

VUV AND EUV IRRADIATION OF CH₄ + NH₃ ICE MIXTURES

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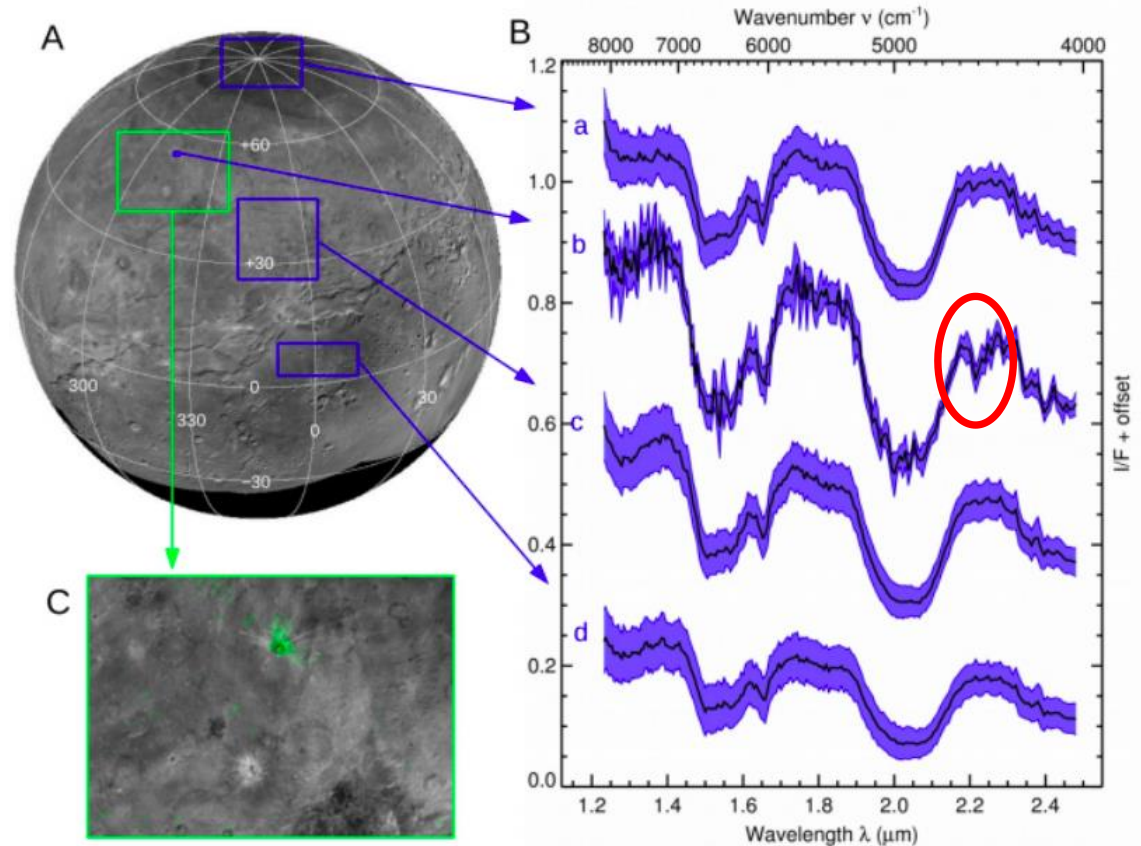
■ Astrophysical Implications

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

Motivation

Ammonia on Organa Crater

- *Ammonia* hydrate ($2.21\mu\text{m}$) was detected all over the surfaces, especially on Organa Crater

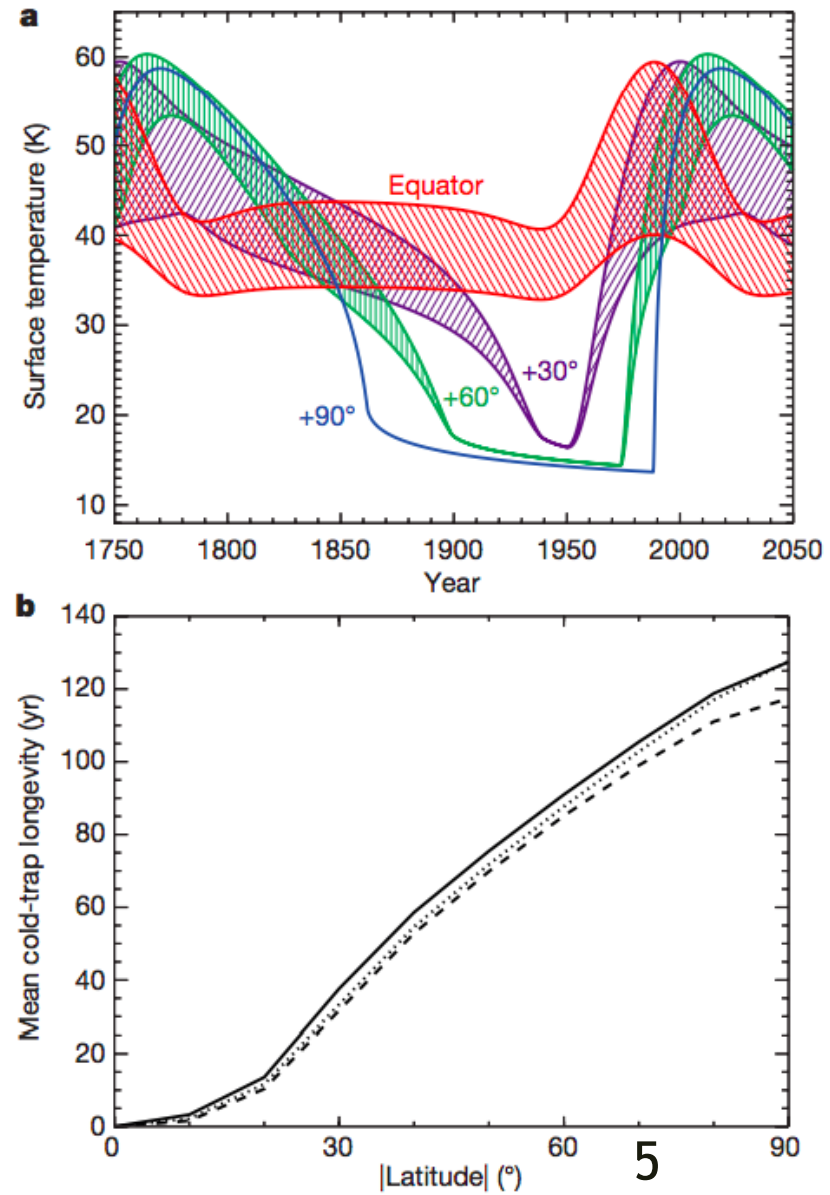


from Grundy et al. (2016)

Surface temperatures at different latitudes

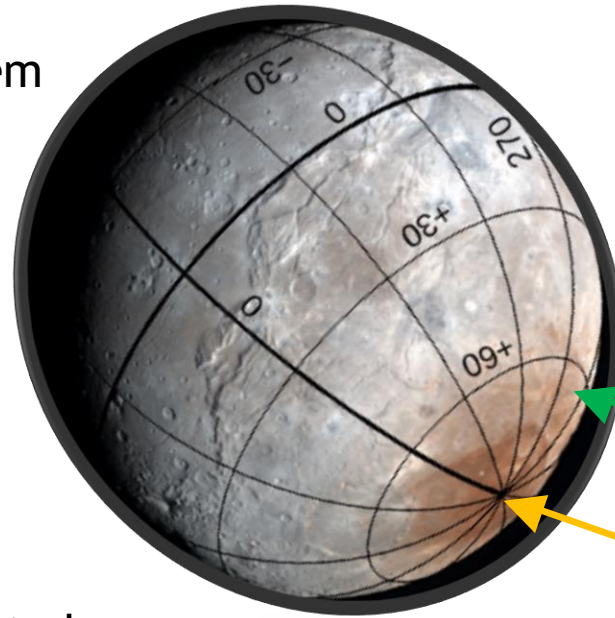
- Thermal model from Grundy et al. (2016) shows the pole position is **below 25 K** for 130 years
- **Methane can condense** on those positions where the temperature is below 25 K.

Quoted from Grundy et al. (2016)



What astrophysical environments are we demonstrating?

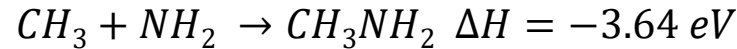
Charon in Pluto system



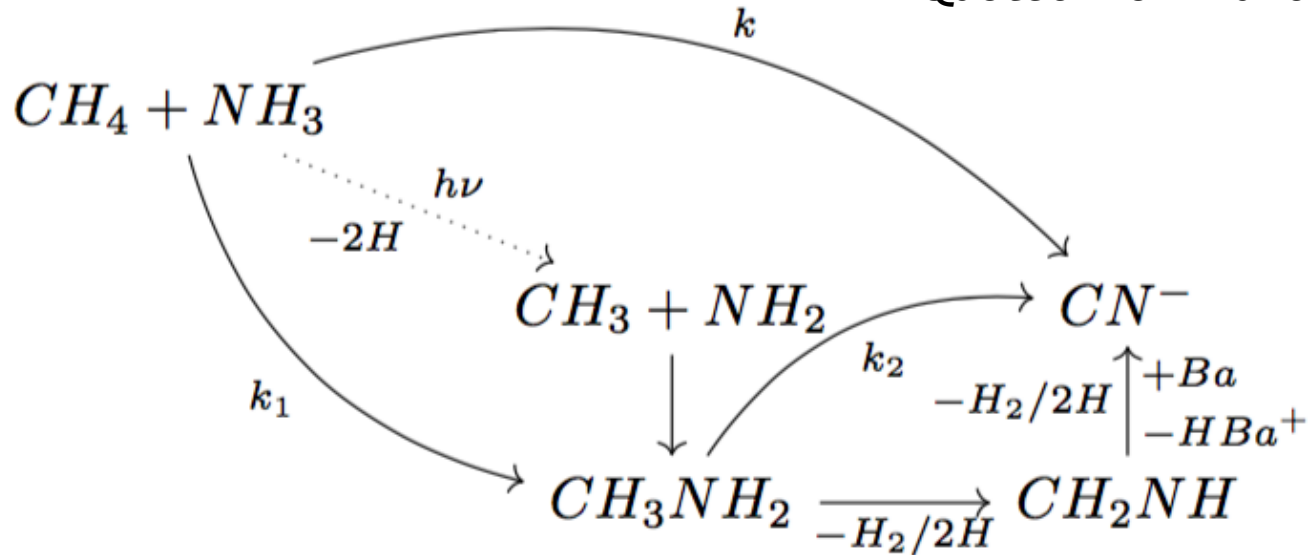
Quoted from Grundy et al.
(2017)

Production mechanism of CN^-

Enthalpy of CH_3NH_2 formation



Quoted from Kundu et al. (2017)



Quoted from Kim and Kaiser (2011)

Production of CN^-

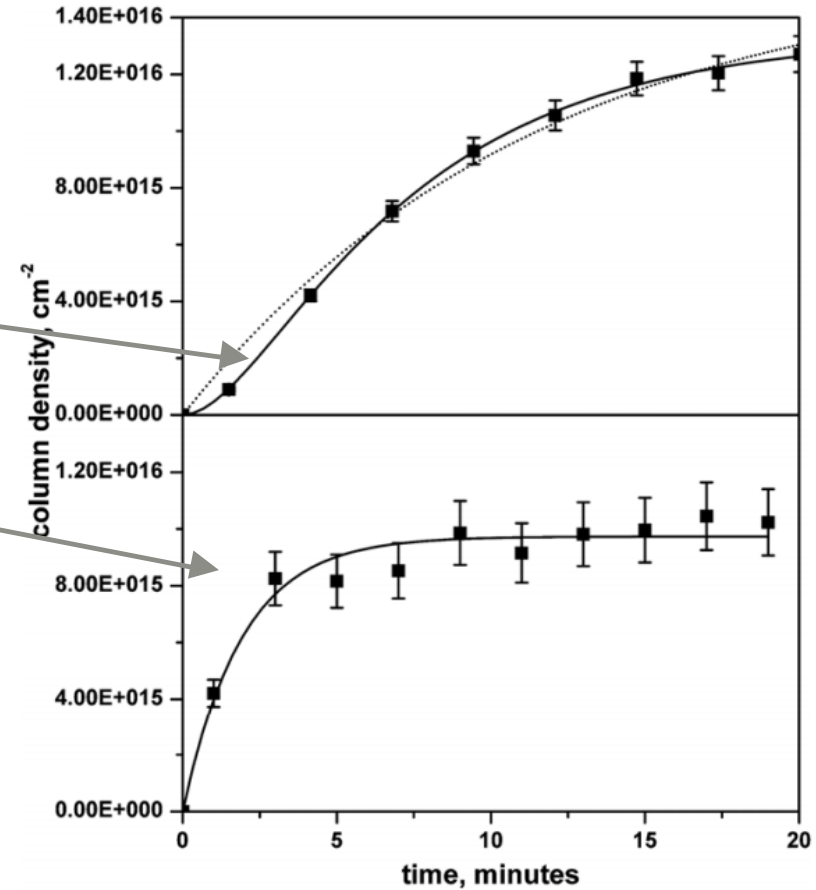
- 2 steps/1 step?

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:

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



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
- How about EUV and VUV photons?
 - We try to study the mechanism by VUV and EUV photons

Short Summary

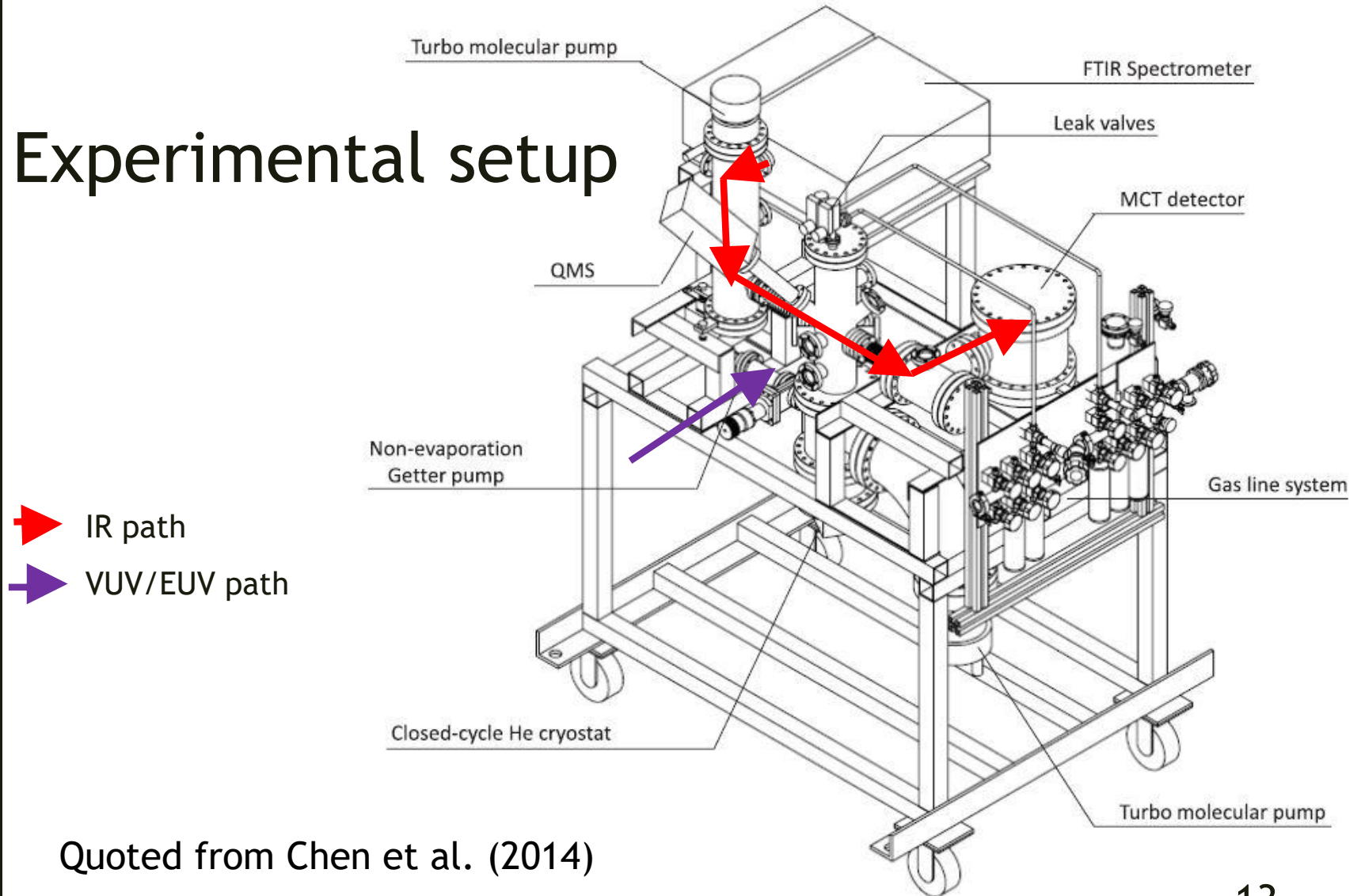
- 1. To compare with **previous studies**
 - *Kim and Kaiser ($\text{CH}_4:\text{NH}_3$ **3:1**) and Kundy et al. (2017) ($\text{CH}_4:\text{NH}_3$ **3:2**)*
 - *We perform experiment of **$\text{CH}_4+\text{NH}_3 = 3:2$***
 - *Variation of photon sources: from VUV to EUV*
- 2. To simulate the **surface of Charon**
 - *Different relative proportion of **$\text{CH}_4:\text{NH}_3 = 1:5, 1:10, 1:20$***

Methodology

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	--	--

Experimental setup



Quoted from Chen et al. (2014)

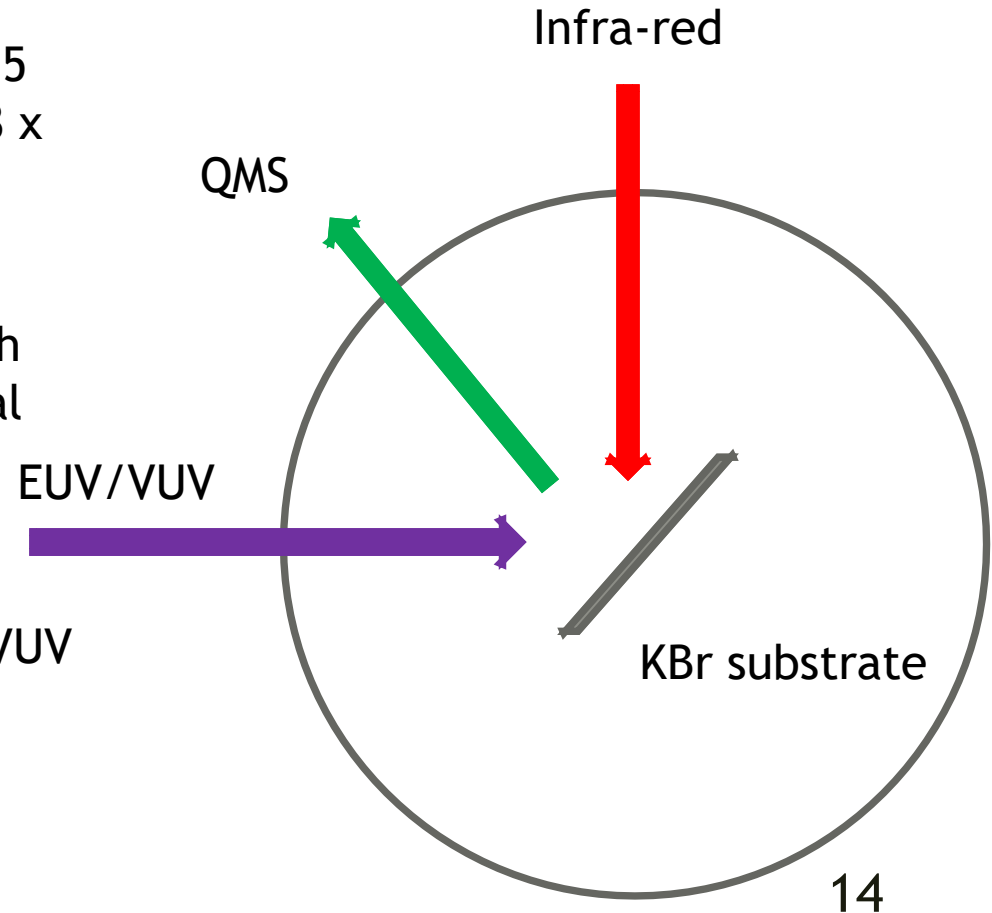
Experimental Protocol

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

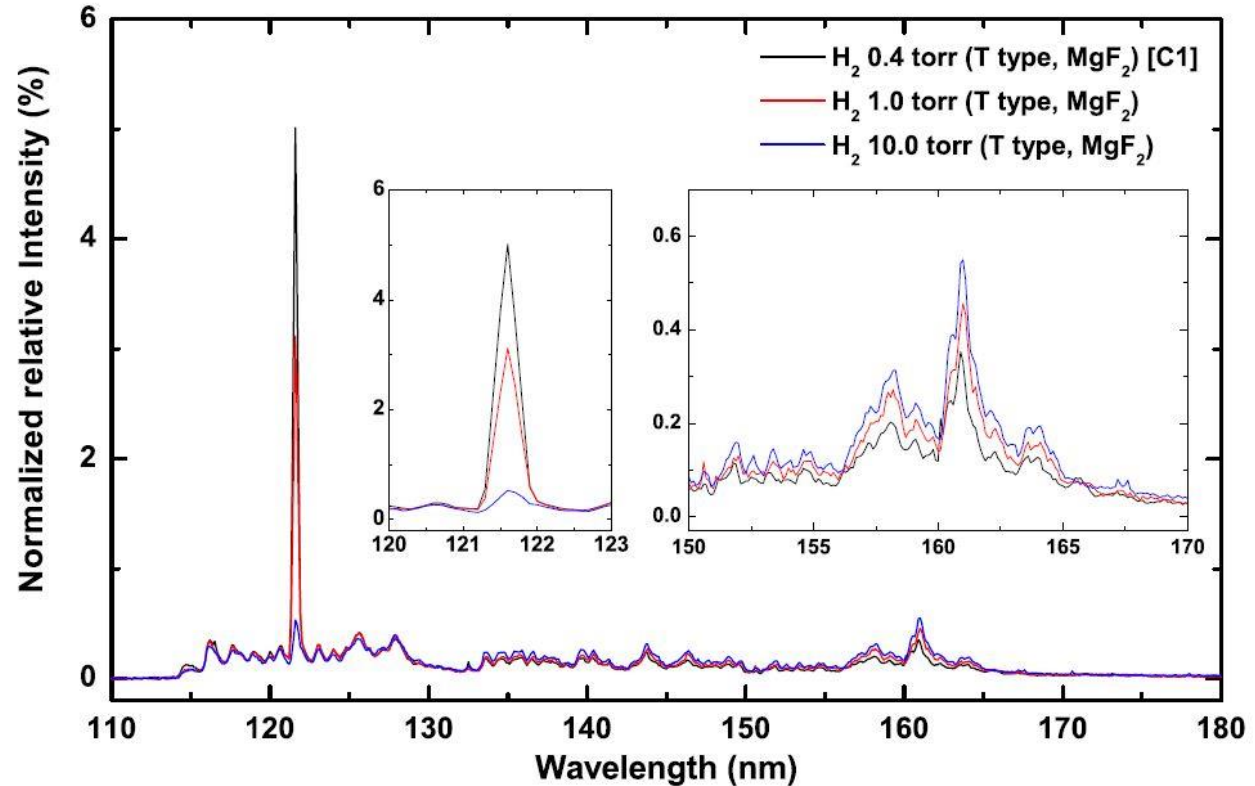
Irradiate the samples by EUV/VUV

Warm-up with 1 K/min



The spectrum of VUV (MDHL) energy source

- H₂ 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

Transmittance $T(\nu)$ is defined by:

$$\blacksquare \quad T(\nu) = \frac{I(\nu)}{I_o(\nu)}$$

Absorbance $\tau(\nu)$ is defined by:

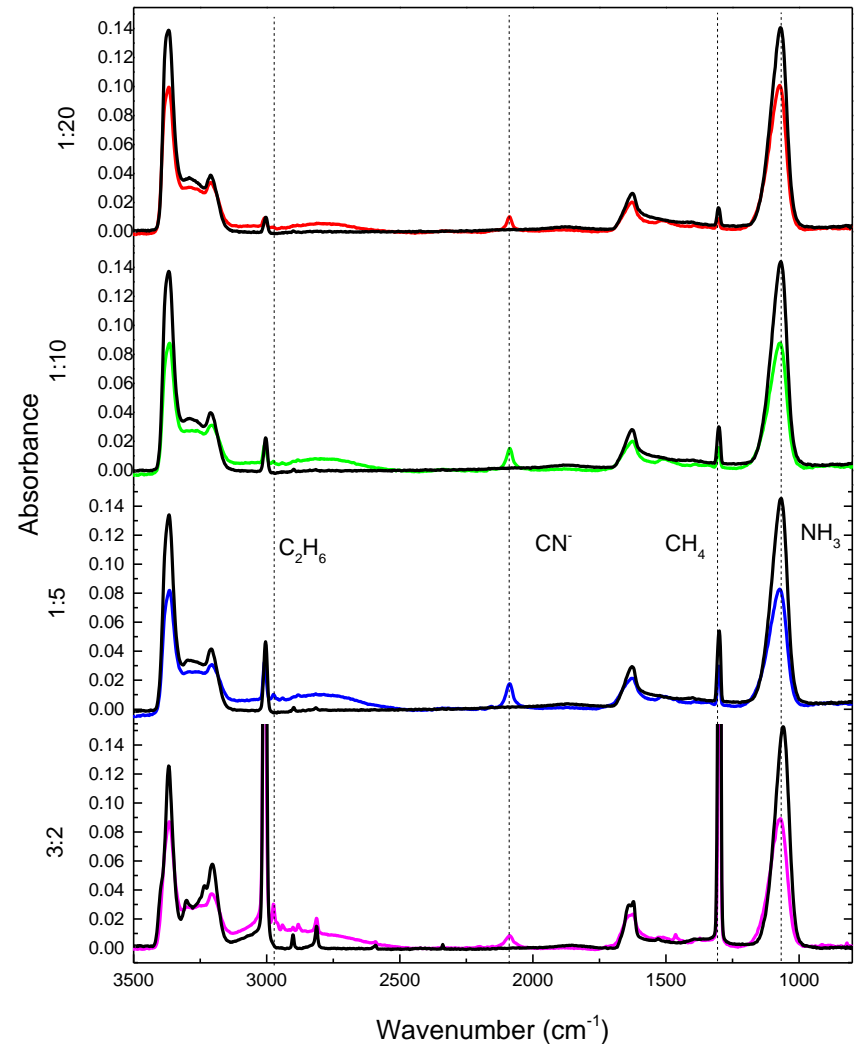
$$\blacksquare \quad \tau(\nu) = -\ln T = -\ln \left(\frac{I(\nu)}{I_o(\nu)} \right) = n l \sigma(\nu)$$

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

Column density N is defined by:

$$\blacksquare \quad N = \frac{\int \tau(\nu) d\nu}{A(\nu)}$$

- where N is column density (molecules cm^{-2}), $A(\nu)$ 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⁻

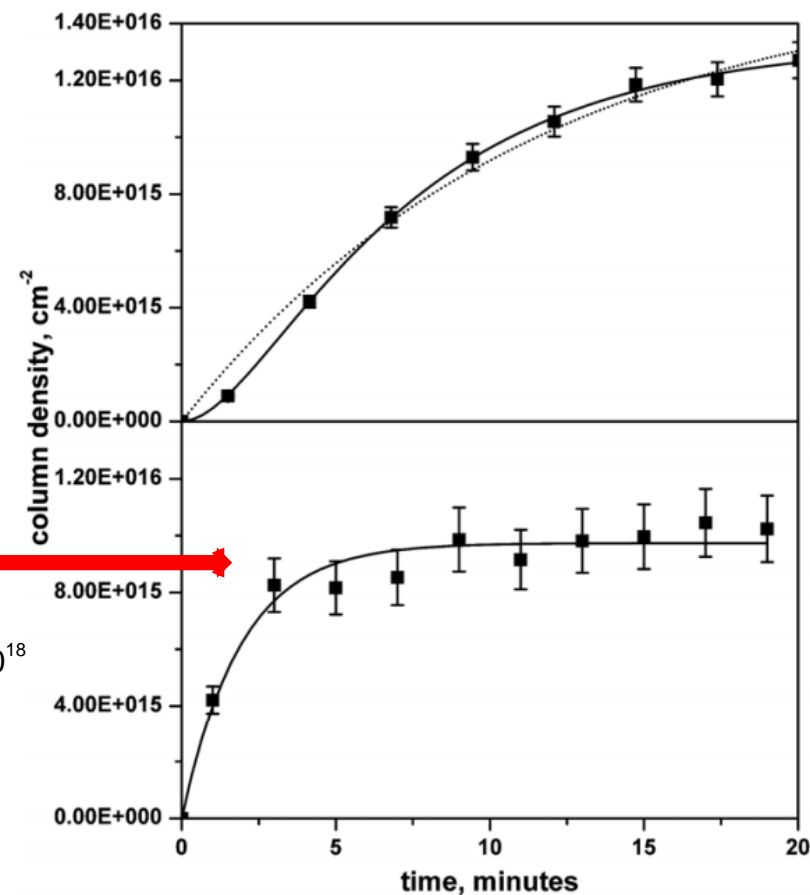
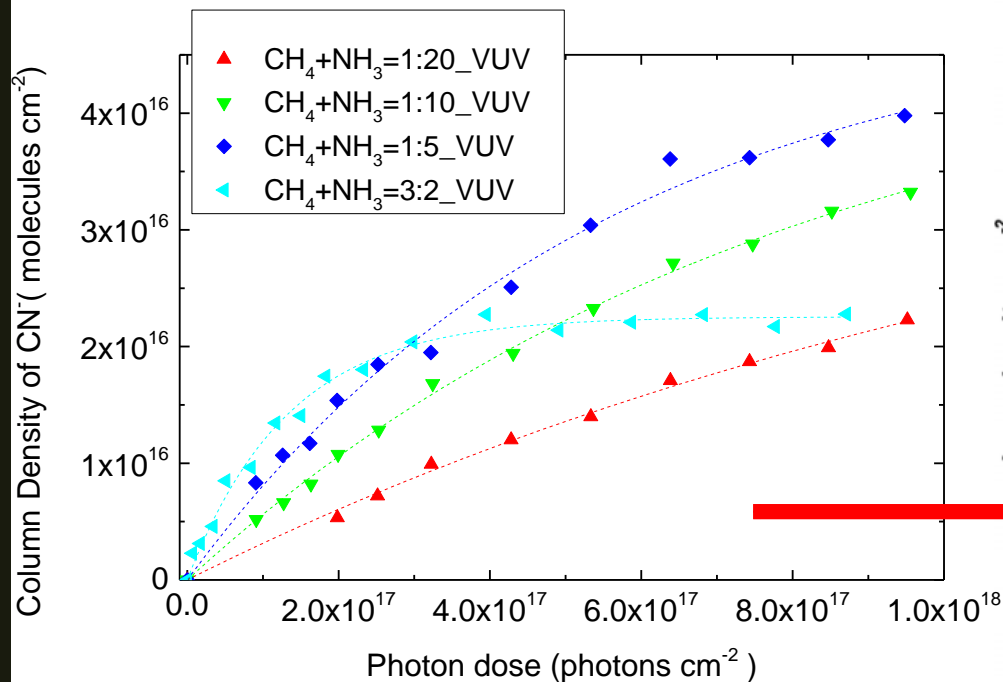
■ $[CN^-] = \left(1 + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} - \frac{k_2 e^{-k_1 t}}{k_2 - k_1}\right) [A]_o$

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

VUV experiments with CH ₄ +NH ₃ ice mixtures			
Ratio	A (x10 ¹⁶ molecules cm ⁻²)	k ₁ (x10 ⁻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(x10 ¹⁶ molecules cm ⁻²)	k ₁ (× 10 ⁻³ s ⁻¹)	k ₂ (× 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	»1

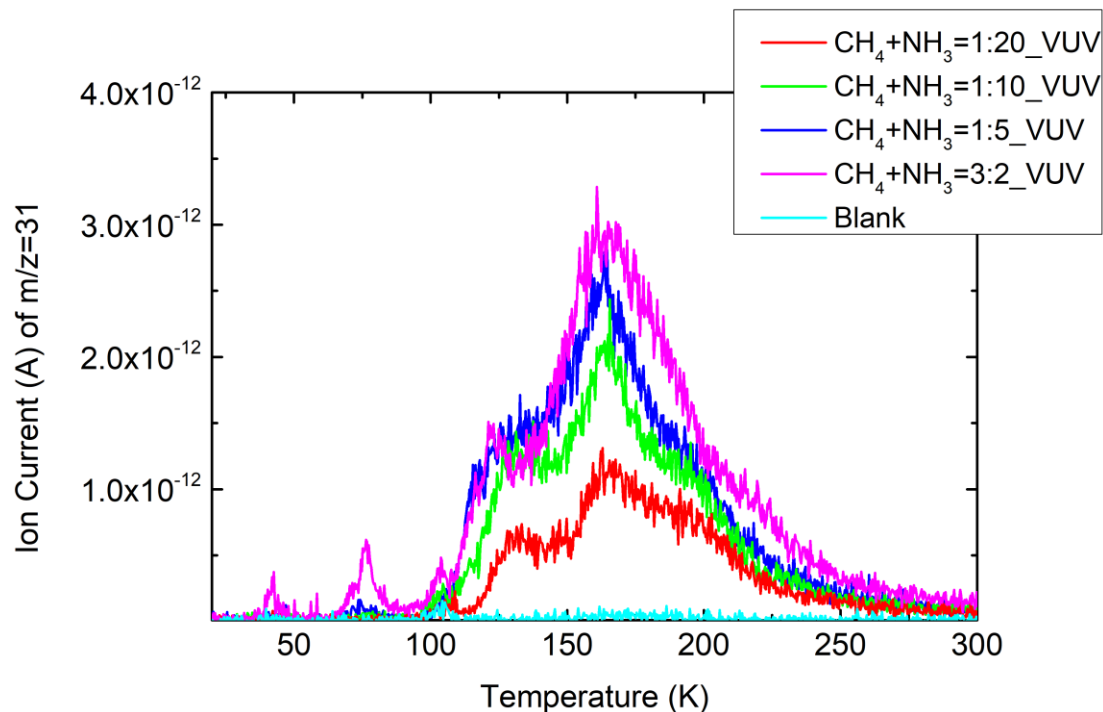
A represents the amount of CN⁻ we may obtain when irradiated the ice for infinitely long.

1. Production of CN⁻



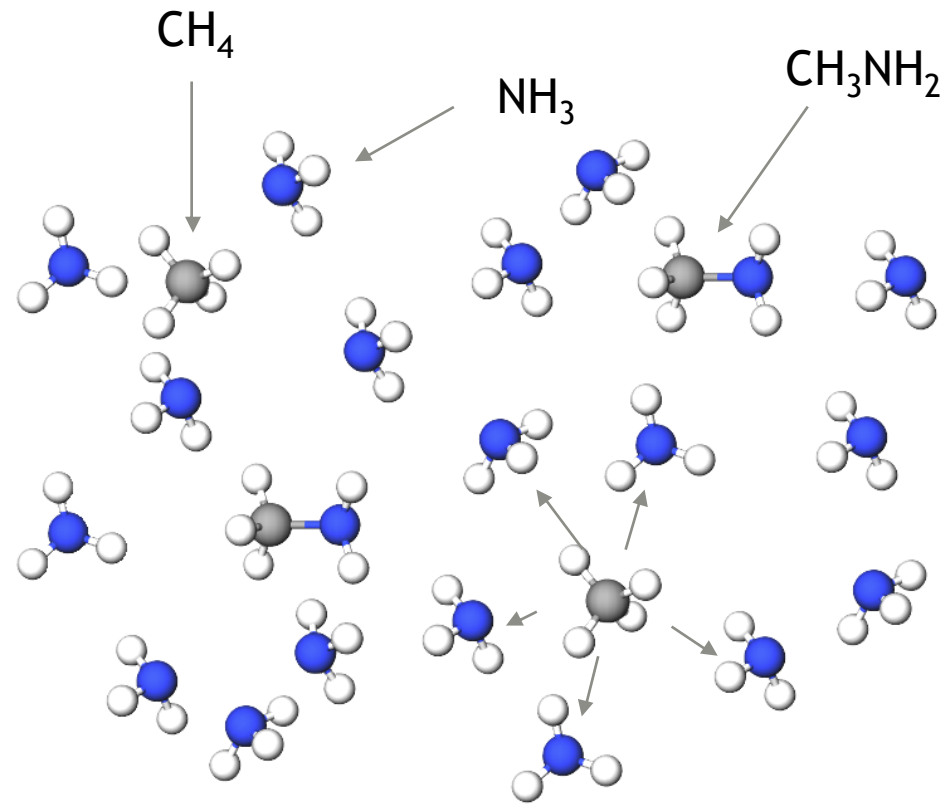
1. Production of CN^-

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



2. The scenario for NH_3 dominating ice mixtures

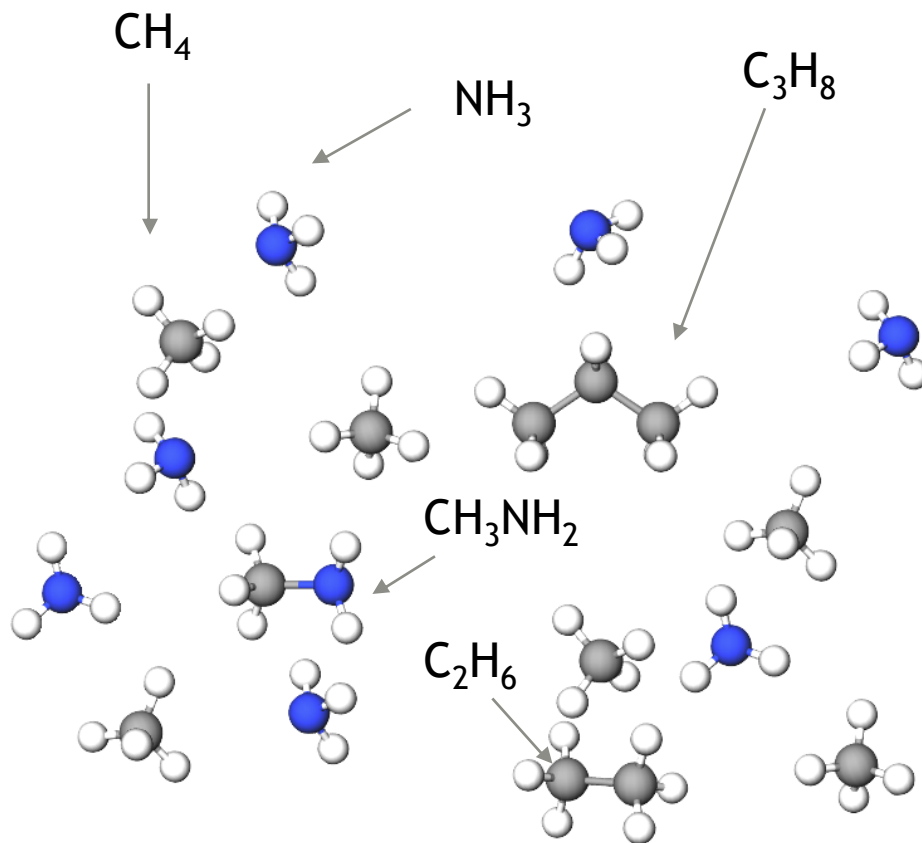
Once CH_4 becomes CH_3 radical, it can easily form CH_3NH_2 and hence become CN^- .



A diagram of $\text{CH}_4:\text{NH}_3 = 1:5$

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)

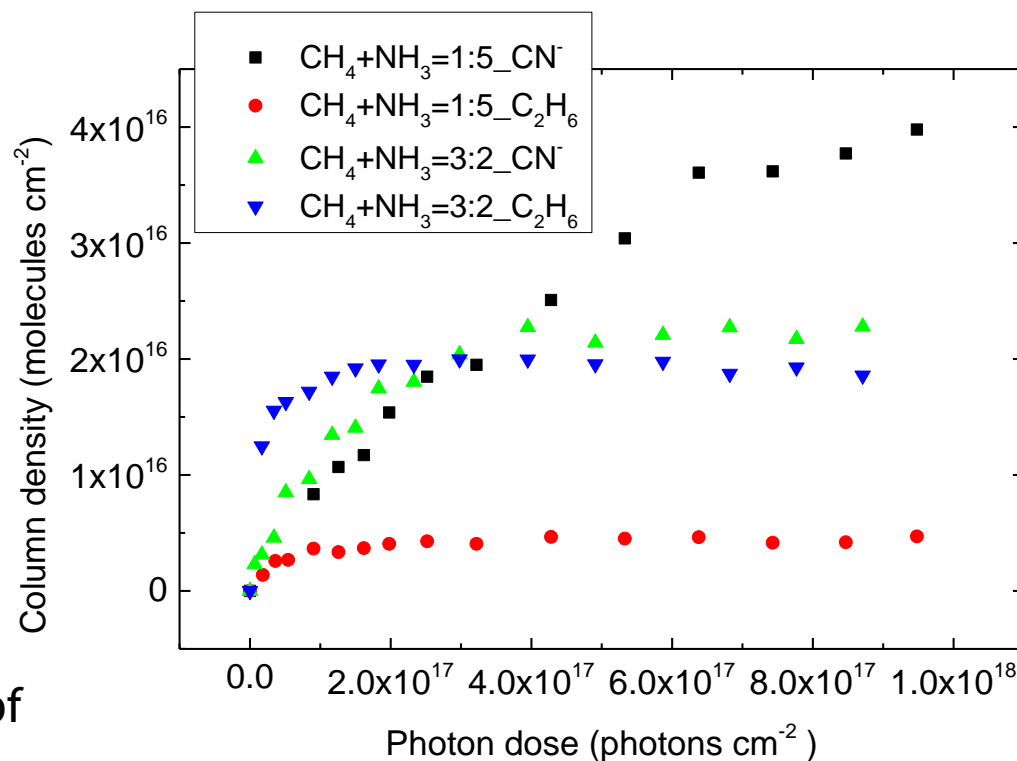


A diagram of $\text{CH}_4 + \text{NH}_3 = 3:2$

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

$\text{CH}_4:\text{NH}_3$	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.



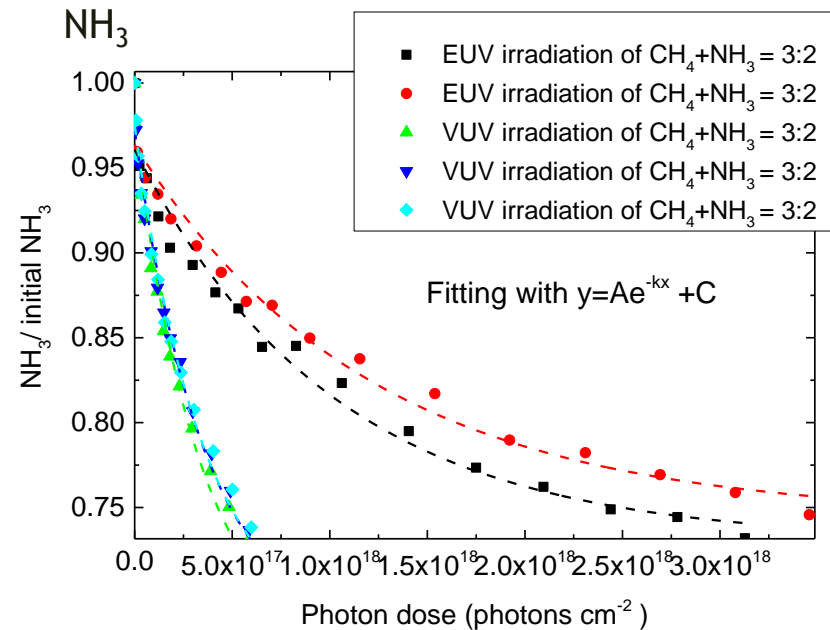
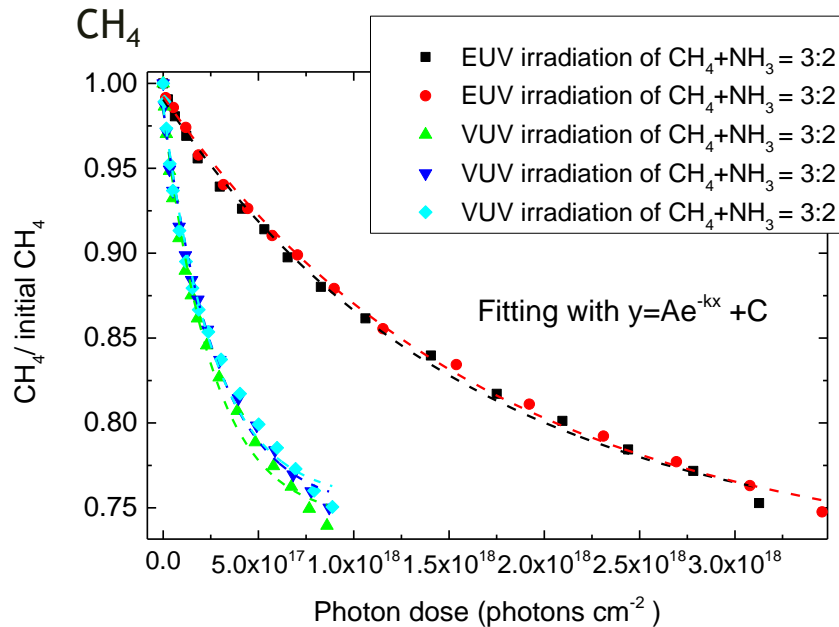
3. Energy needed for forming radicals by EUV (40.1 eV) and VUV (9.27 eV)

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))

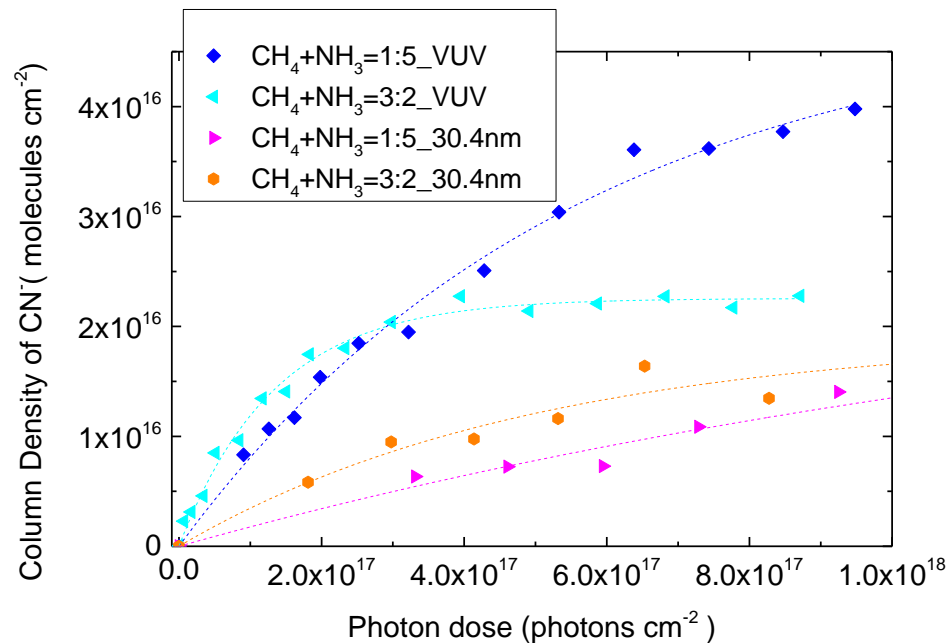
3. Destruction cross-section of EUV (40.1 eV) and VUV (9.27 eV)

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



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:

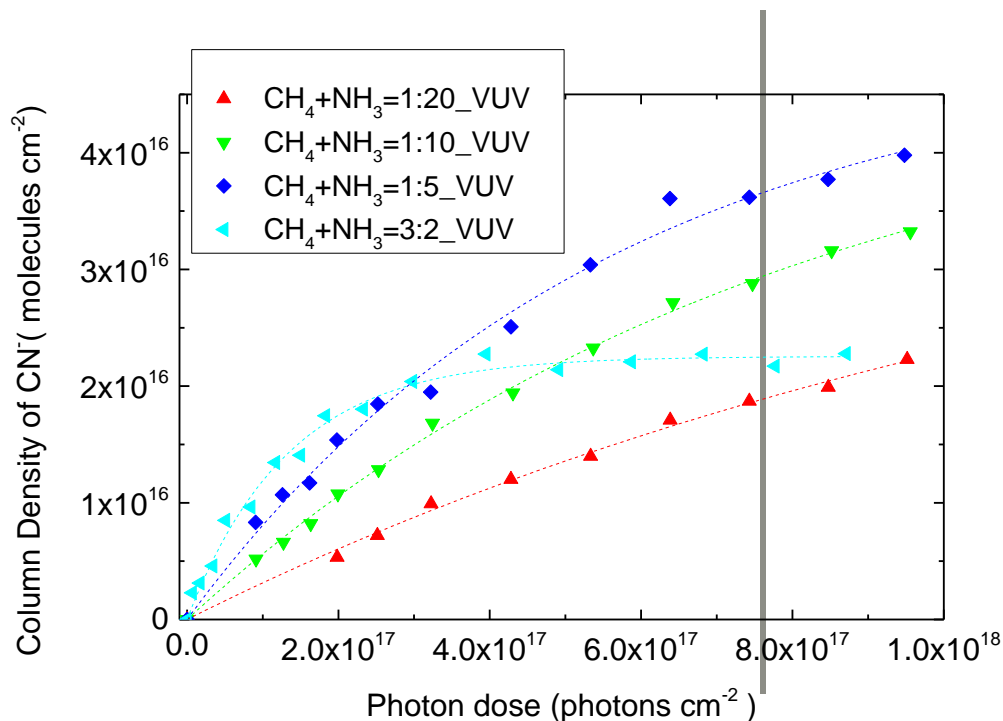
- Ly α exposure: $1.9 \times 10^9 \text{ eV cm}^{-2} \text{ s}^{-1}$
(Grundy et al. 2016)

→ photon dose: $7.64 \times 10^{17} \text{ photons cm}^{-2}$

- CH₄ deposition rate:
(Hoey et al. 2017)

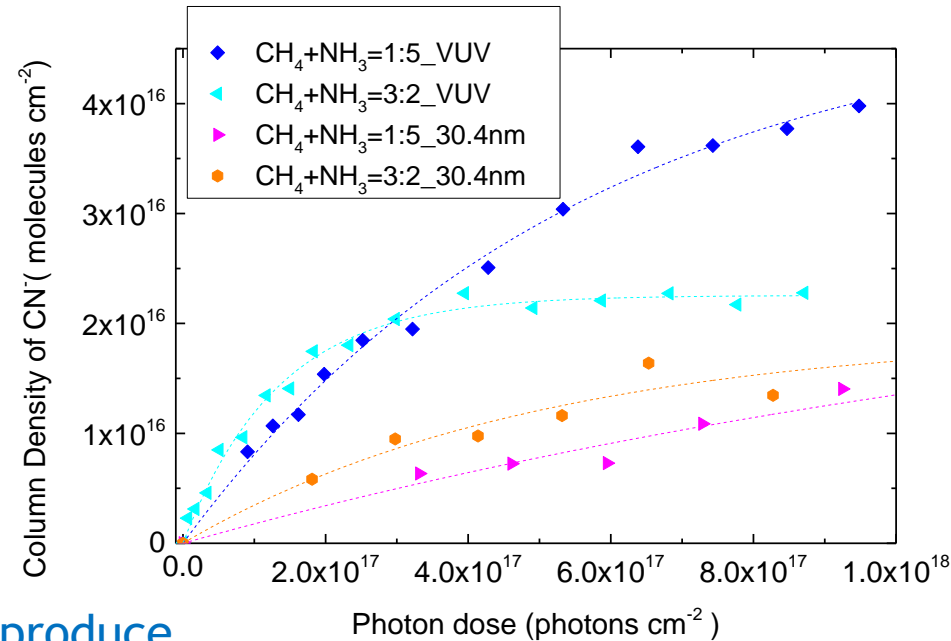
→ ~110-150 ML in 130 earth years

CH ₄ +NH ₃ 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

- 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- α exposure: $1.9 \times 10^9 \text{ eV cm}^{-2} \text{ s}^{-1}$
- EUV exposure: $8.7 \times 10^7 \text{ eV cm}^{-2} \text{ s}^{-1}$



Ly- α is the main energy source to produce CN⁻ on Charon

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

Production yield and production rates

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

