

VUV AND EUV IRRADIATION OF CH₄ + NH₃ ICE MIXTURES

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Contents

- Introduction
 - *CN⁻ formation mechanisms:*
 - 2 different groups results
 - *3:2 CH₄+NH₃ ice mixtures*
 - *What astrophysical environments are we demonstrating?*
 - Charon
 - NH₃
 - *Ammonia on Organa Crater*
 - CH₄
 - *Deposition rate of methane on Charon*
 - *Surface temperatures at different latitudes*
 - 1:5 ,1:10 and 1:20 CH₄+NH₃ ice mixtures

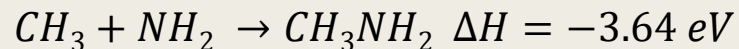
Contents

- Methodology
 - *Experimental setup*
 - *The spectrum of VUV (MDHL) energy source*
 - *Experimental Configurations*
- Results
 - *Production of CN^-*
 - *The relations between CN^- and C_2H_6*
 - *CN^- formation efficiency of EUV (40.1 eV) and VUV (9.27 eV)*
- Astrophysical Implications
 - *Understand CN^- formation after winter on surface of Charon*

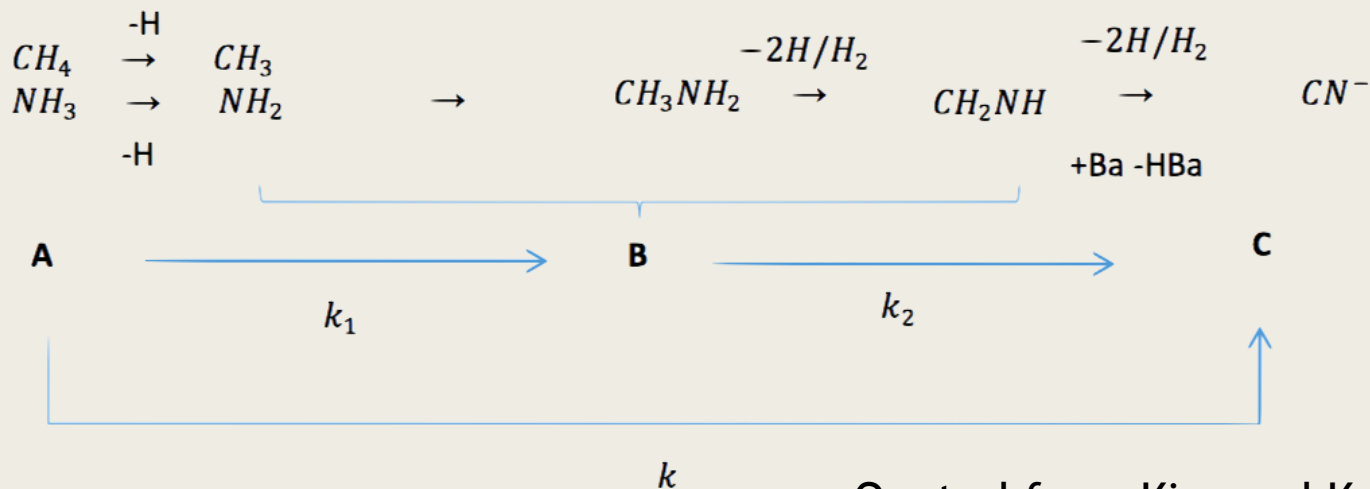
Introduction

Production mechanism of CN^-

Enthalpy of CH_3NH_2 formation



Quoted from Kundu et al. (2017)



Quoted from Kim and Kaiser (2011)

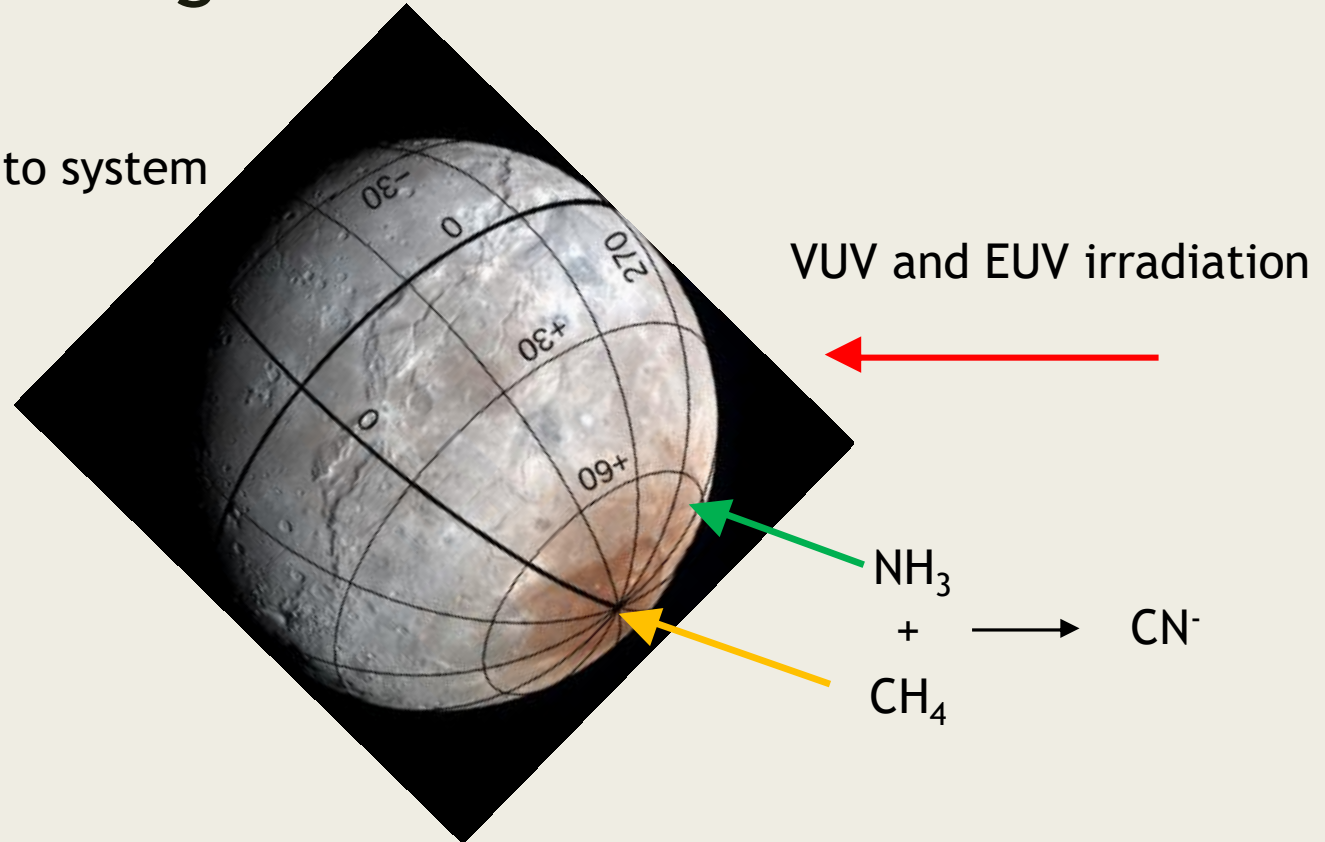
Production mechanism of CN^-

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?

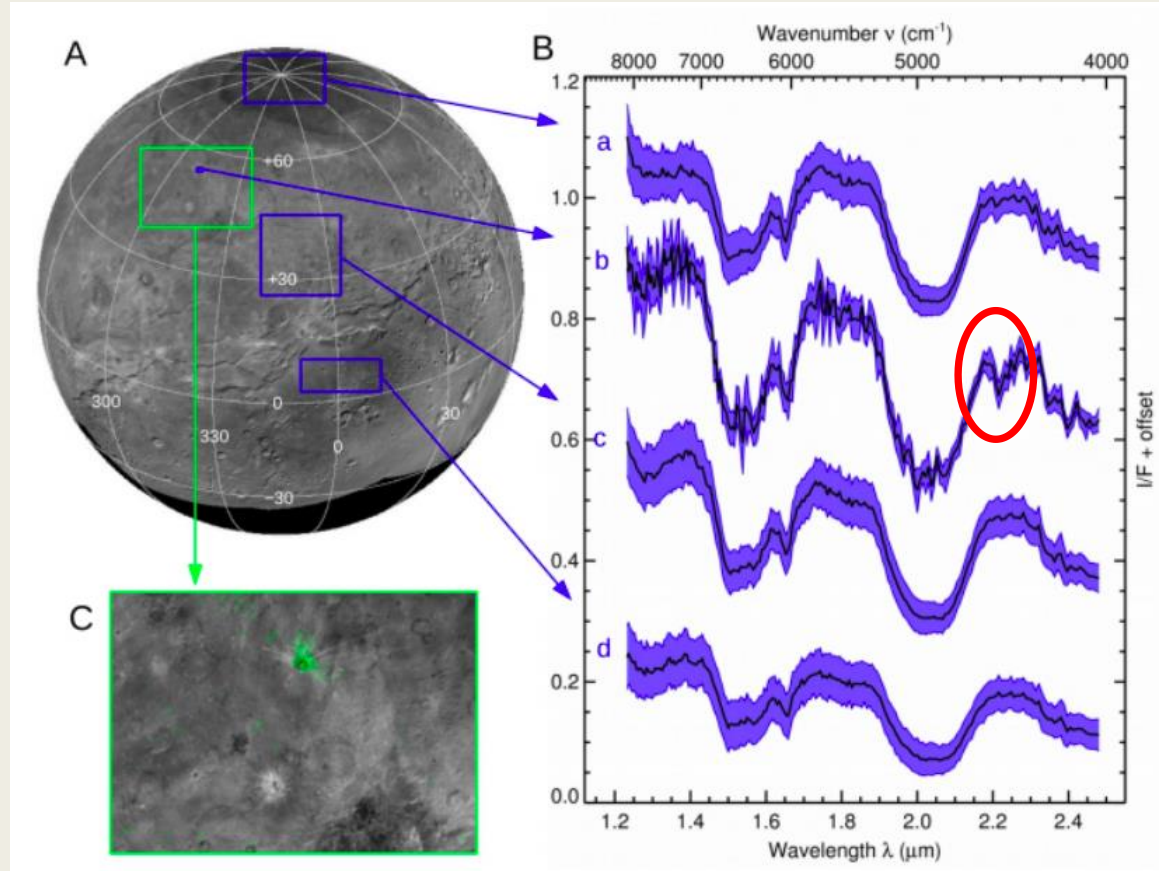
What astrophysical environments are we demonstrating?

Charon in Pluto system



Ammonia on Organa Crater

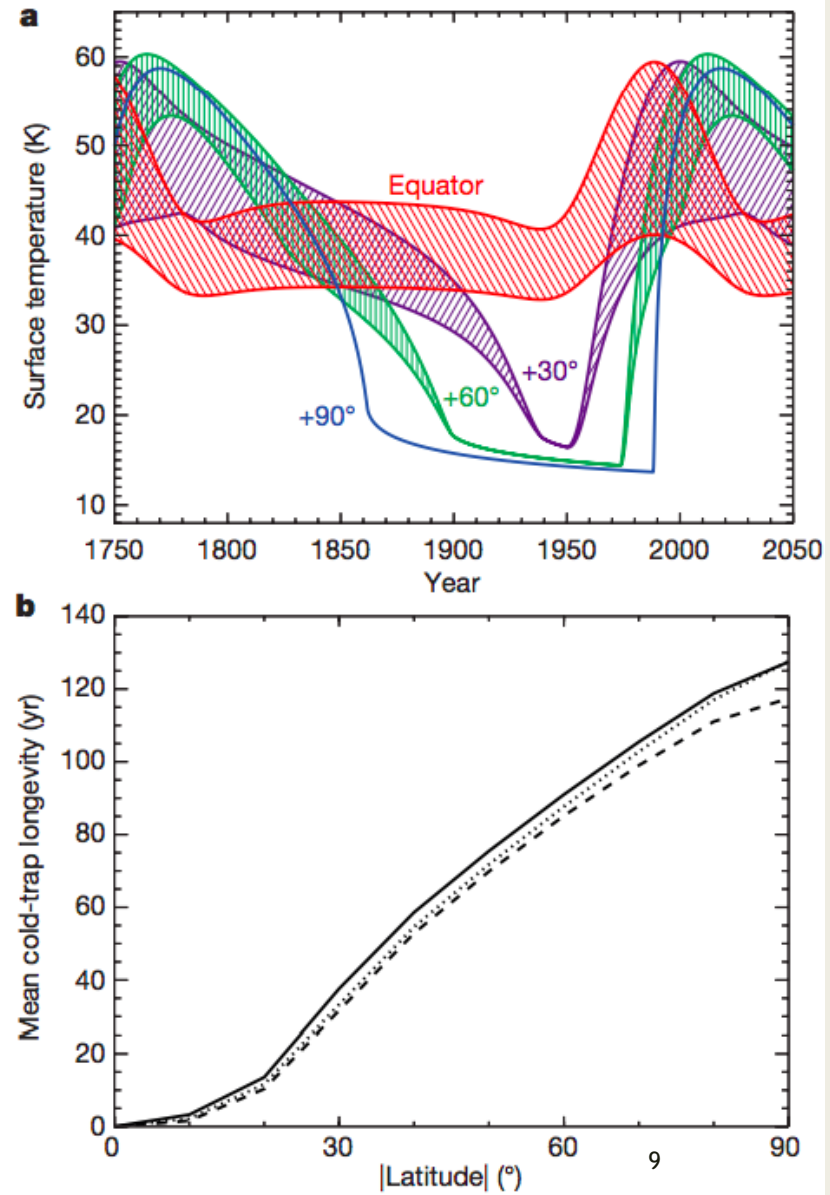
- *Ammonia was detected all over the surfaces, especially on Organa Crater*



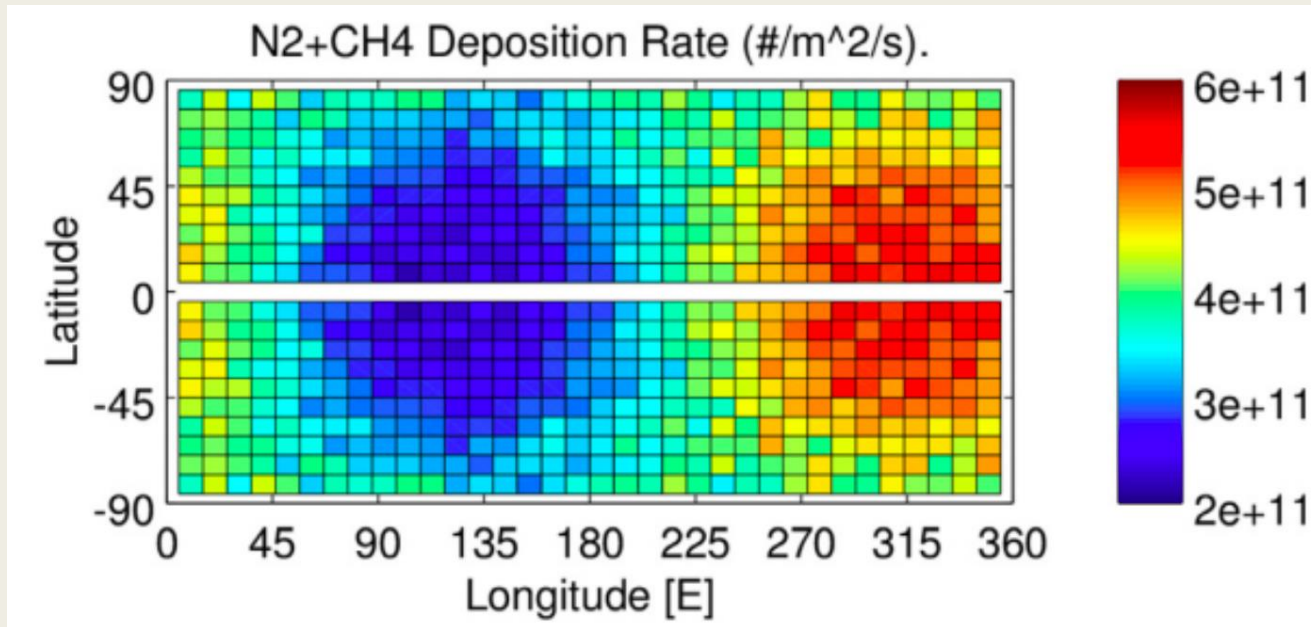
Surface temperatures at different latitudes

- ▶ 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



quoted from Hoey et al. (2017)

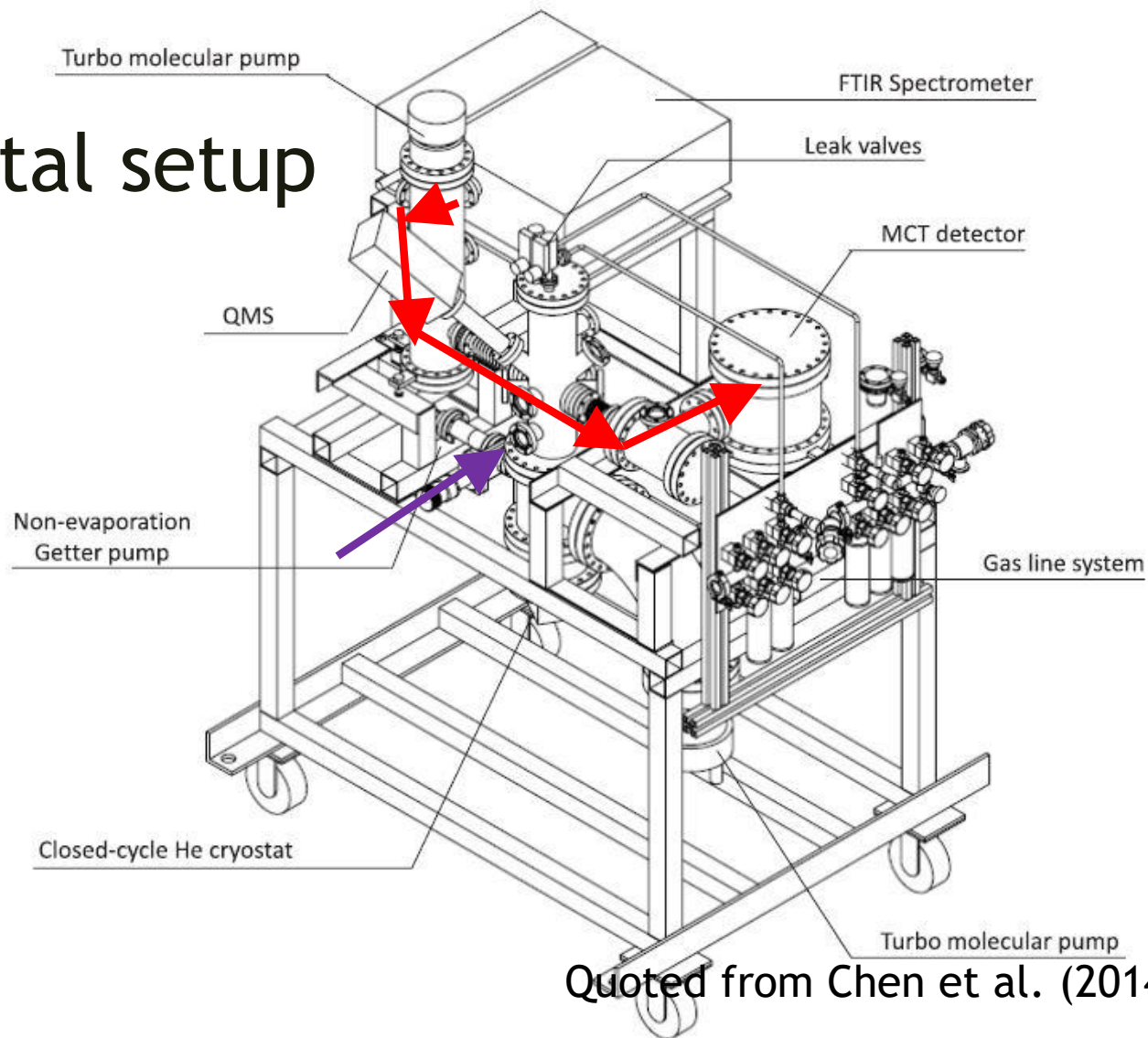
Motivation

- 1. To compare with previous studies
 - *Experiment: $\text{CH}_4 + \text{NH}_3 = 3:2$*
 - *Confirm mechanism of CN^-*
- 2. To simulate the surface of Charon
 - *Experiment: $\text{CH}_4 + \text{NH}_3 = 1:5, 1:10, 1:20$*
 - *Variation of photon sources: from VUV to EUV*

Methodology

Experimental setup

- ➡ IR path
- ➡ VUV/EUV path



Quoted from Chen et al. (2014)

Experimental Protocol

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



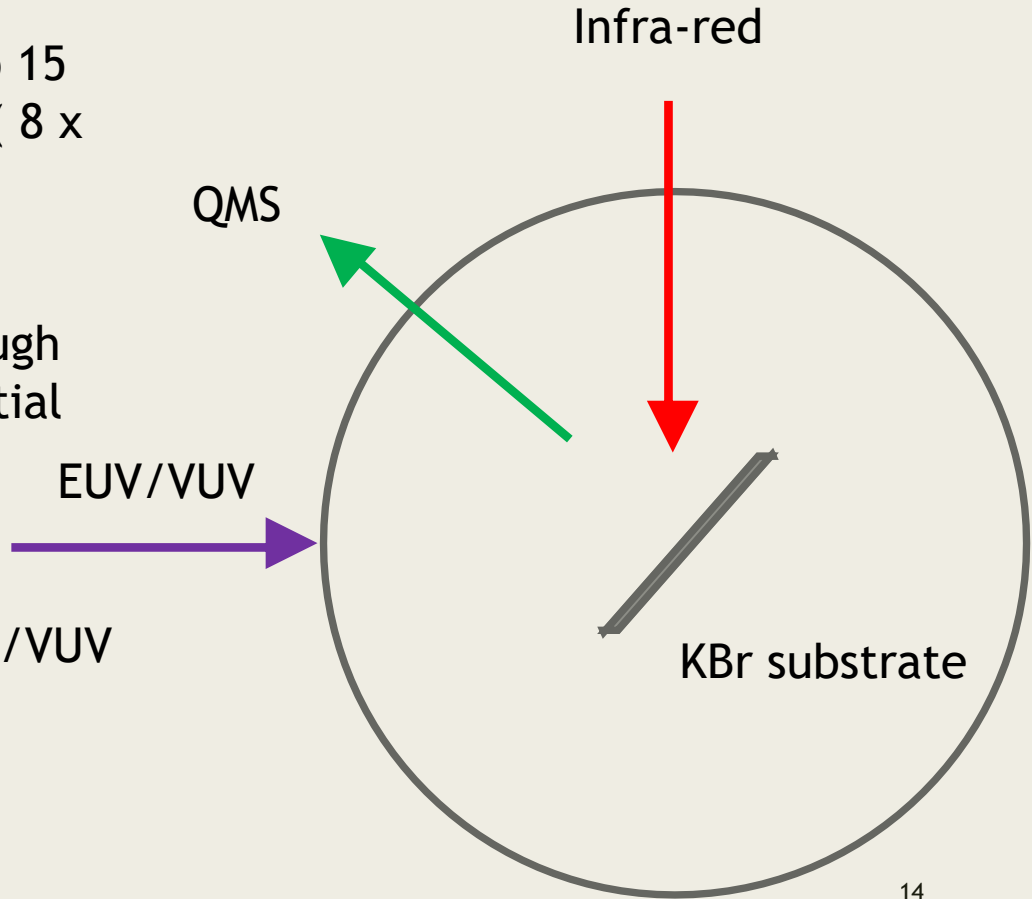
Deposit the ice mixtures through leak valve, with different partial pressures of CH_4 and NH_3



Irradiate the samples by EUV/VUV

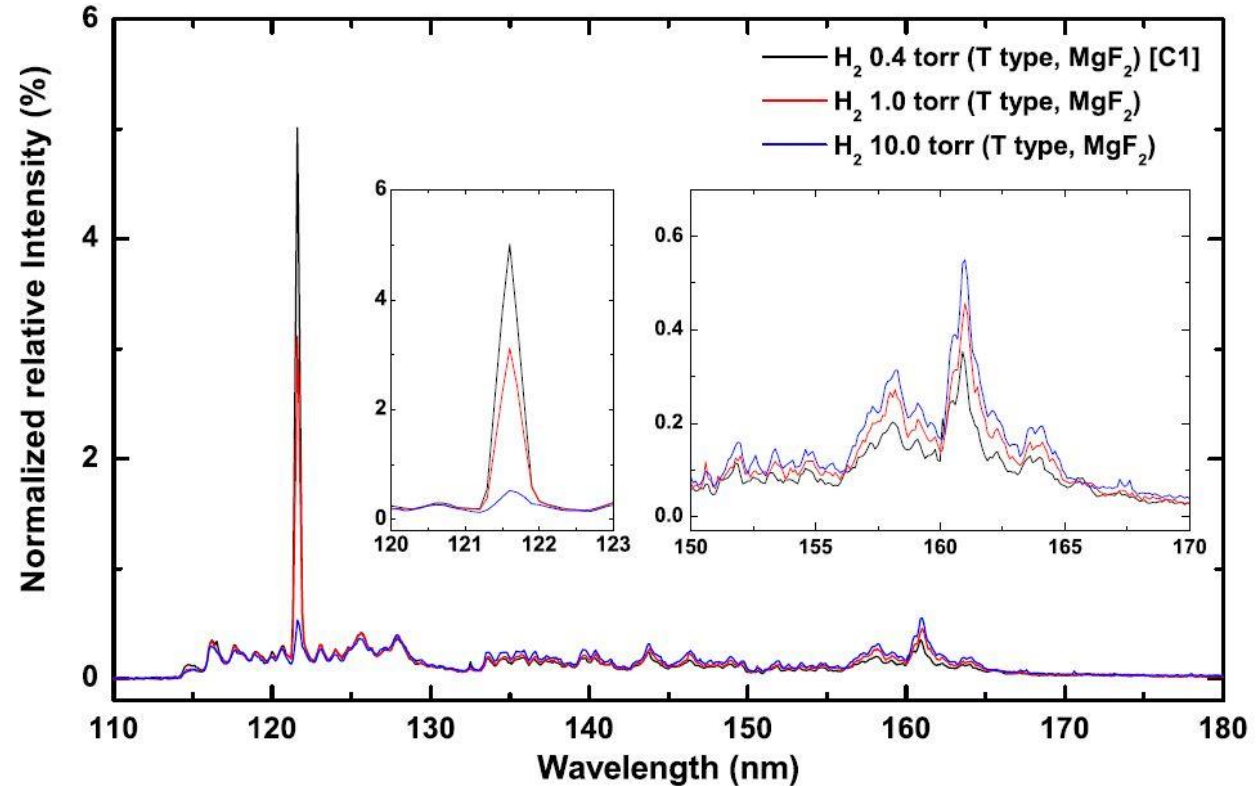


Warm-up with 1 K/min



The spectrum of VUV (MDHL) energy source

- 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)

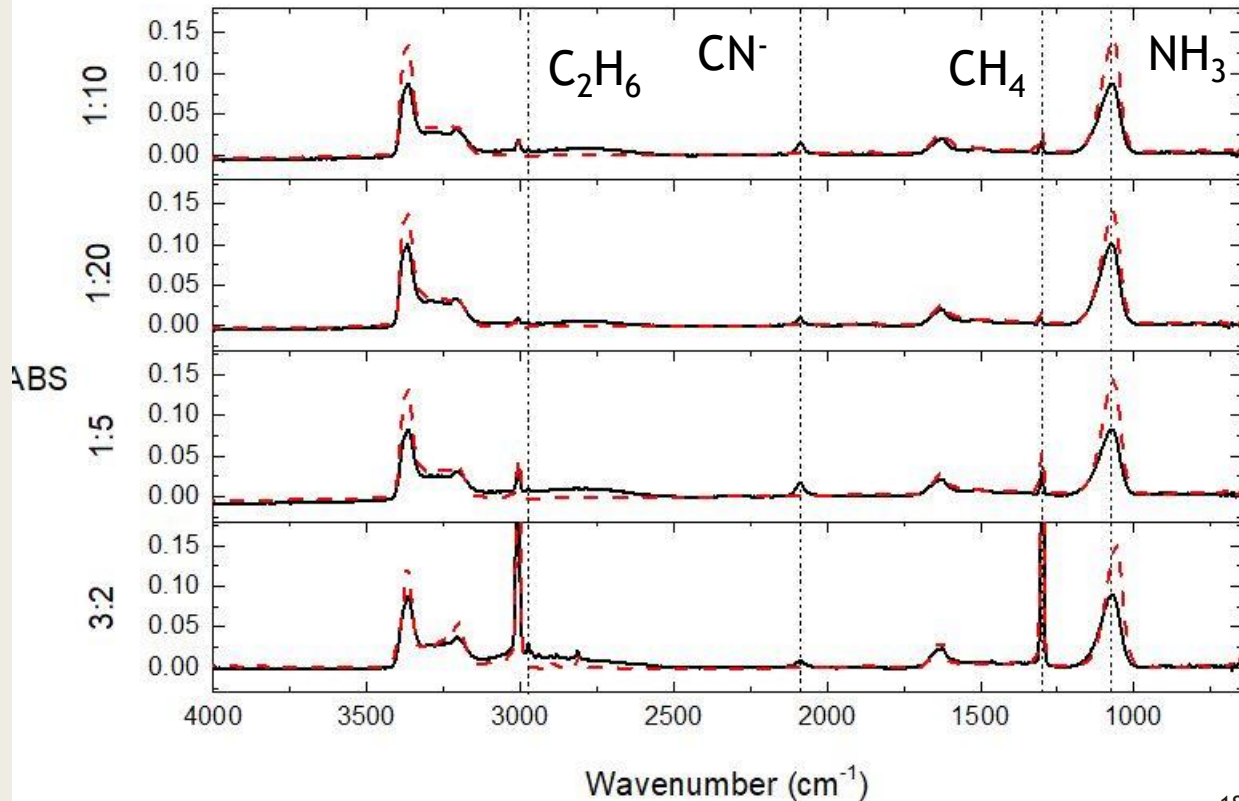
Experimental Configurations

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

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 $T(\nu)$ is defined by:

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

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

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

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

Column density N is defined by:

- $N = \frac{\int a(\nu) d\nu}{A(\nu)}$

Where N is column density (molecules cm^{-2}) $A(\nu)$ is the absorption strength (A-value) (cm molecule^{-1}) from literatures

1. Production of CN^-

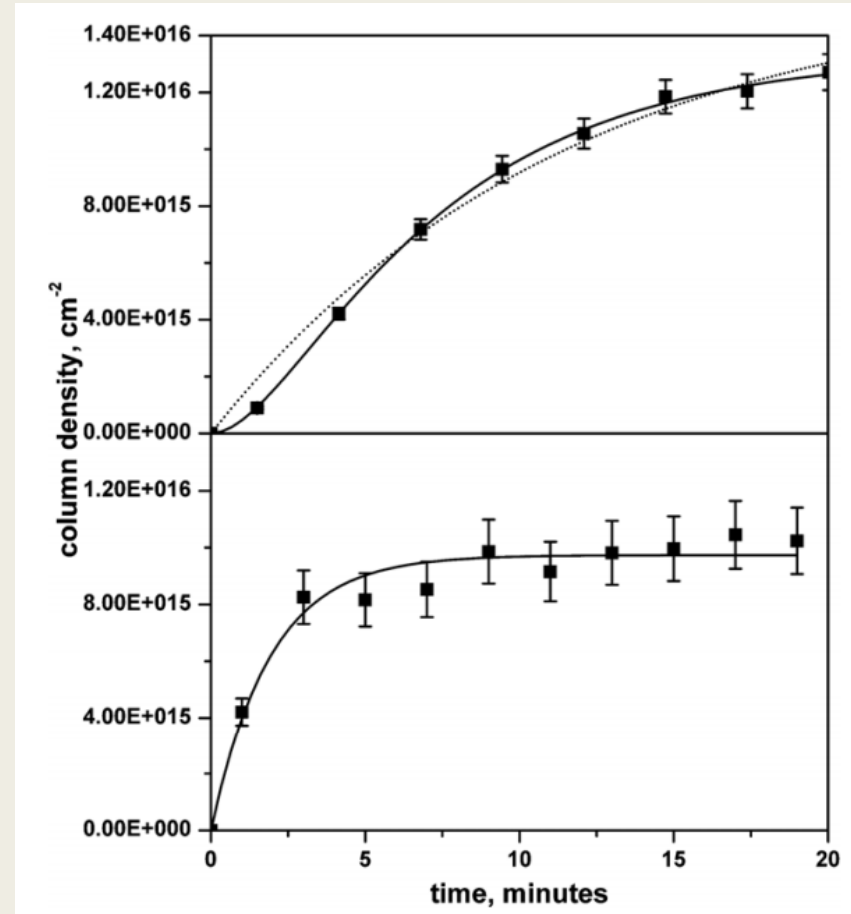
- 2 steps/1 step?

2 steps 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:

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

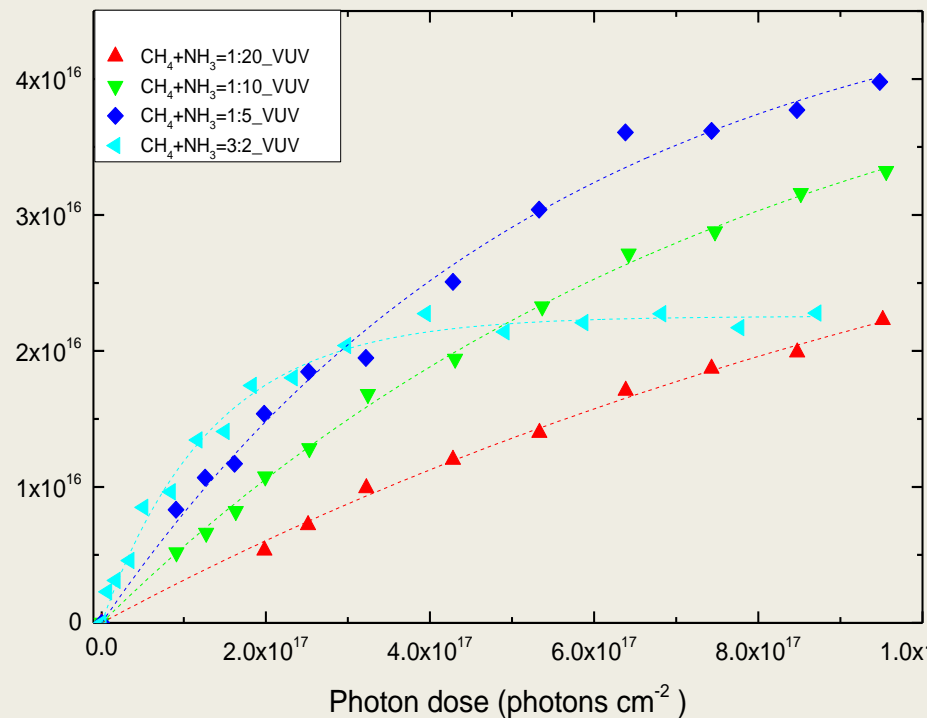


Quoted from Kim and Kaiser (2011)

1. Production of CN⁻

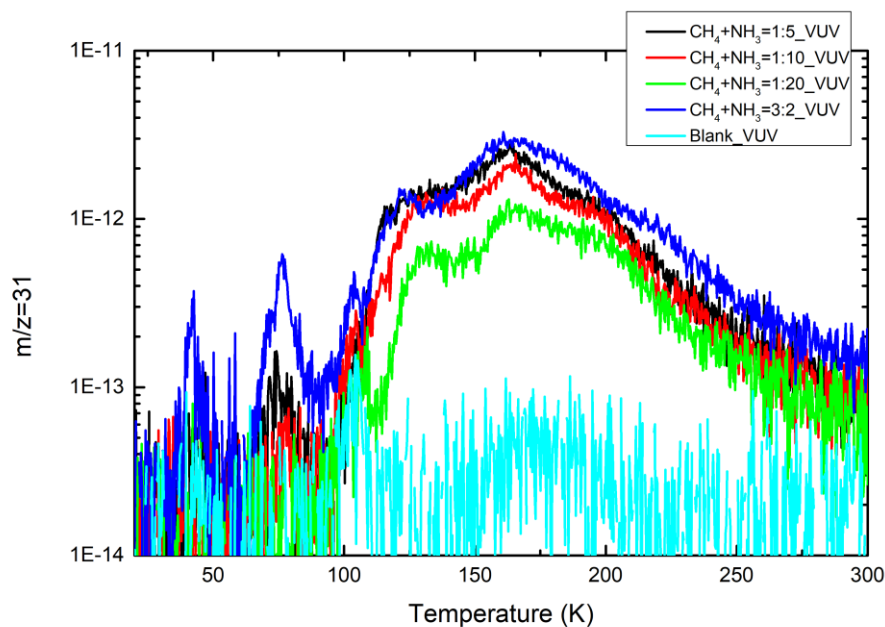
■ 2 steps/1 step?

light source	Ratio of CH ₄ +NH ₃	A (x10 ¹⁶ molecules cm ⁻²)	k (x10 ⁻¹⁸ photon ⁻¹) ^{±2}
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



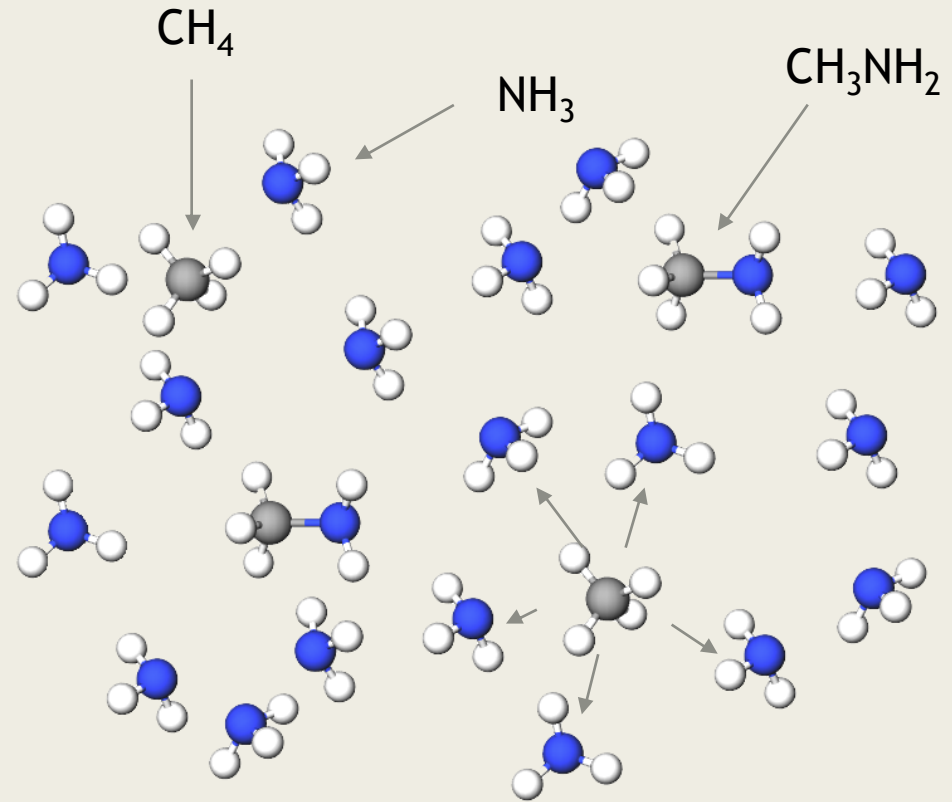
1. Production of CN⁻

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

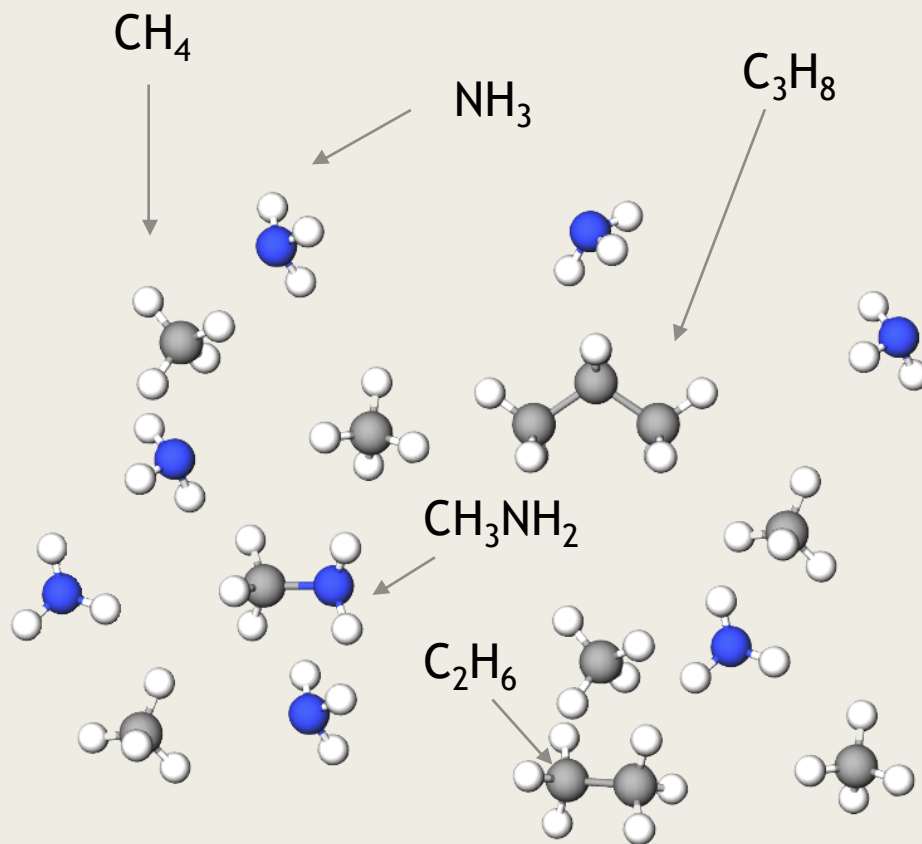
- Once CH_4 becomes CH_3 radical, it can easily form methylamine and hence become CN^- .



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

2. The scenario for CH₄ dominating ice mixtures

- CH₂NH₃ (formed by CH₃ + NH₂) has a competing relationship with C₂H₆ (formed by 2 CH₃) and C₃H₈ (formed by CH₂ + C₂H₆ or C₂H₄ + CH₄)
- Once CH₄ becomes CH₃ radical, it reacts with either NH₂ or CH₃ radicals, forming CH₃NH₂ or C₂H₆ respectively

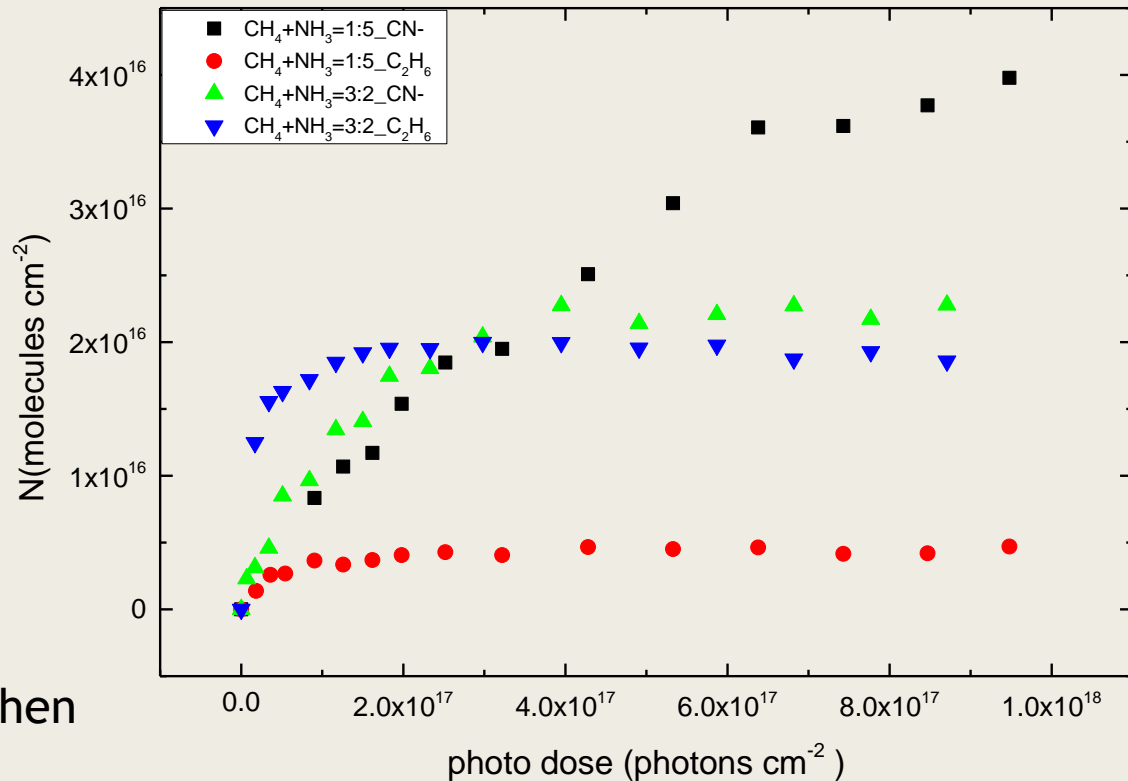


A diagram of CH₄+NH₃ = 3:2

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

$\text{CH}_4:\text{NH}_3$	C_2H_6 (ML)	CN^- (ML)
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.



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

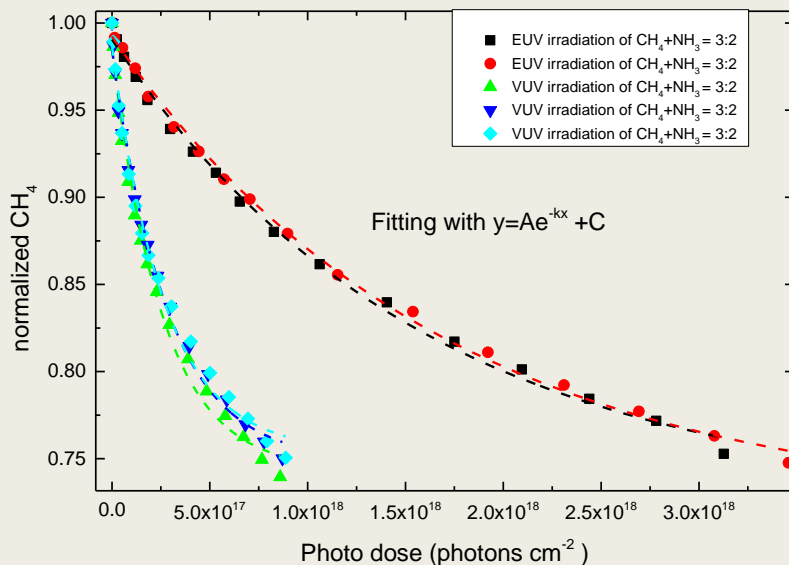
Radicals \ species	CH ₄	NH ₃
- 1 H	4.55 eV	4.67 eV
-2 H	4.78 eV	4.38 eV
-3 H	9.19 eV	7.63 eV

(quoted from Kundu et al. (2017))

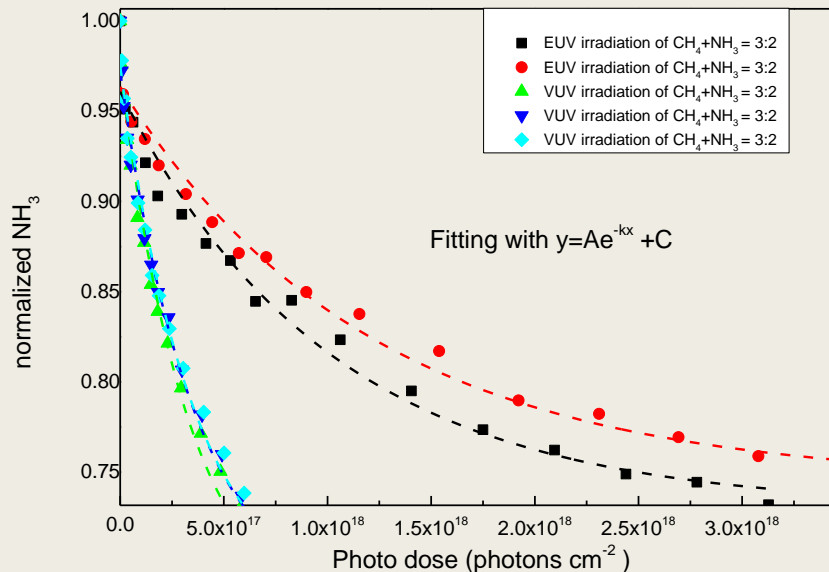
3. CN⁻ formation efficiency of EUV (40.1 eV) and VUV (9.27 eV)

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

CH₄

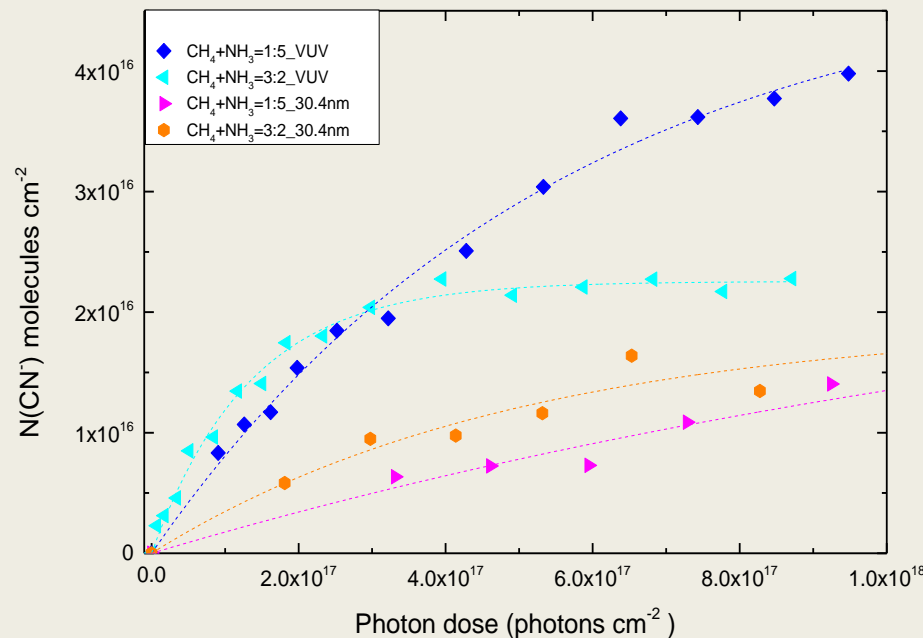


NH₃



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

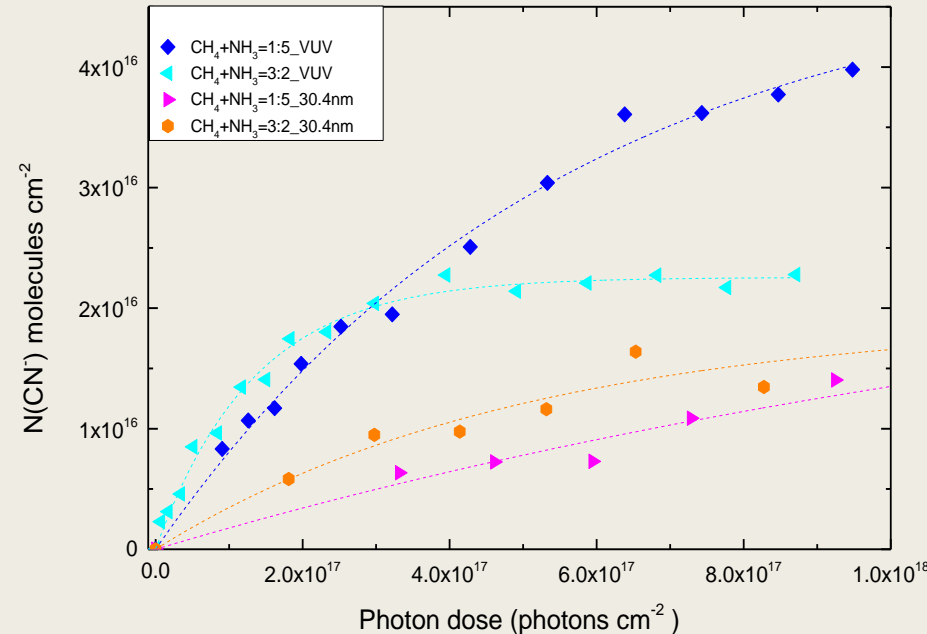
k (photons ⁻¹)	CH ₄ (x 10 ⁻¹⁸)	NH ₃ (x10 ⁻¹⁸)
VUV (MDHL)	3.70±0.18	2.89±0.10
EUV (30.4nm)	0.61±0.03	0.91±0.11
Destruction cross-section ratio	6.06±0.07	3.18±0.12
k (photon ⁻¹)	CH ₄ to NH ₃ 3:2 (x 10 ⁻¹⁸)	CH ₄ to NH ₃ 1:5 (x10 ⁻¹⁸)
VUV (MDHL)	8.21±0.70	1.93±0.19
EUV (30.4nm)	1.92±1.99	0.63±0.37
CN ⁻ production 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 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: $8.7 \times 10^7 \text{ eV cm}^{-2} \text{ s}^{-1}$



Understand CN⁻ formation after winter on surface of Charon

Surface composition after 1 Pluto winter:

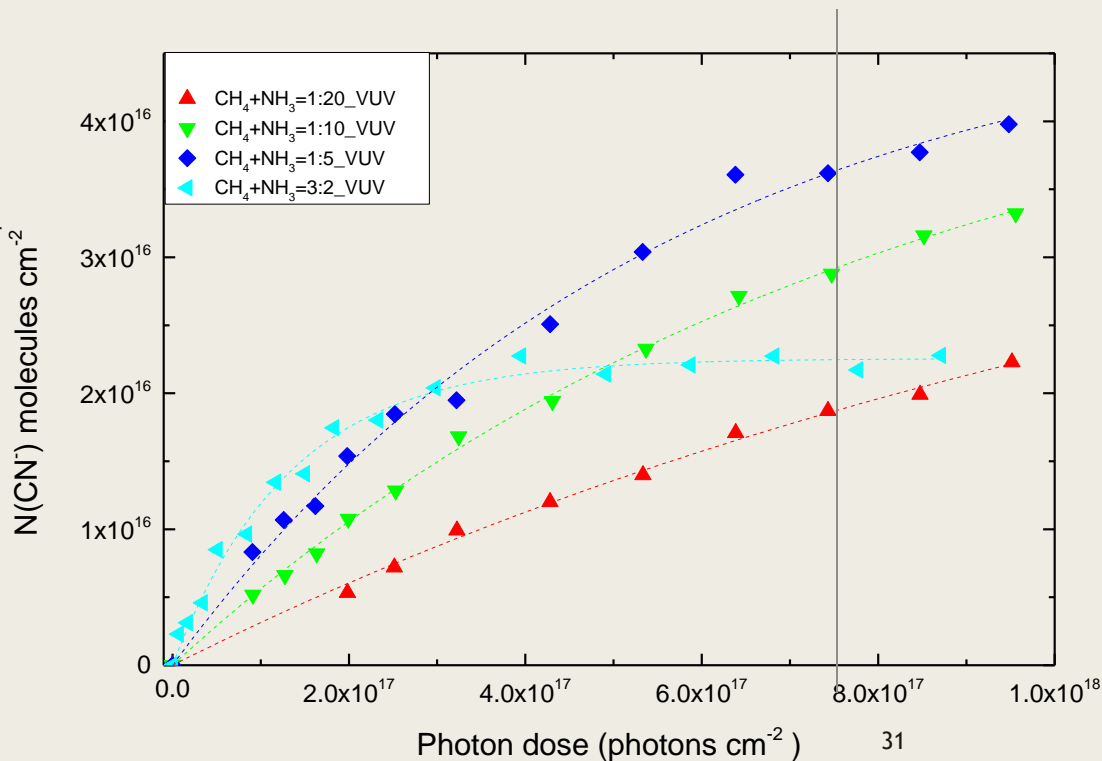
■ Ly α exposure: $1.9 \times 10^9 \text{ eV cm}^{-2} \text{ s}^{-1}$ (Grundy et al. 2016)

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

■ CH₄ deposition rate: $2\text{-}6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ (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.