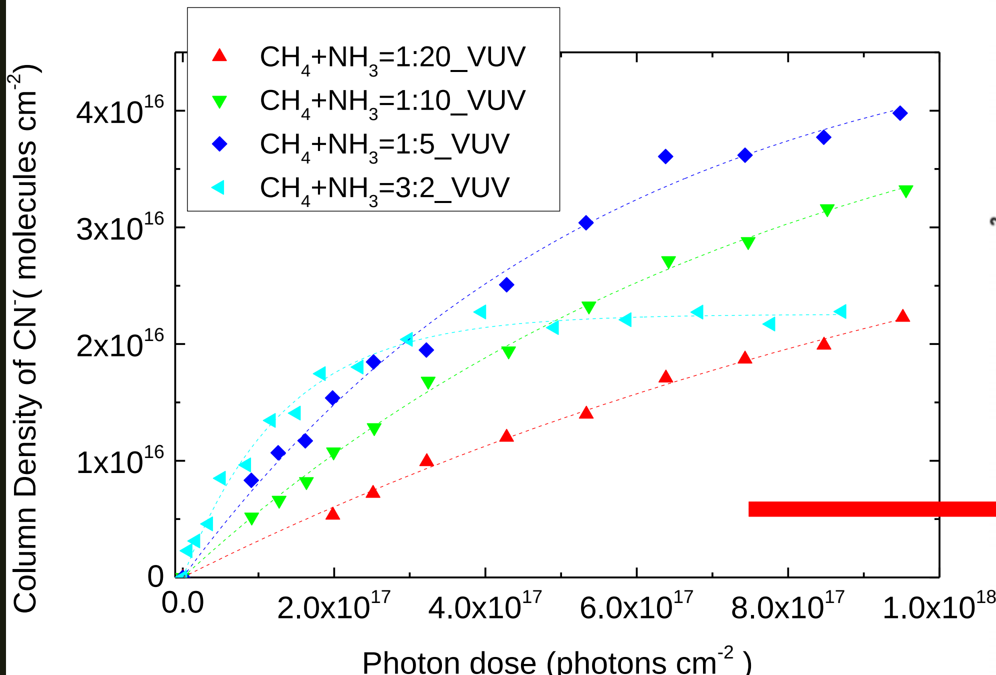
- $N = \frac{\int \tau(v)dv}{A(v)}$

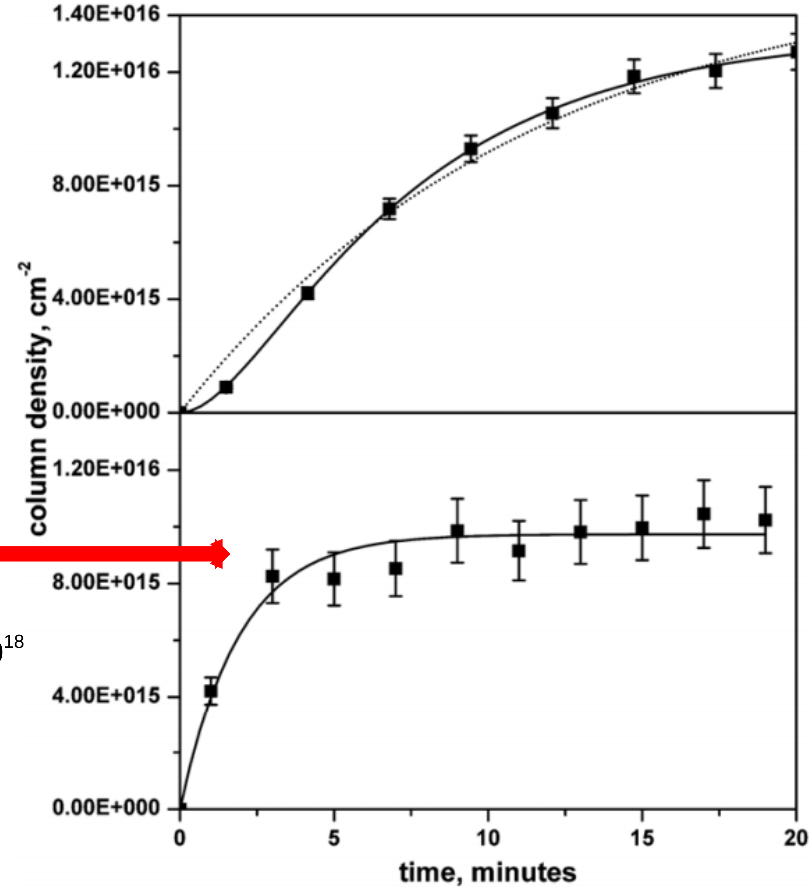
$A(v)$: absorption strength (A-value) (cm molecule$^{-1}$)




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 $CN^-$



# 1. Production of CN⁻

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

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

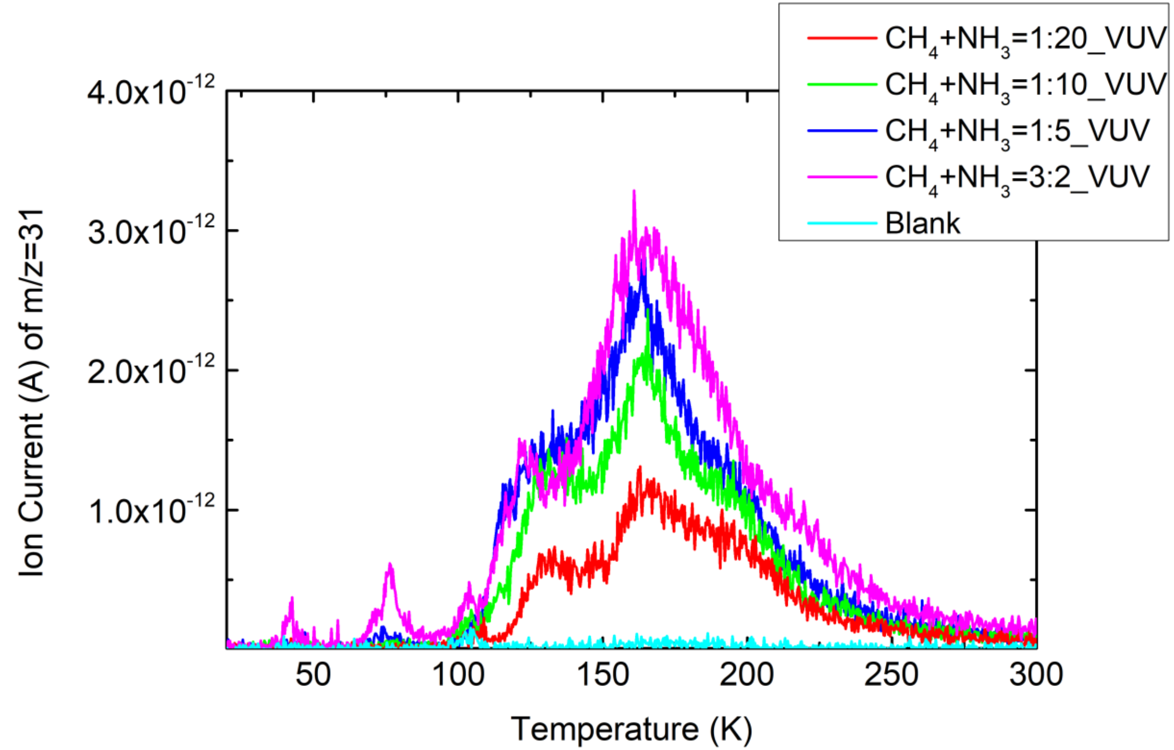
| VUV experiments with $CH_4+NH_3$ ice mixtures | | | |
|---|---|---|---|
| Ratio | A (x$10^{16}$ molecules $cm^{-2}$) | $k_1$ (x$10^{-18}$ $photon^{-1}$) | $k_2$ ($photon^{-1}$) |
| 1:20 | 4.75 ± 0.40 | 0.70 ± 0.09 | >1 |
| 1:10 | 4.51 ± 0.18 | 1.33 ± 0.13 | >1 |
| 1:5 | 4.61 ± 0.18 | 1.93 ± 0.19 | >1 |
| 3:2 | 2.24 ± 0.03 | 8.21 ± 0.70 | >1 |
| Quotated from Kim and Kaiser[2] | | | |
| Ratio | A(x$10^{16}$ molecules $cm^{-2}$) | $k_1$ ($\times 10^{-3}$ $s^{-1}$) | $k_2$ ($\times 10^{-3}$ $s^{-1}$) |
| 0.1 $\mu$A $e^-$ with $CH_4+NH_3$ ice mixtures | | | |
| 3:1 | 1.3 ± 0.0 | 2.7 ± 0.3 | 8.9 ± 1.6 |
| 1 $\mu$A $e^-$ 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 $CN^-$

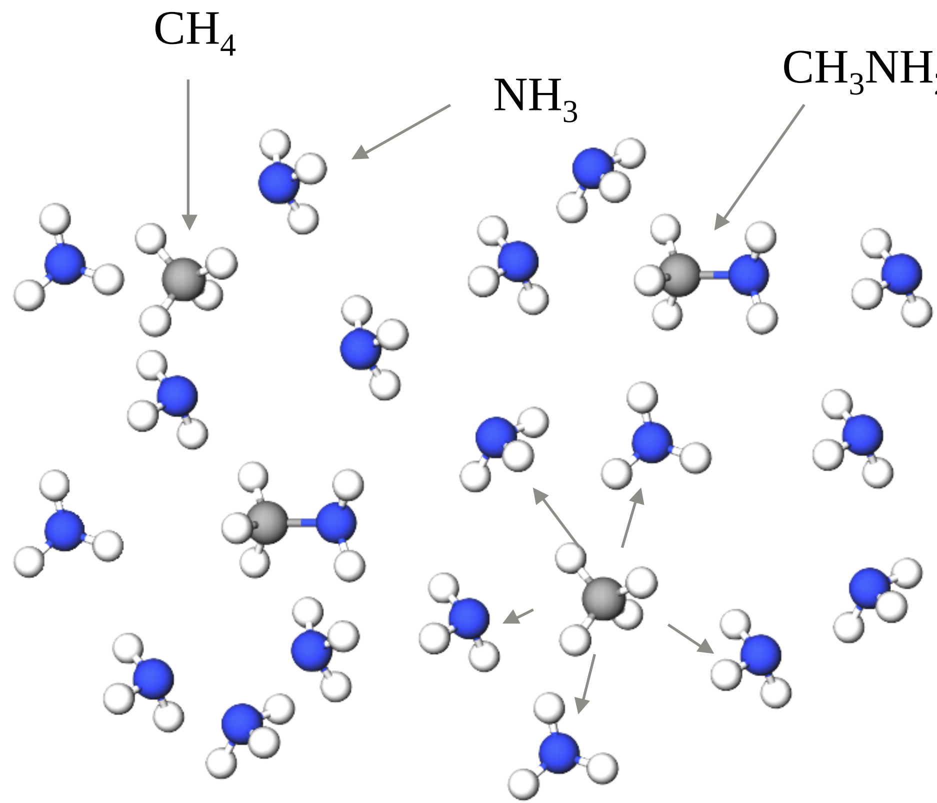
Methylamine ($CH_3NH_2$) with m/z=31 is detected by QMS

CN$^-$ is formed via a 2 step mechanism.



# 2. The scenario for $NH_3$ dominating ice mixtures

Once $CH_4$ becomes $CH_3$ radical, $CH_3NH_2$ can be easily formed and hence become CN$^-$.

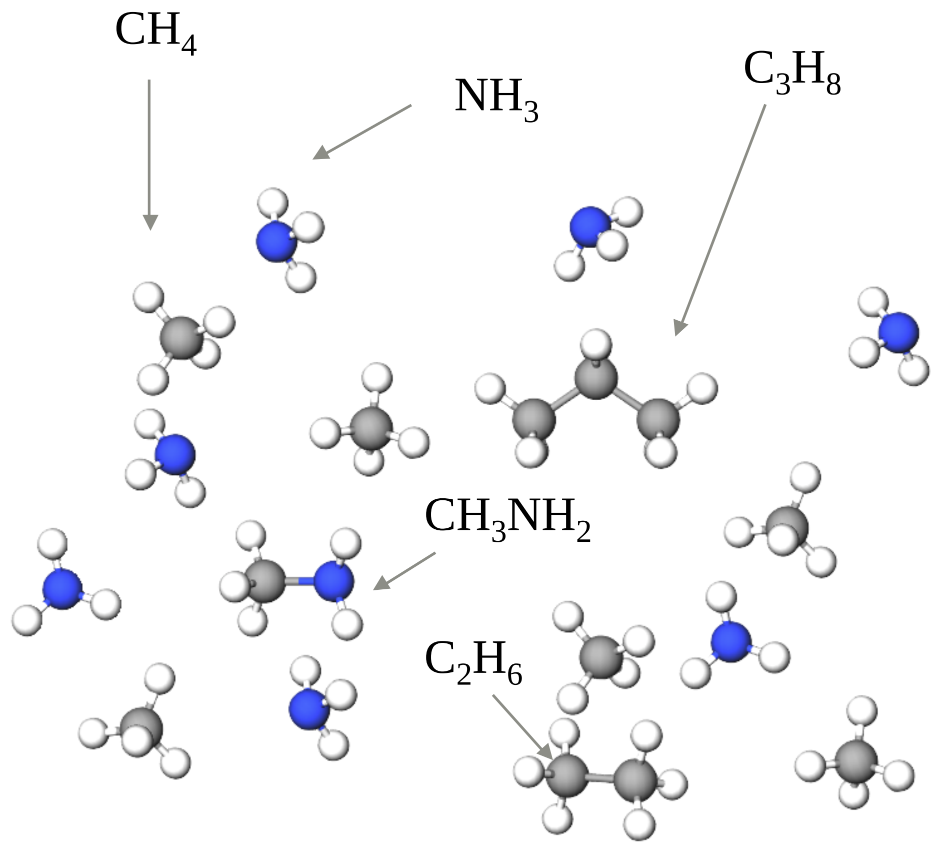



A diagram of $CH_4$:$NH_3$ = 1:5

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

$CH_3NH_2$ (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 $C_2H_4$ + $CH_4$)

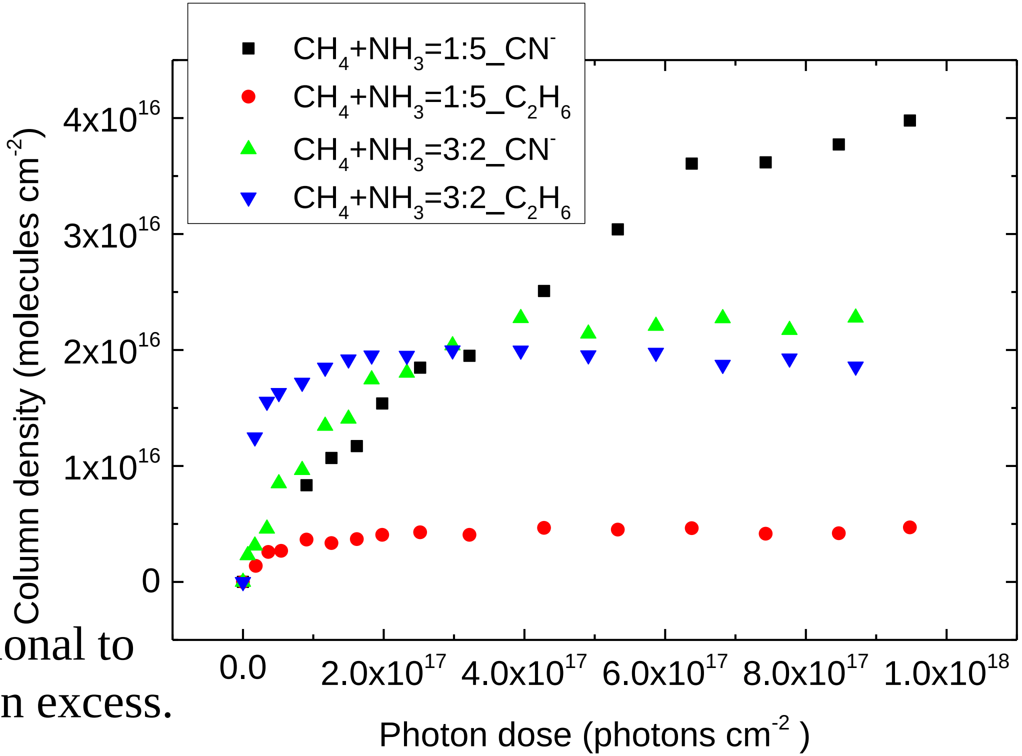
$C_2H_6$ can form easier than $NH_3$ dominating case




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

# 2. The relations between $CN^-$ ($NH_3$ dominant) and $C_2H_6$ ($CH_4$ dominant)

| $CH_4:NH_3$ | $C_2H_6$ (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 |

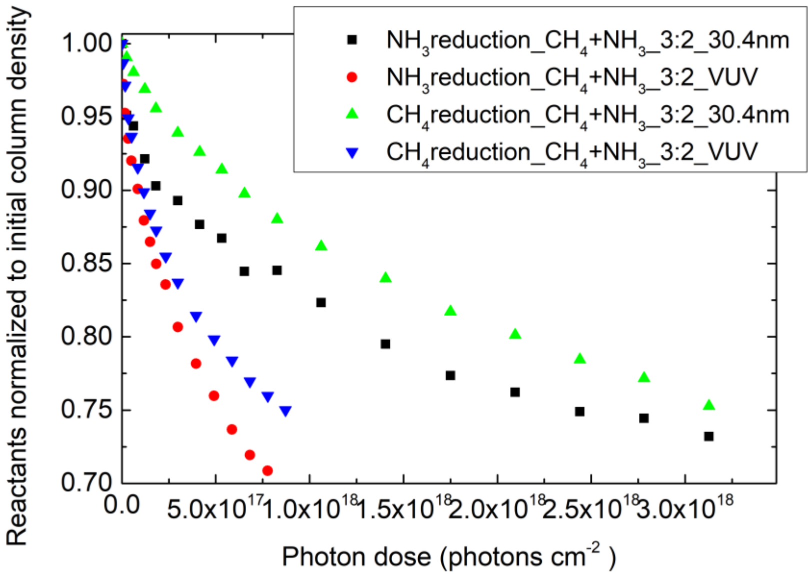



Concentration of $CN^-$ is not proportional to initial amount of $CH_4$ when $CH_4$ is in excess.

# 3. Rate constant of reactants by EUV (40.1 eV) and VUV (9.27 eV)

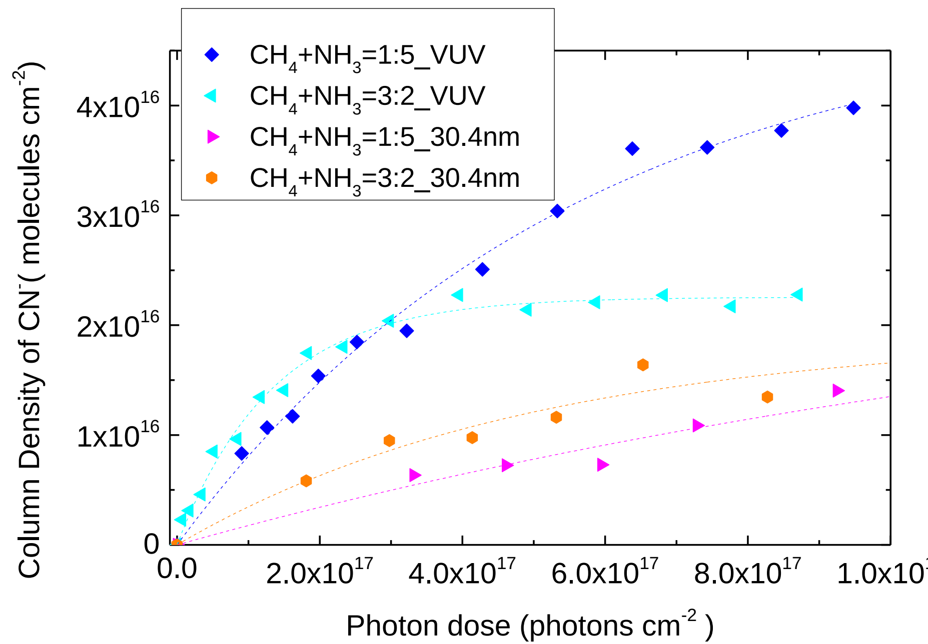
- Fitting with $y = Ae^{-kx} + C$ (first order decay)

| Ratio of $CH_4+NH_3$ | 3:2 | | 1:5 | |
|---|---|---|---|---|
| k (photons$^{-1}$cm$^2$) | $CH_4$ (x $10^{-18}$) | $NH_3$ (x$10^{-18}$) | $CH_4$ (x $10^{-18}$) | $NH_3$ (x$10^{-18}$) |
| VUV (MDHL) | 3.70±0.18 | 2.89±0.10 | 2.70±0.07 | 1.17±0.12 |
| EUV (30.4nm) | 0.61±0.03 | 0.91±0.11 | 0.49±0.02 | 0.56±0.06 |
| Destruction cross-section ratio | 6.06±0.07 | 3.18±0.12 | 5.52±0.07 | 2.07±0.13 |



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

| k (photon $^{-1}$cm$^2$) | $CH_4 : NH_3$ 3:2 (x $10^{-18}$) | $CH_4 : NH_3$ 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 |
| Destruction cross-section ratio ($CH_4$) | 6.06±0.07 | 5.52±0.07 |
| Destruction cross-section ratio ($NH_3$) | 3.18±0.12 | 2.07±0.13 |



# 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)

# Astrophysical Implications

# Estimate the column density of $CN^-$ formed after winter on Charon (from result 2)

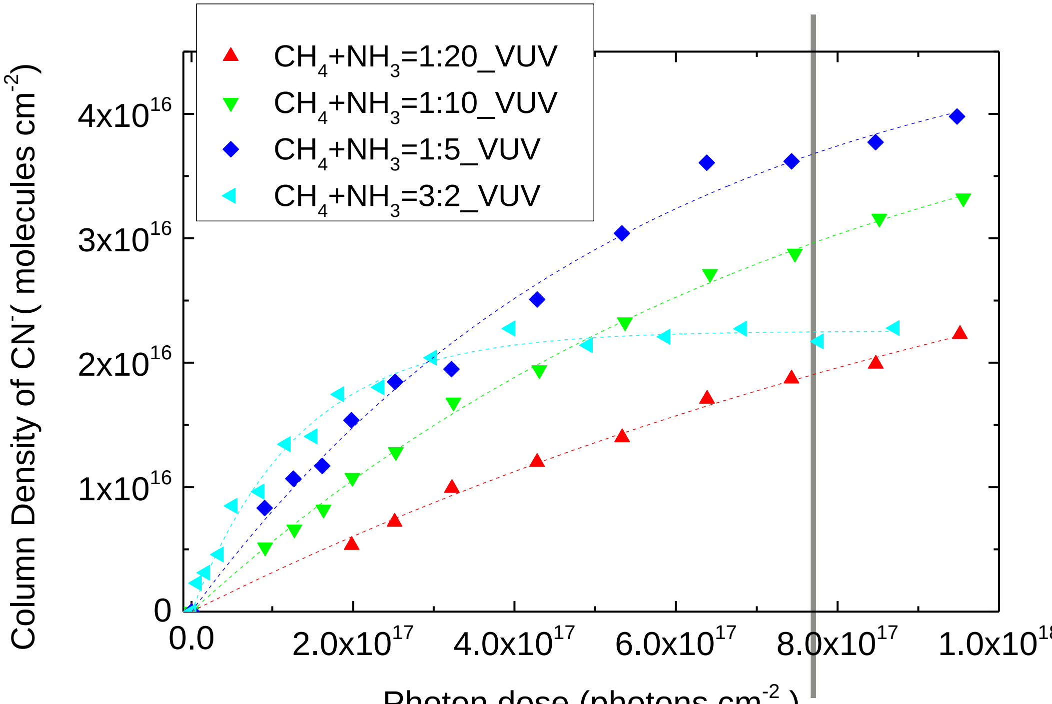
Ly-α flux: 1.9 x $10^9$ eV $cm^{-2}$ $s^{-1}$ (Grundy et al. 2016)

→photon dose after 1 Pluto winter $7.64 \times 10^{17}$ photons $cm^{-2}$

$CH_4$ after winter ~173 ML

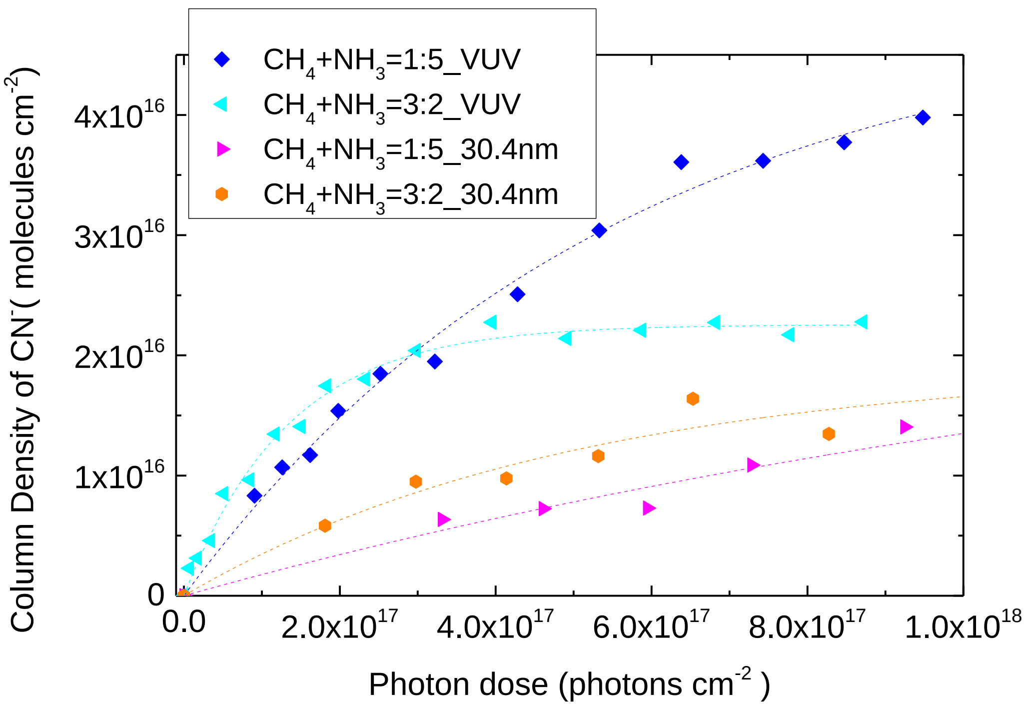
Assume the column density of $NH_3$ is 600 ML

| $CH_4$:$NH_3$ | $CH_4$ (ML) | $CN^-$ (ML) |
|---|---|---|
| 1:5 | 120 | 36.6 |
| 1:10 | 60 | 29.5 |
| 1:20 | 30 | 18.9 |
| 3:2 | 900 | 22.5 |



# Ly-α is the main photon source to produce $CN^-$ on Charon (from result 3)

- VUV(19.1% of which is Ly-α) will produce $CN^-$ 3.06 - 4.28 times more efficient than EUV
- It is expected that Ly- α will produce $CN^-$ more efficient than EUV
- Ly- α flux is 1 order of magnitude more intense than EUV irradiations at 39.1 A.U. (Grundy et al. 2016)
  - Ly-α flux: $1.9 \times 10^9$ eV $cm^{-2}$ $s^{-1}$
  - EUV flux: $8.7 \times 10^7$ eV $cm^{-2}$ $s^{-1}$



# Conclusion

- 1. Detection of methylamine implies that $CN^-$ is formed via a 2 step mechanism.
- 2. Formation of $CN^-$ is not proportional to the initial column density of $CH_4$ when $CH_4$ is in excess.
  - This implies that we have to experimentally estimate the column density of $CN^-$ after Charon winter for further investigations.
- 3. The reduced destruction cross-section of EUV (30.4nm) irradiation is the main factor of reducing the formation rate of $CN^-$.
  - This implies that Ly-α (VUV) is the main photon source to produce $CN^-$ on Charon.

Q & A

# Production yield and production rates

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