

VUV AND EUV IRRADIATION OF CH₄ + NH₃ ICE MIXTURES

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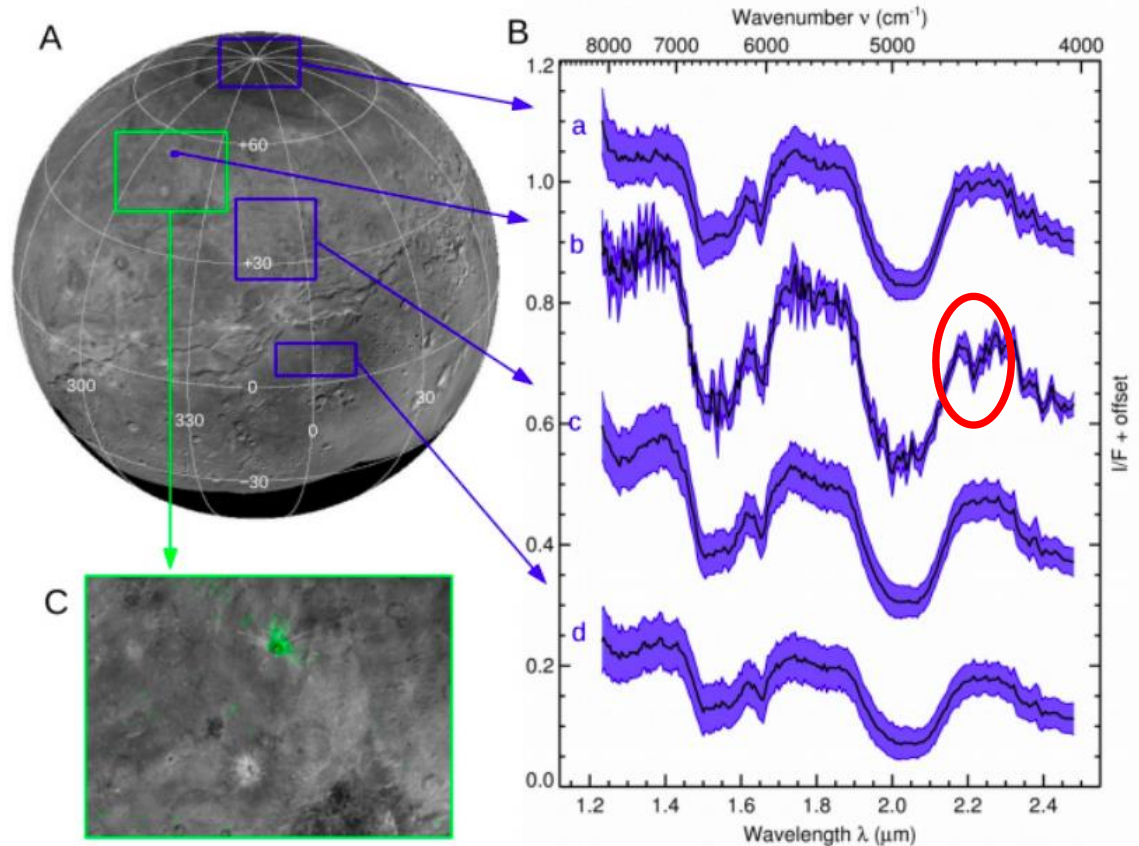
■ Astrophysical Implications

- *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

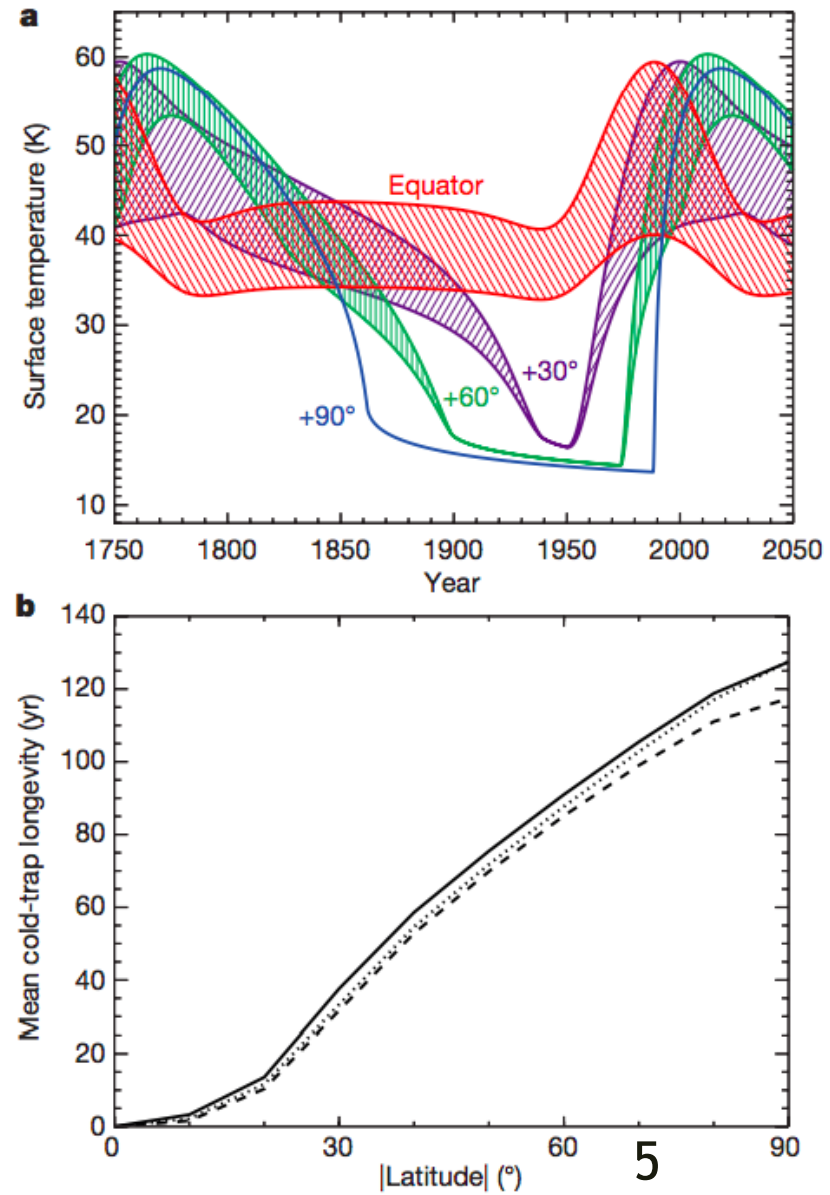


from Grundy et al. (2016)

Surface temperatures at different latitudes

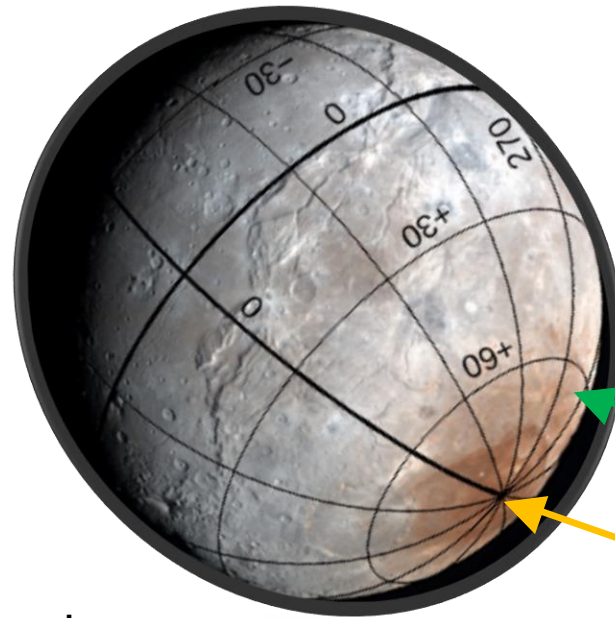
- Thermal model from Grundy et al. (2016) shows the pole position is **below 25 K** for 130 years
- **Methane can condense** on those positions where the temperature is below 25 K.

Quoted from Grundy et al. (2016)



What astrophysical environments are we demonstrating?

Charon in Pluto system



VUV and EUV irradiation



NH_3

+

CH_4

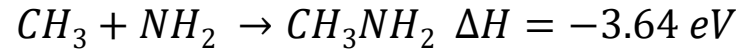


CN^-

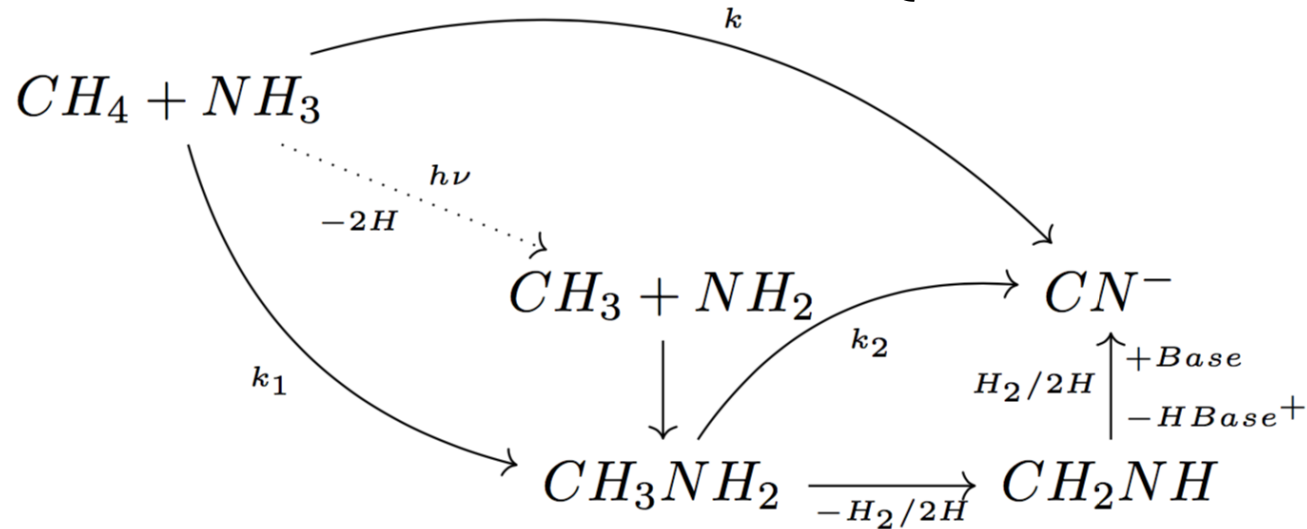
Quoted from Grundy et al.
(2017)

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^-

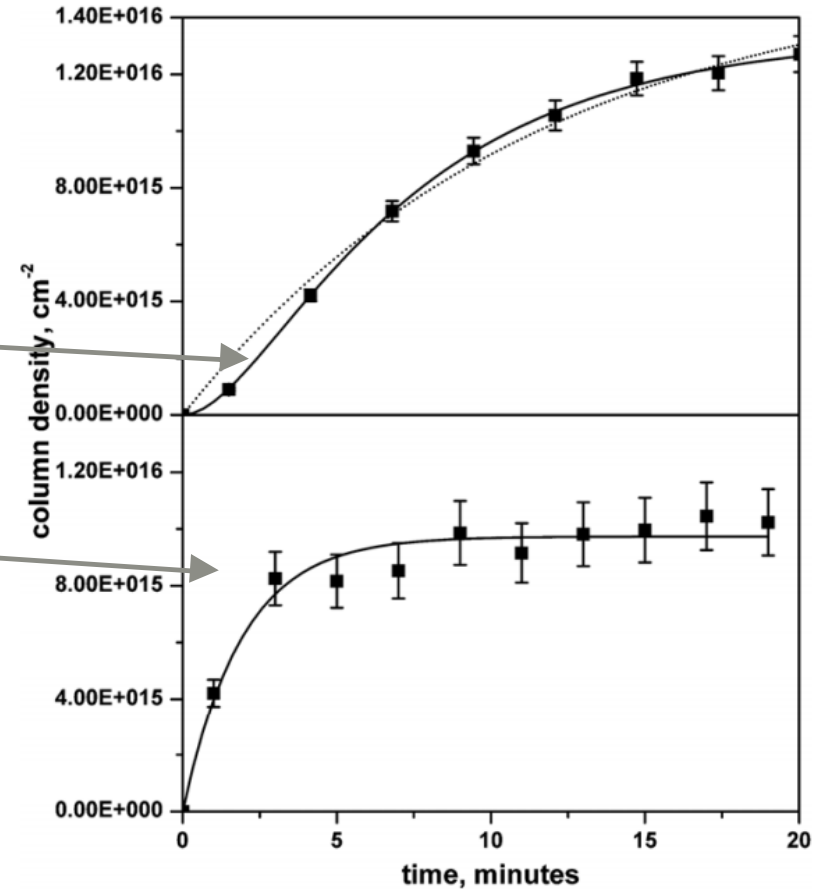
- 2 steps/1 step?

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

Experimental Protocol:

- 1. To compare with **previous studies**
 - *Kim and Kaiser* ($\text{CH}_4:\text{NH}_3$ **3:1**) (5 keV e^-)
 - *Kundy et al.* ($\text{CH}_4:\text{NH}_3$ **3:2**) (1-90 eV e^-)
 - *We perform* ($\text{CH}_4:\text{NH}_3$ **3:2**)
photon sources: VUV (9.27 eV) and EUV (40.8 eV)
- 2. To simulate the **surface of Charon**
 - *Different relative proportion of*
 $\text{CH}_4:\text{NH}_3$ 1:5, 1:10, 1:20

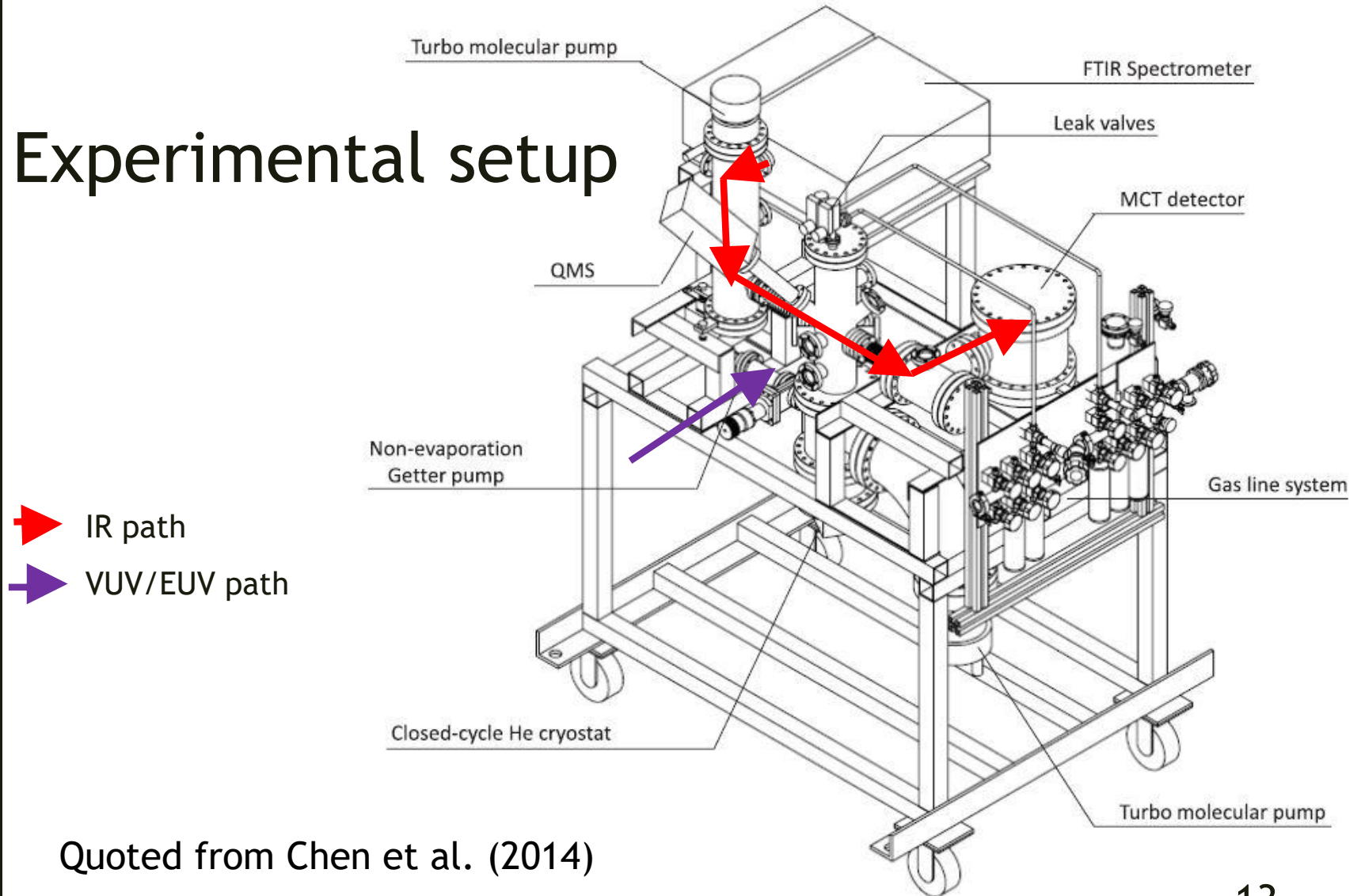
Methodology

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	--	--

Different initial amount of CH₄ correspond to different ratio of CH₄:NH₃ ice mixtures

Experimental setup



Quoted from Chen et al. (2014)

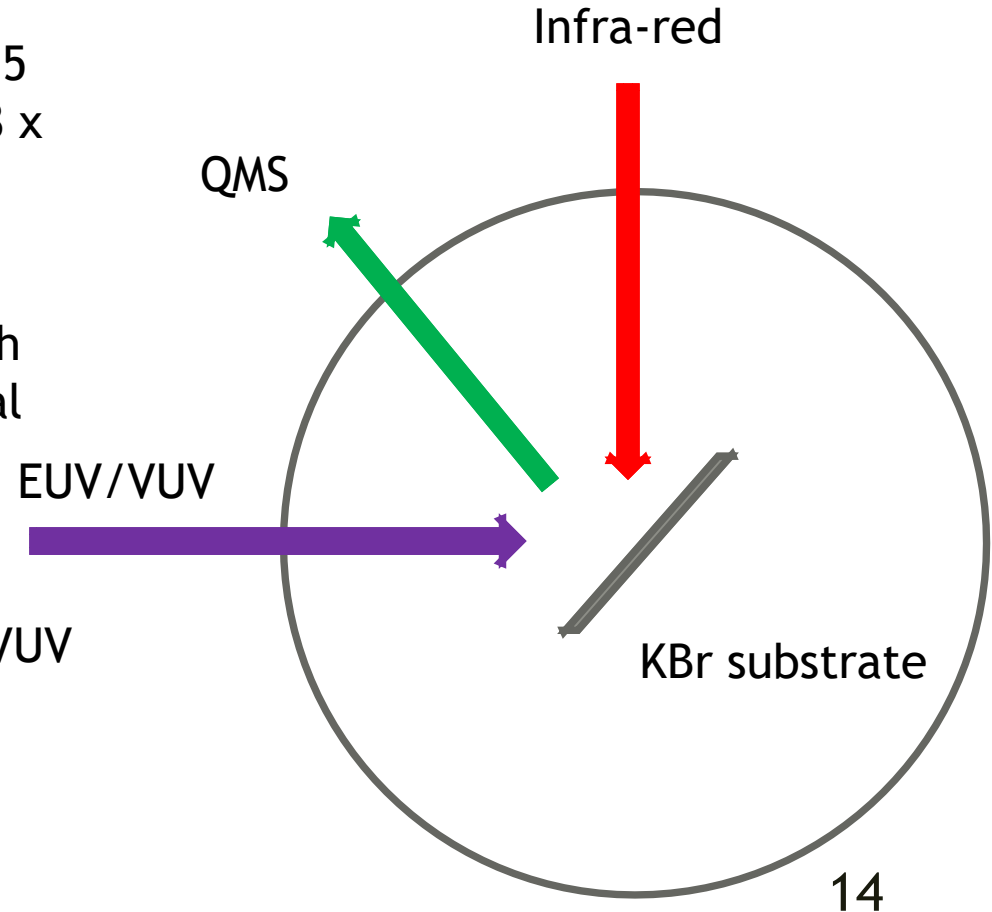
Experimental Procedure

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

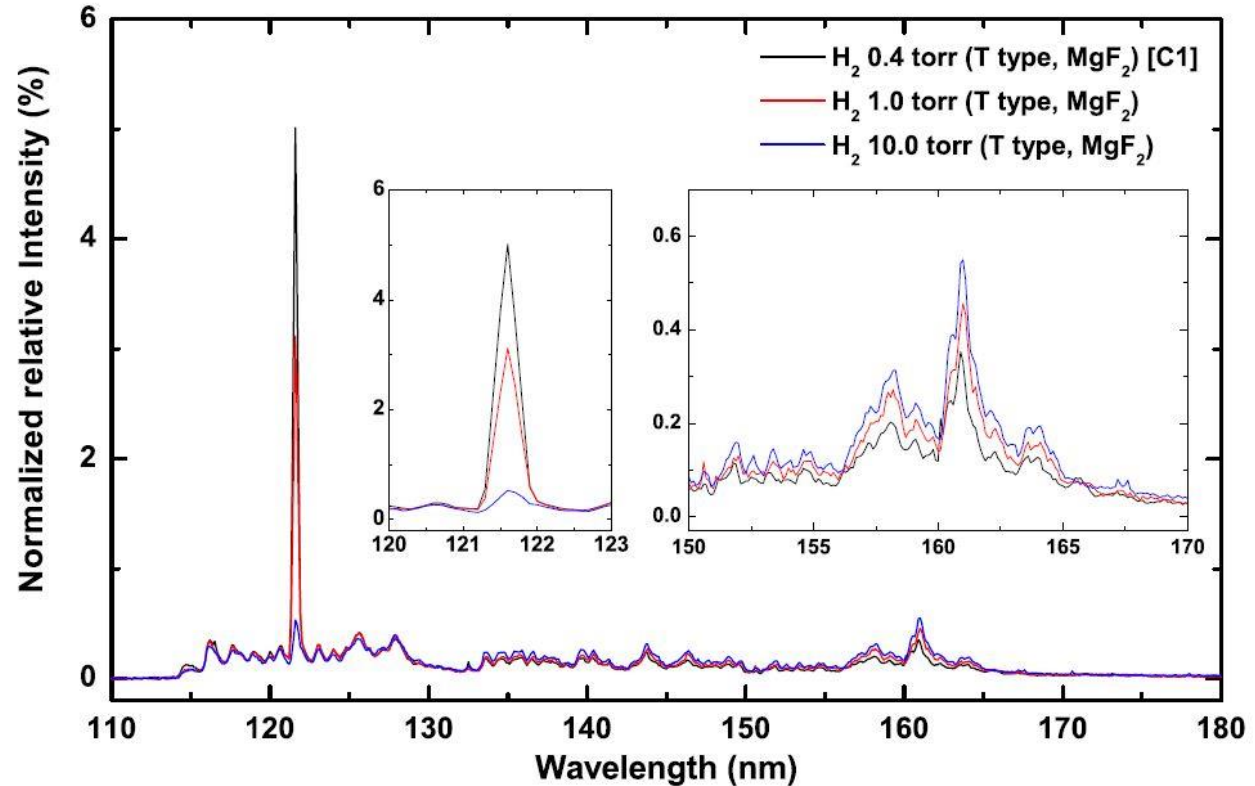
Irradiate the samples by EUV/VUV

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

Absorbance $\tau(\nu)$:

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

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

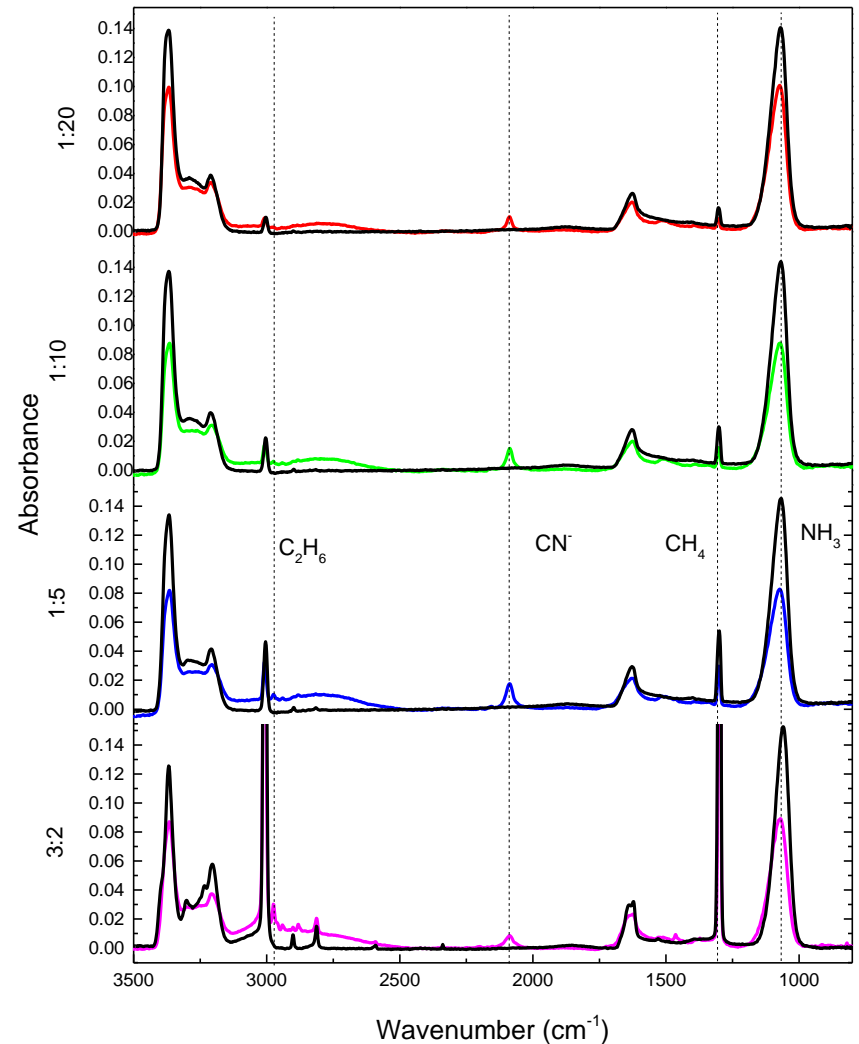
l : path length (cm)

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

Column density N :

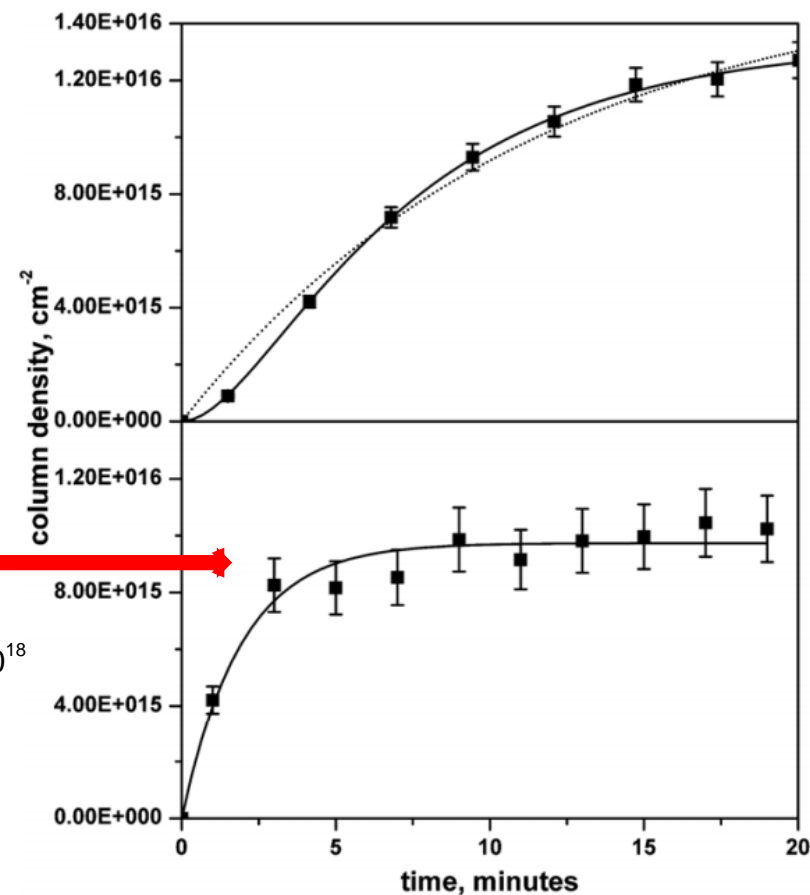
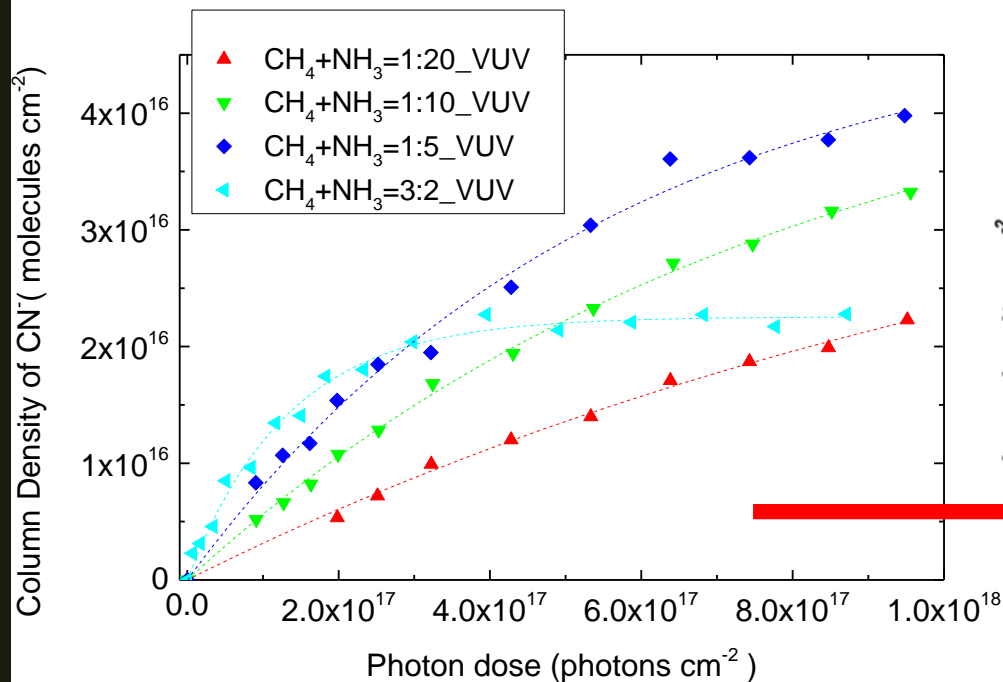
$$\blacksquare \quad N = \frac{\int \tau(\nu) d\nu}{A(\nu)}$$

$A(\nu)$: 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⁻



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

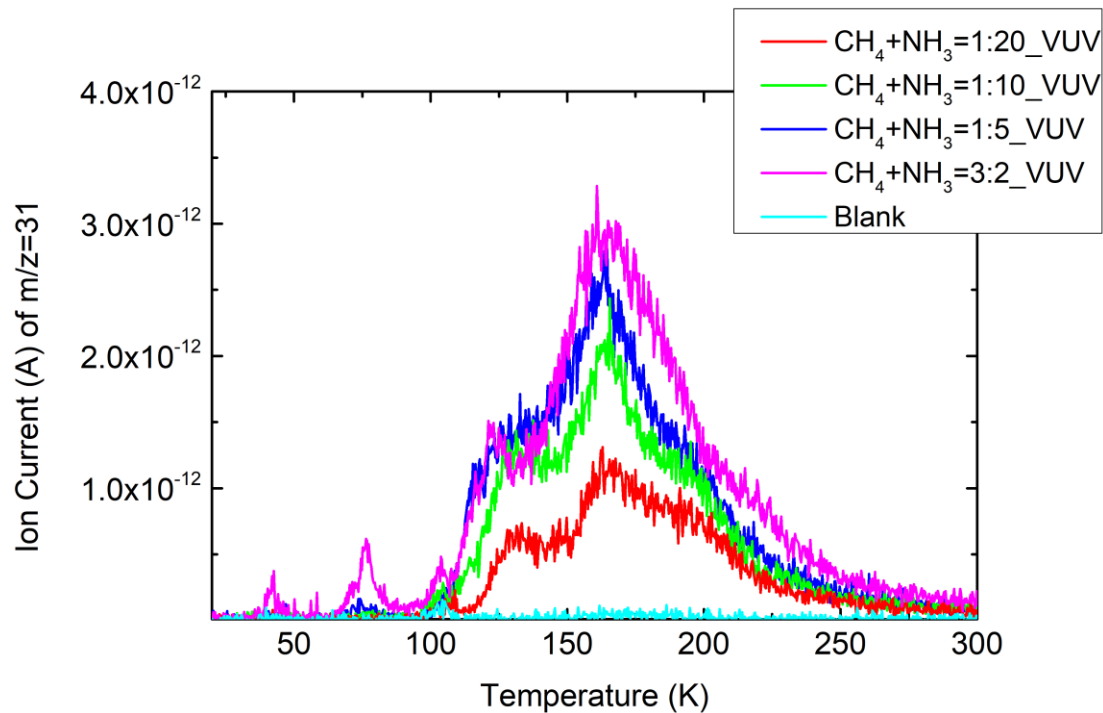
VUV experiments with CH ₄ +NH ₃ ice mixtures			
Ratio	A (x10 ¹⁶ molecules cm ⁻²)	k ₁ (x10 ⁻¹⁸ photon ⁻¹)	k ₂ (photon ⁻¹)
1:20	4.75 ± 0.40	0.70 ± 0.09	>1
1:10	4.51 ± 0.18	1.33 ± 0.13	>1
1:5	4.61 ± 0.18	1.93 ± 0.19	>1
3:2	2.24 ± 0.03	8.21 ± 0.70	>1
Quotated from Kim and Kaiser[2]			
Ratio	A(x10 ¹⁶ molecules 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^-

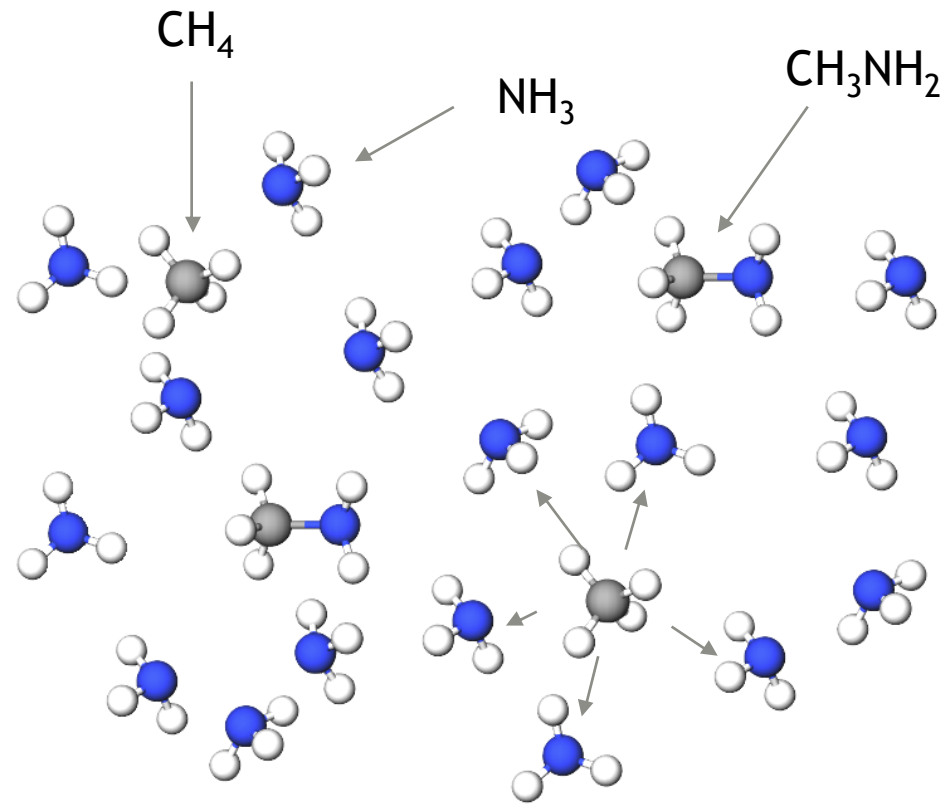
Methylamine
(CH_3NH_2) with
 $m/z=31$ is
detected by QMS

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^- .

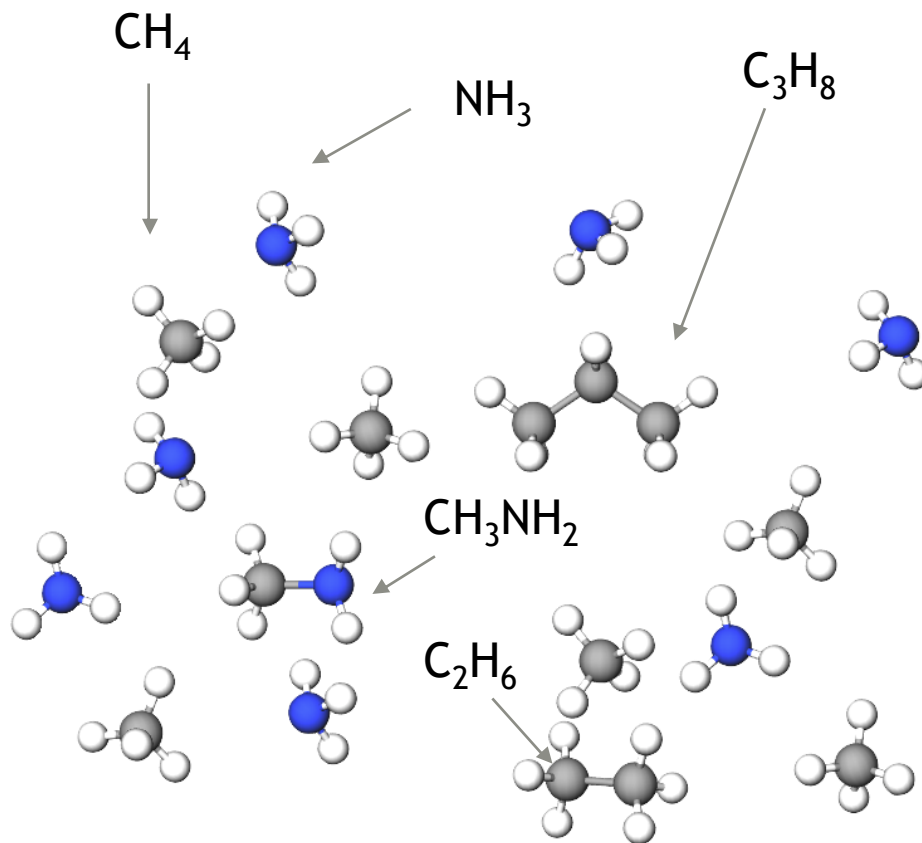


A diagram of $\text{CH}_4:\text{NH}_3 = 1:5$

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

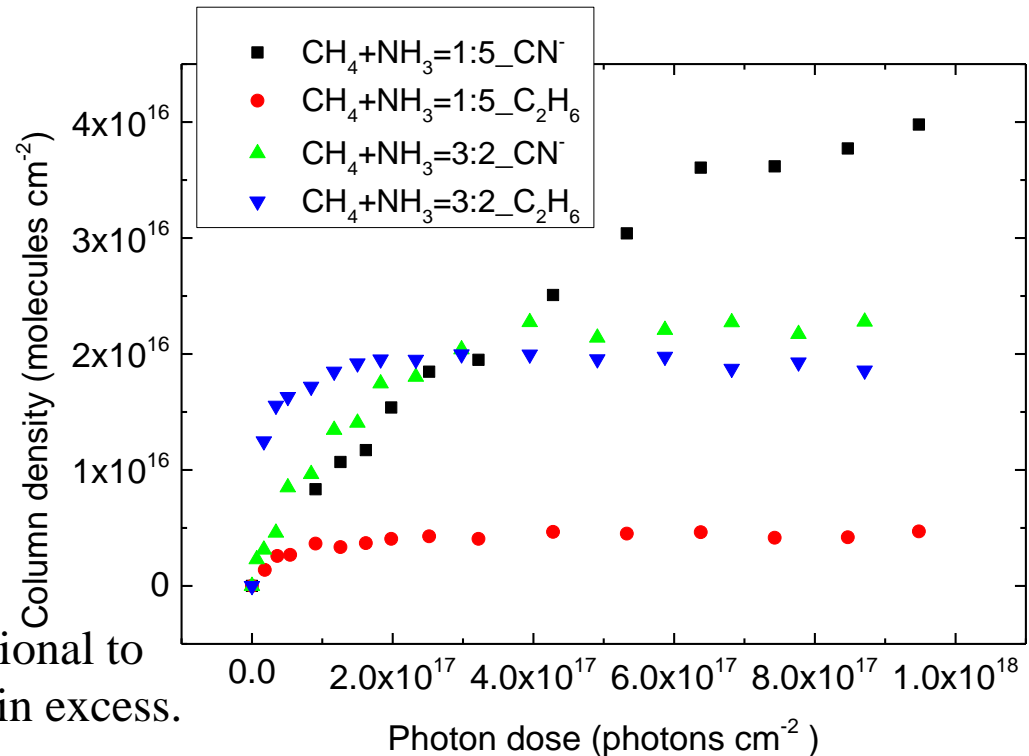


A diagram of $\text{CH}_4 + \text{NH}_3 = 3:2$

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

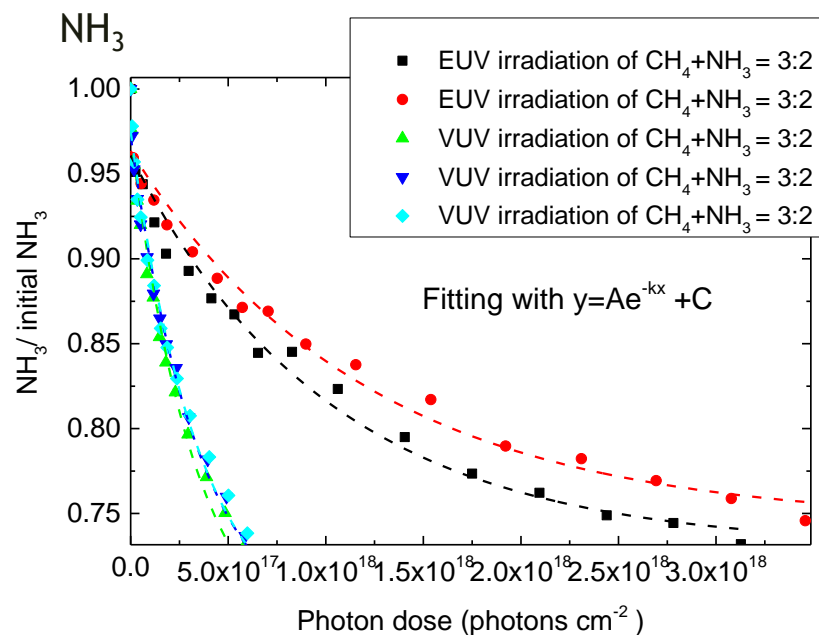
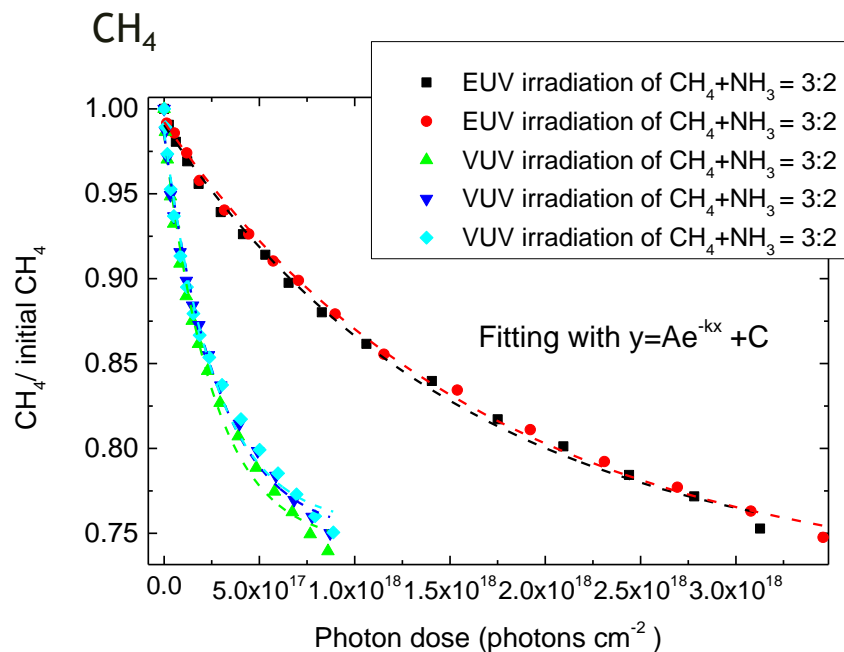
$\text{CH}_4:\text{NH}_3$	C_2H_6 (ML)	CN^- (ML)	Ratio of CN^- to C_2H_6
3:2 (CH_4 dominant)	19.1	23	1.2
1:5 (NH_3 dominant)	4.3	49	11.3

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



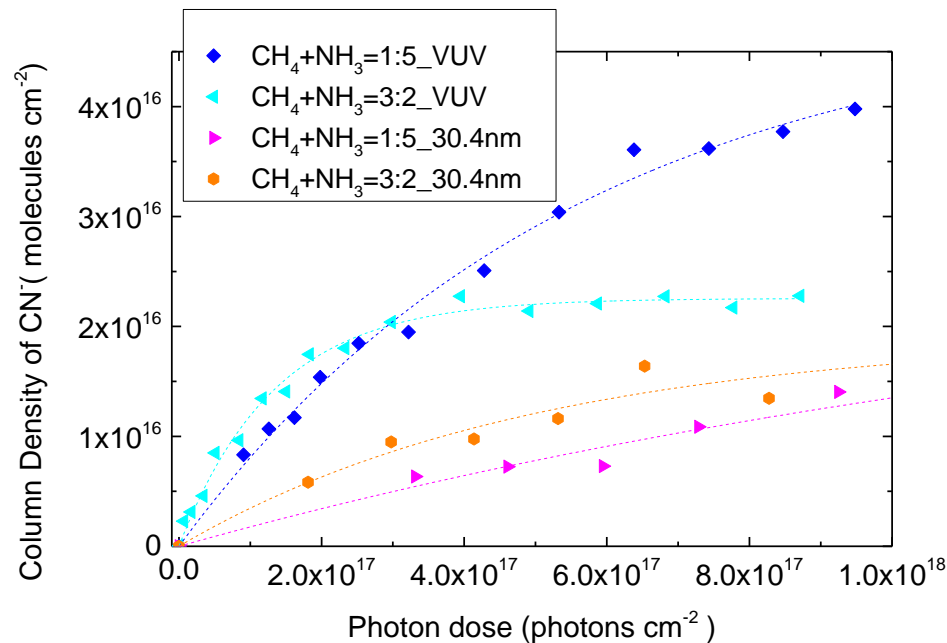
3. Rate constant of reactants by EUV (40.1 eV) and VUV (9.27 eV)

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



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 : NH ₃ 3:2 (x 10 ⁻¹⁸)	CH ₄ : 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



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: $1.9 \times 10^9 \text{ eV cm}^{-2} \text{ s}^{-1}$

(Grundy et al. 2016)

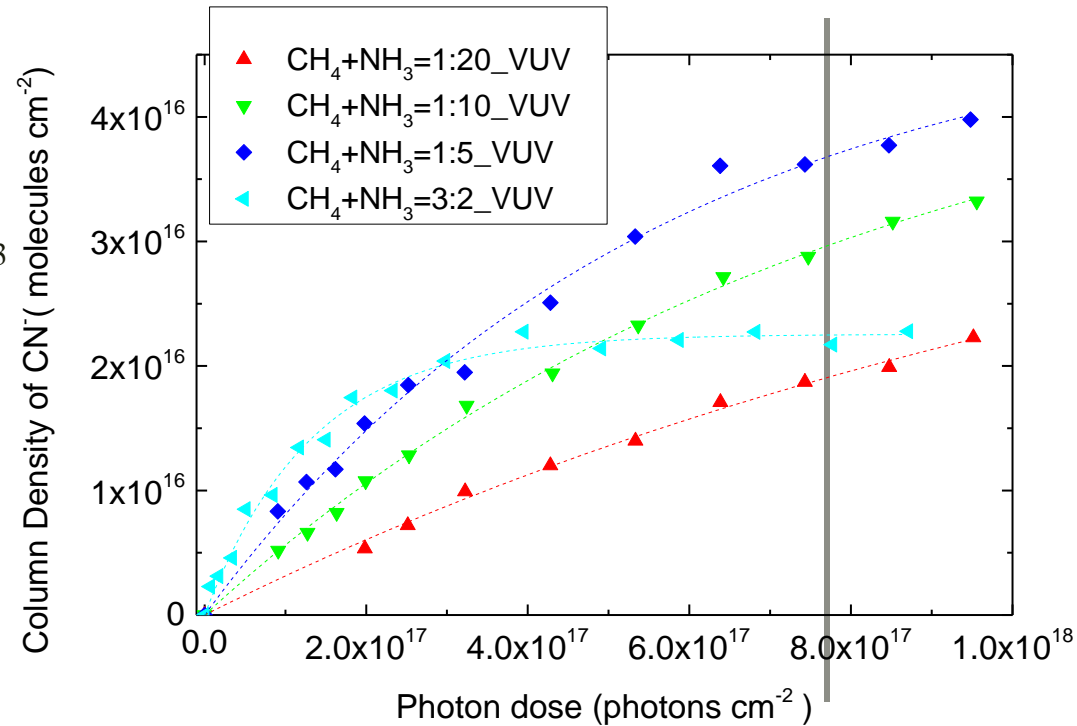
→ photon dose after 1 Pluto winter

$7.64 \times 10^{17} \text{ photons cm}^{-2}$

CH₄ after winter ~173 ML

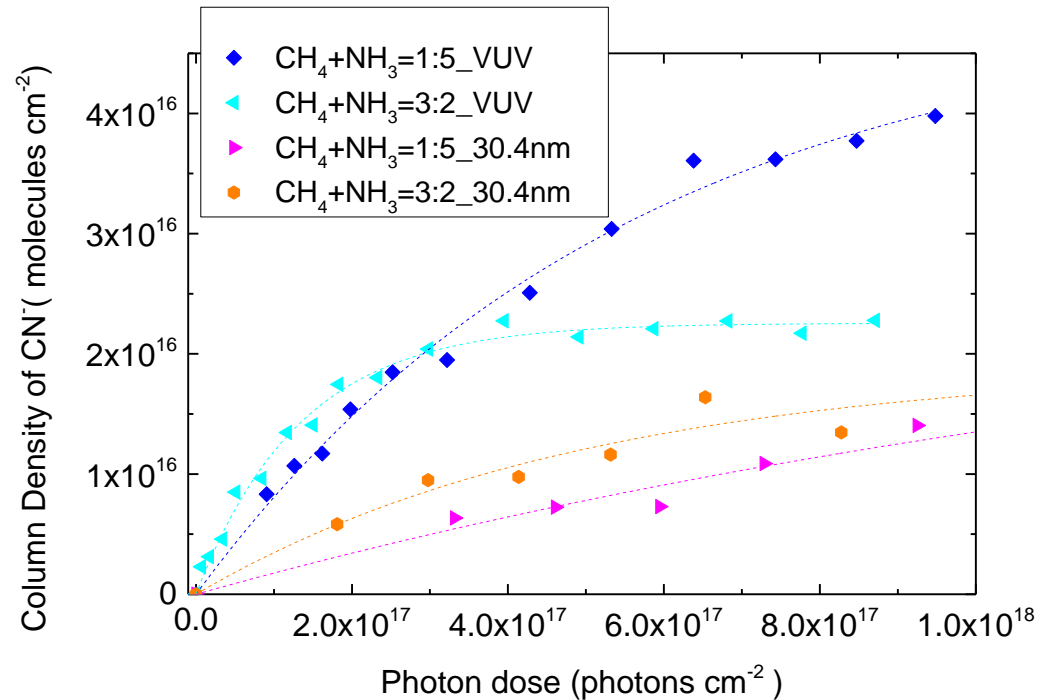
Assume the column density of NH₃ is 600 ML

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



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

