

VUV AND EUV IRRADIATION OF $\text{CH}_4 + \text{NH}_3$ ICE MIXTURES

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Contents

■ Motivation

■ 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 (40.8 eV) and VUV (9.27 eV)

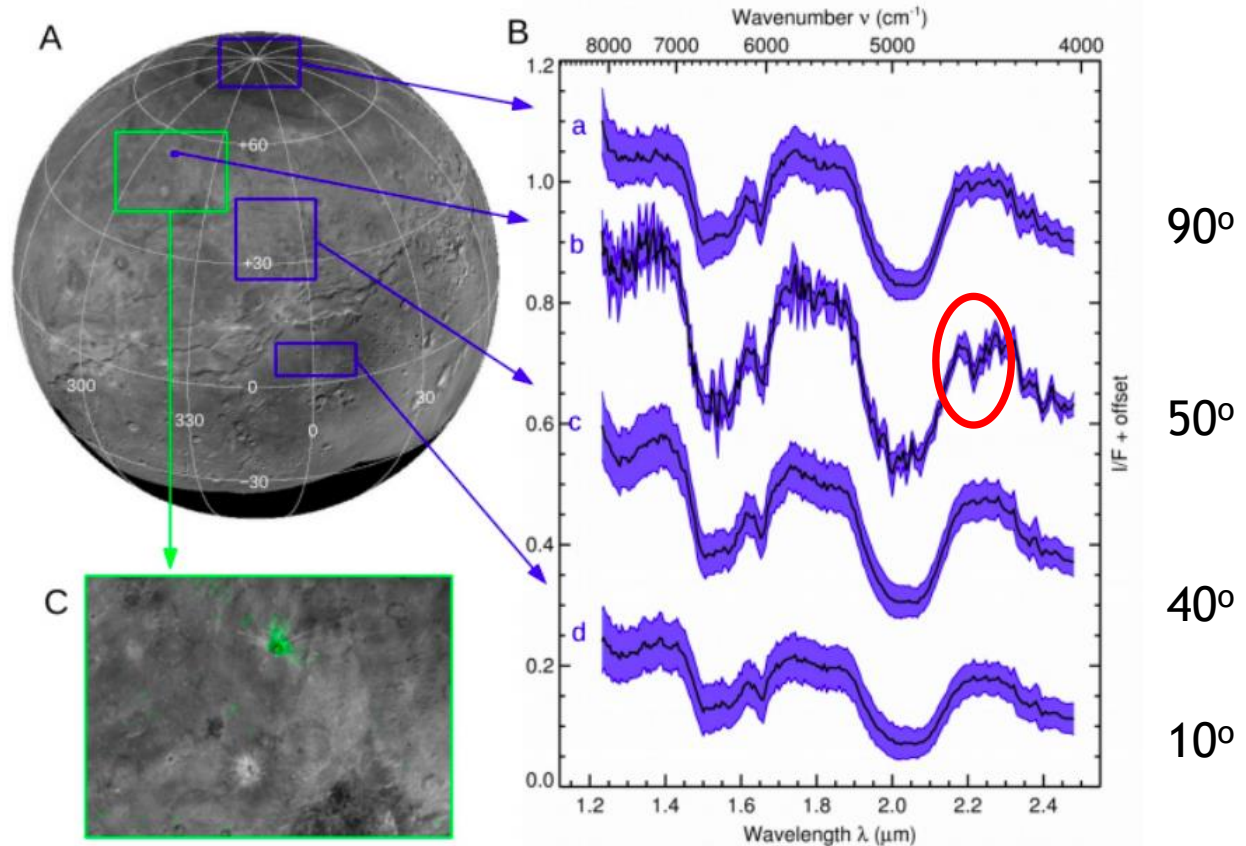
■ Astrophysical Implications

- 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

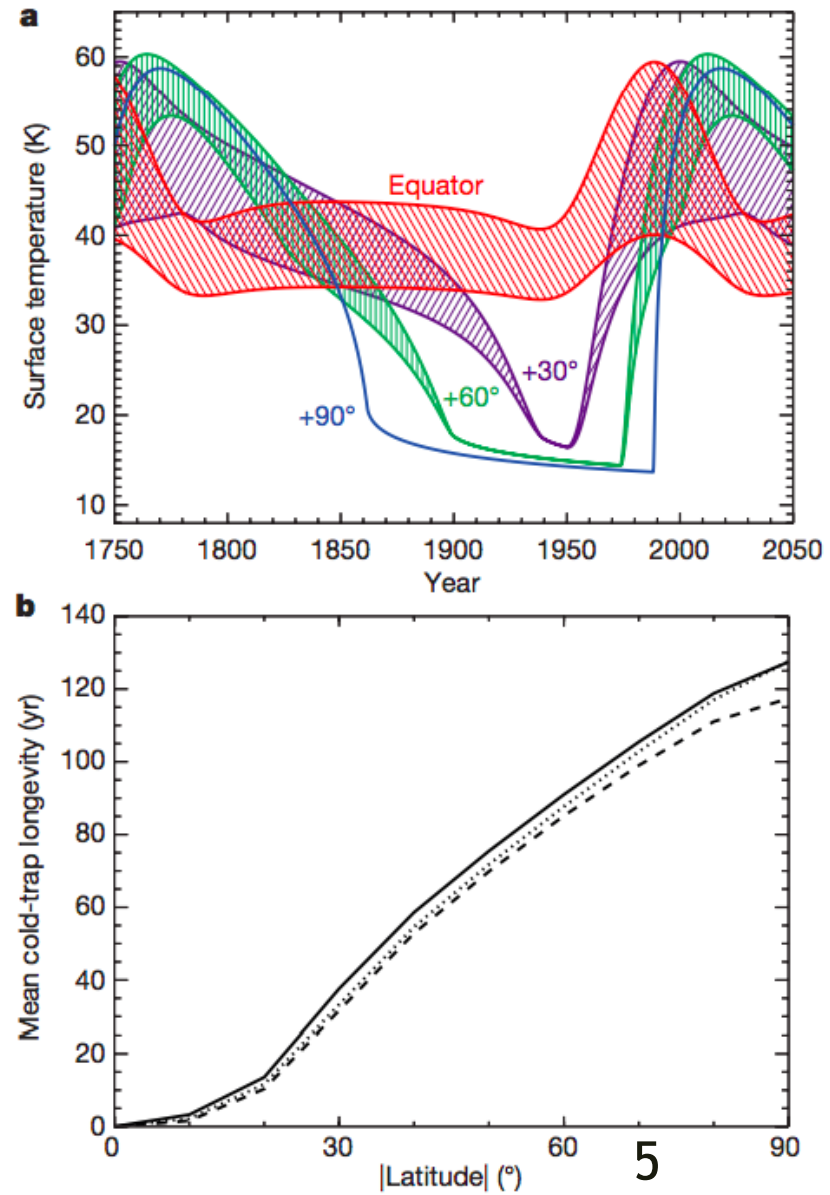


from Grundy et al. (2016)

Surface temperatures at different latitudes

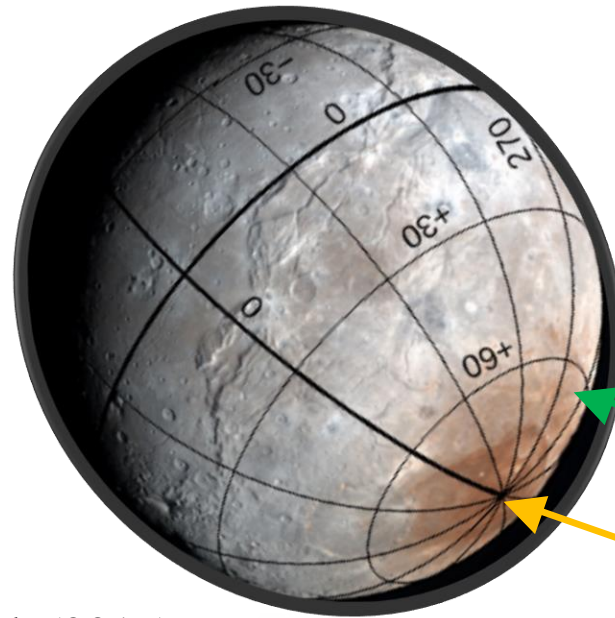
- Thermal model from Grundy et al. (2016) shows the pole position is **below 25 K** for 130 years
- **Methane can condense** on those positions where the temperature is below 25 K.

Quoted from Grundy et al. (2016)

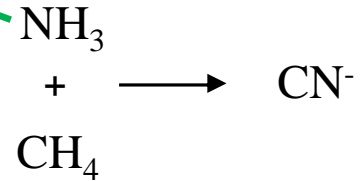


What astrophysical environments are we demonstrating?

Charon in Pluto system



VUV and EUV irradiation



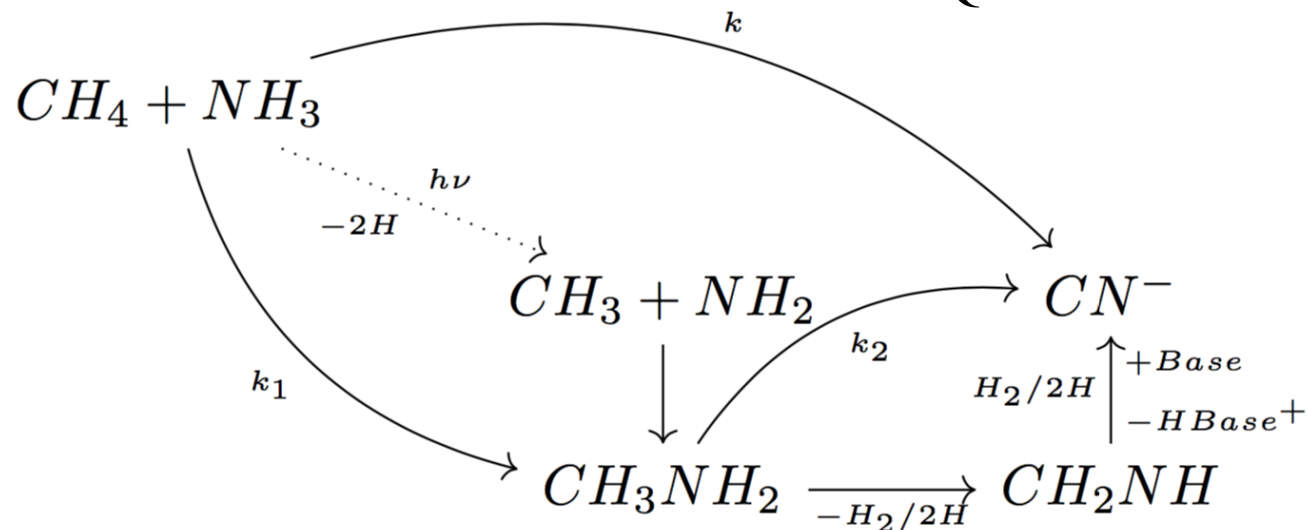
Quoted from Grundy et al. (2017)

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^-

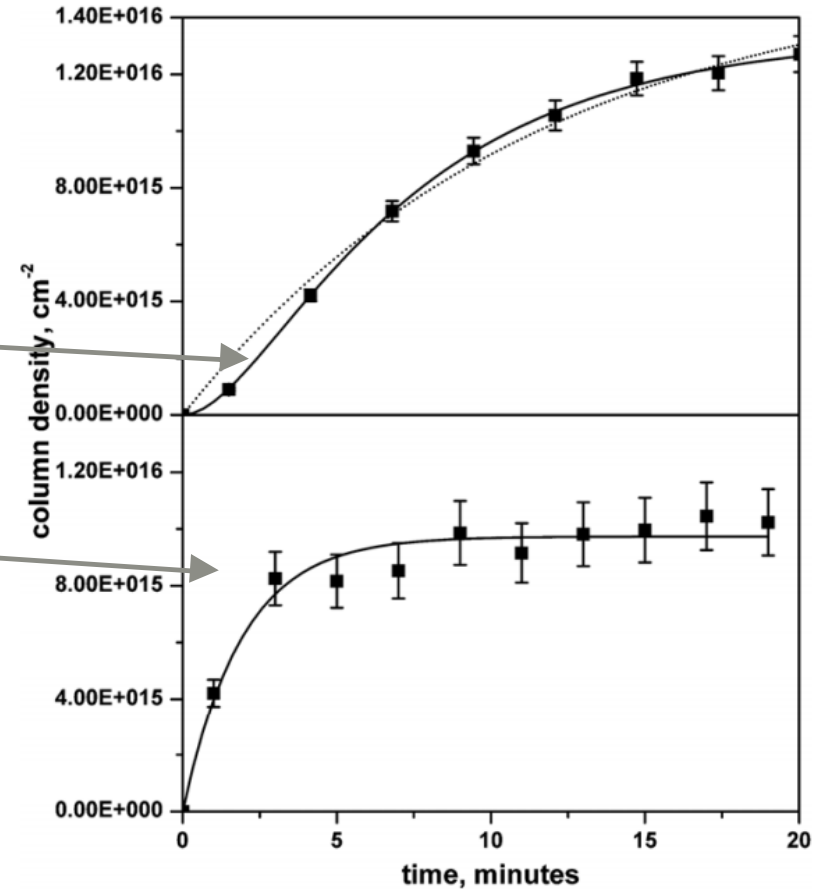
- 2 steps/1 step?

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

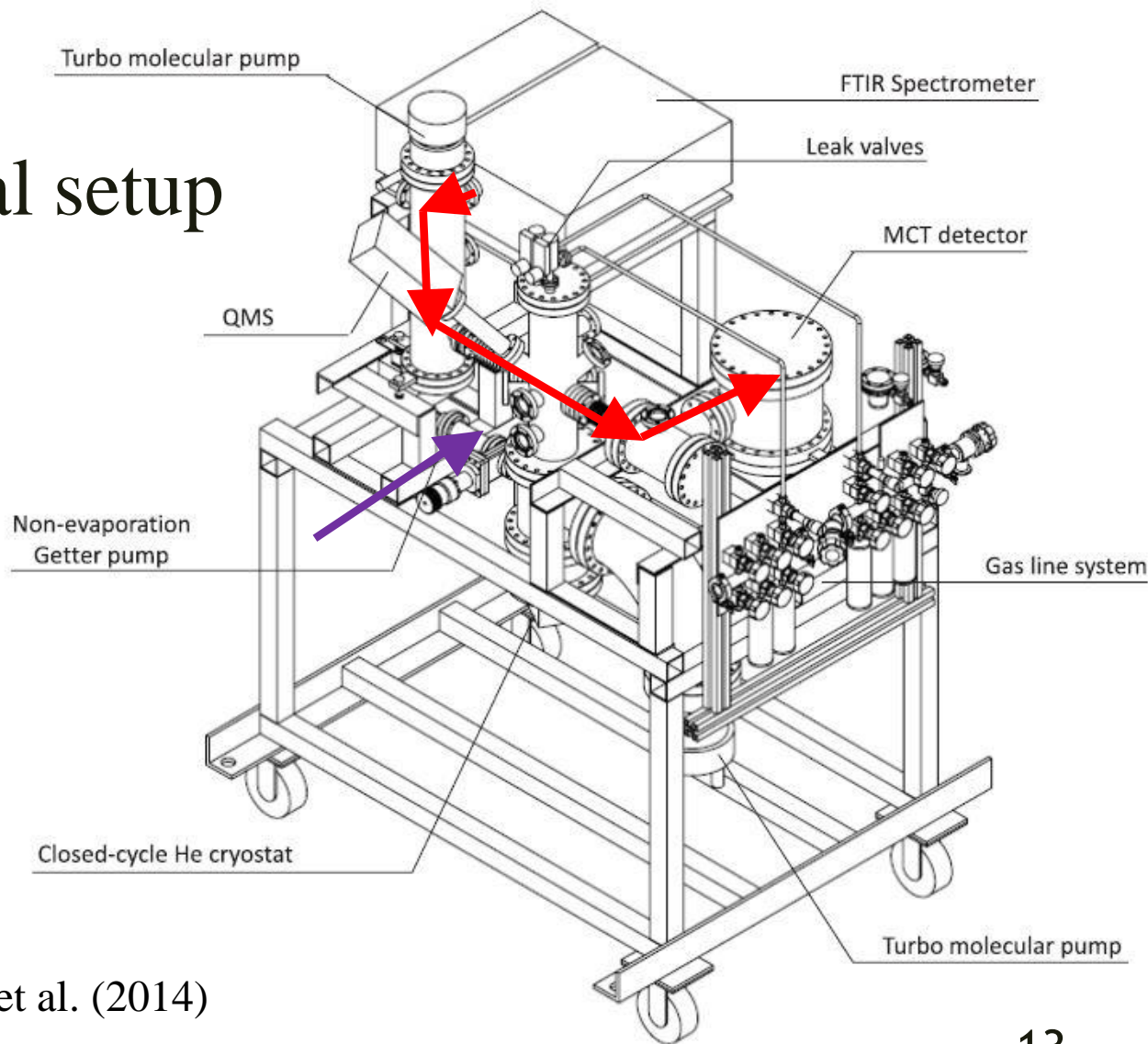
Experimental Configurations

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

- ▶ IR path
- ▶ VUV/EUV path



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)



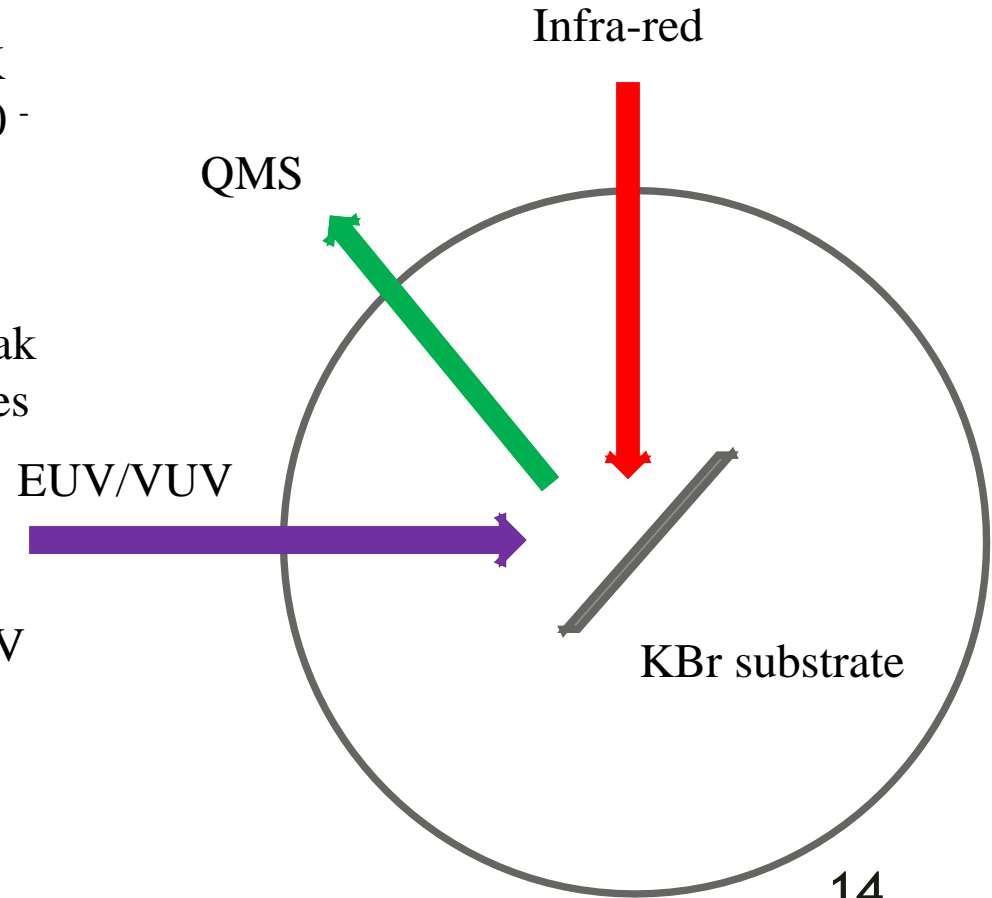
Deposit the ice mixtures through leak valve, with different partial pressures of CH_4 and NH_3



Irradiate the samples by EUV/VUV

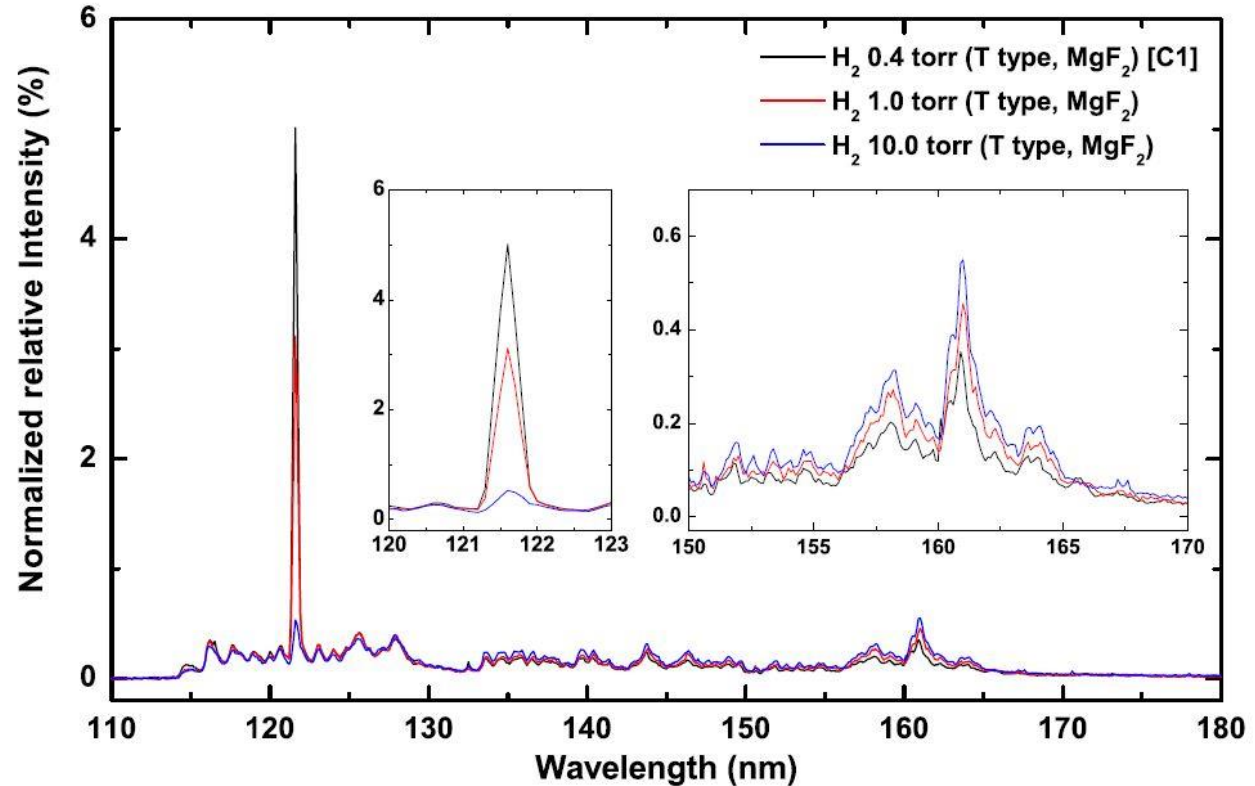


Warm-up with 1 K/min



The spectrum of VUV (MDHL) energy source

- 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 $\tau(\nu)$:

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

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

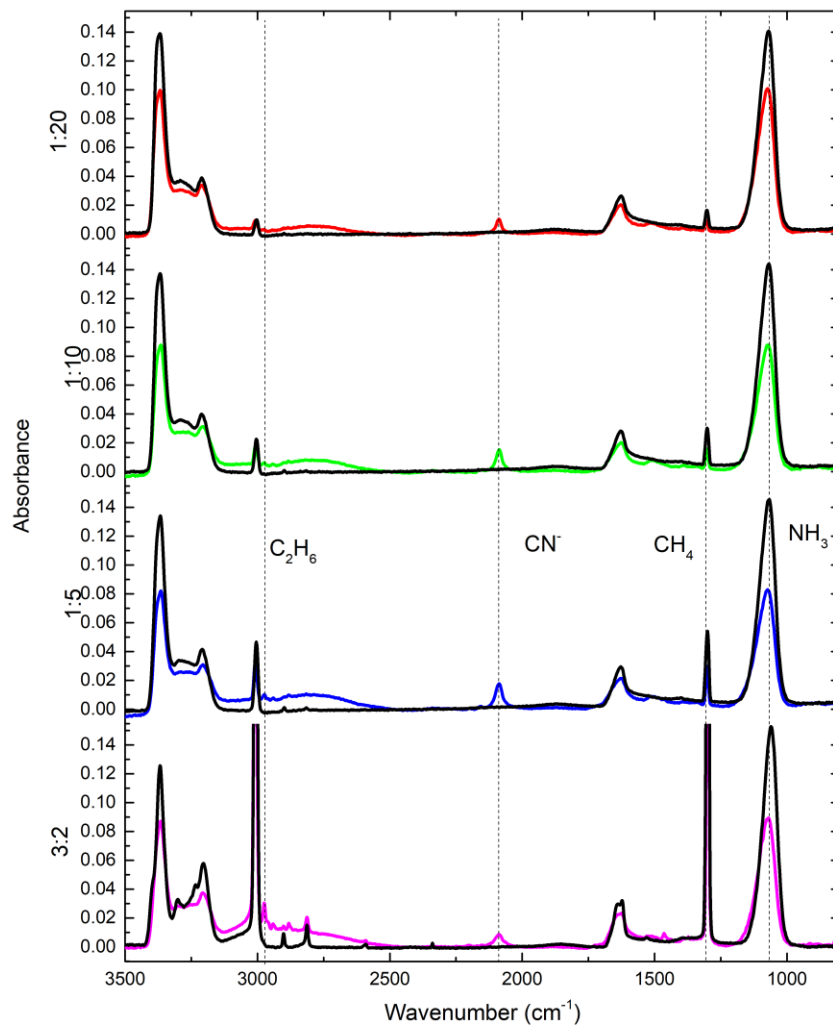
l : path length (cm)

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

Column density N :

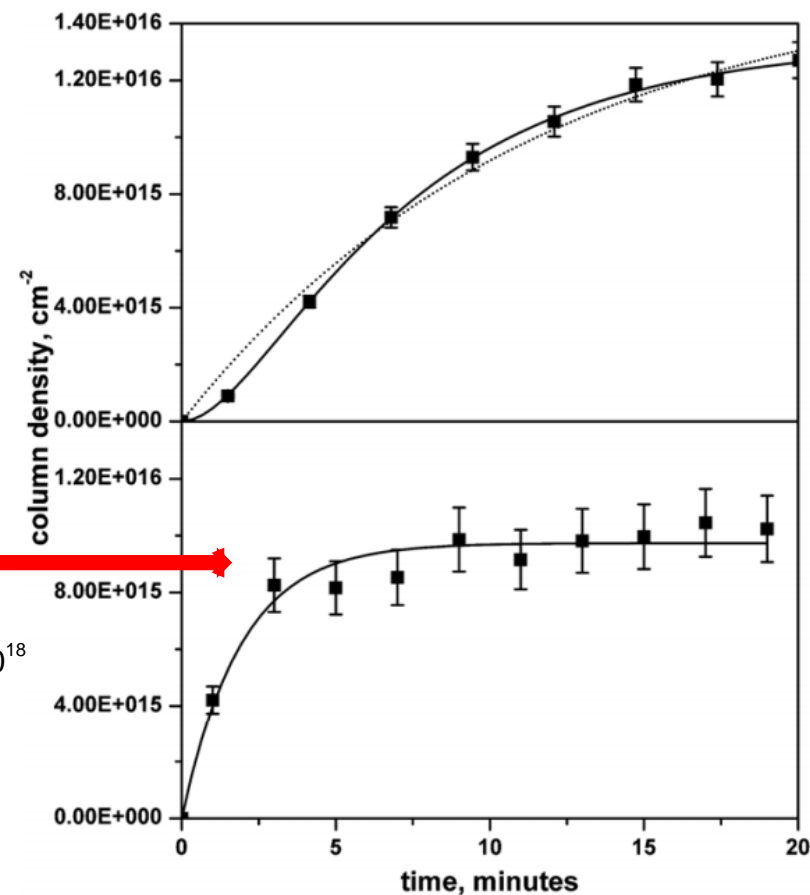
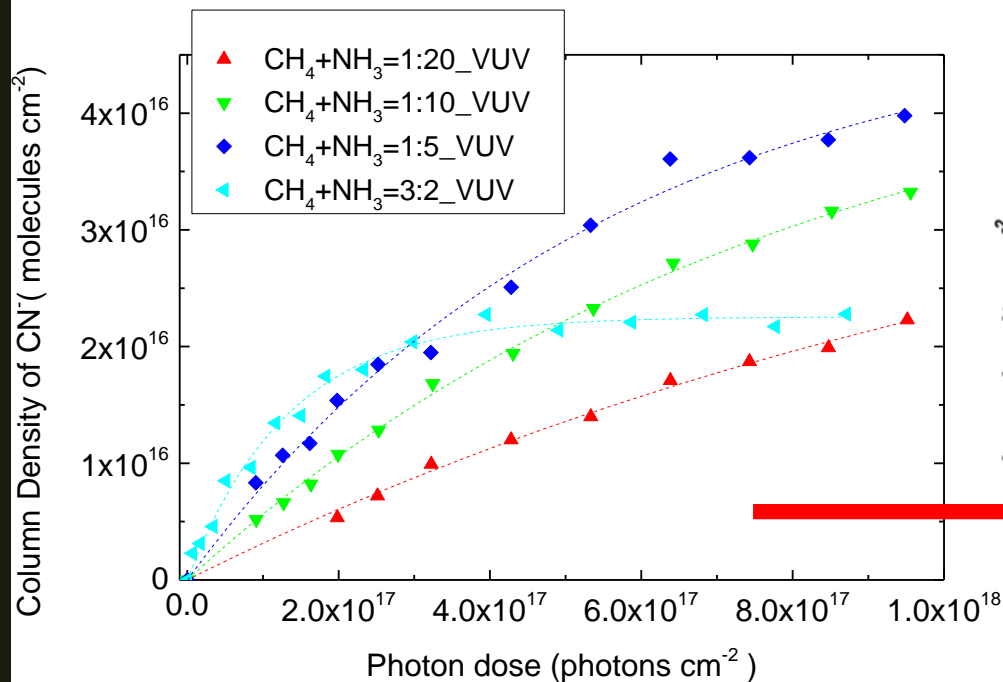
$$\blacksquare N = \frac{\int \tau(\nu) d\nu}{A(\nu)}$$

$A(\nu)$: 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^-

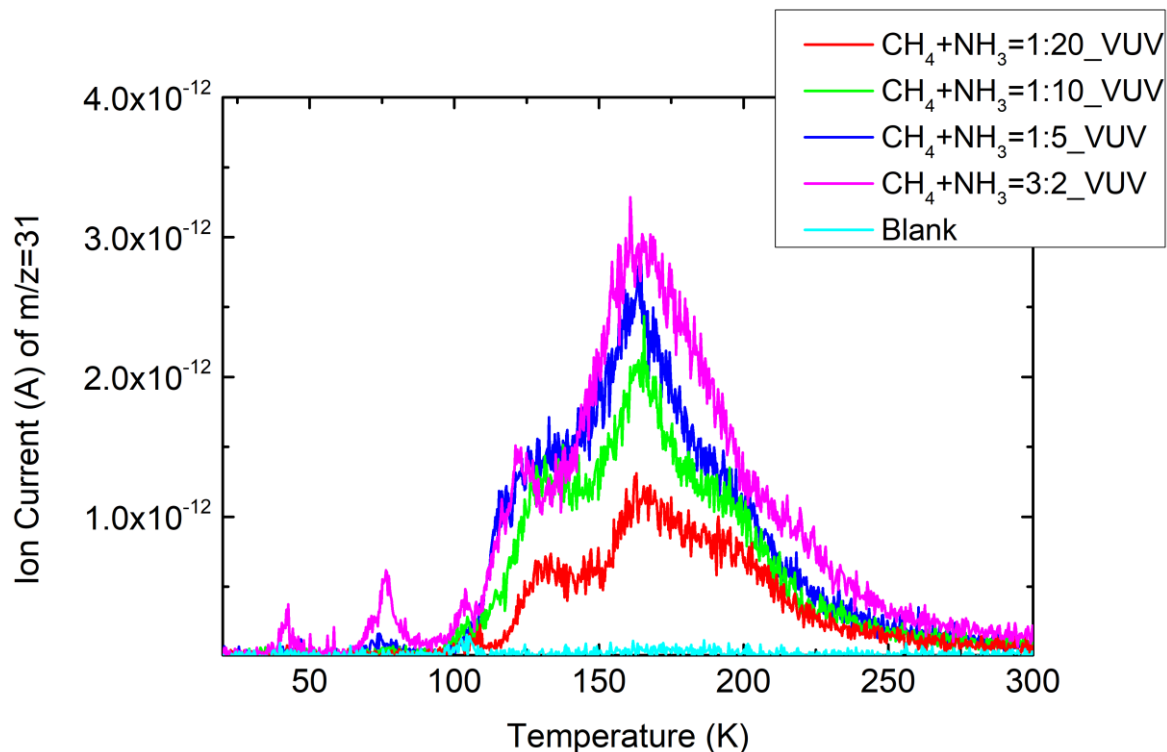
■ $[CN^-] = \left(1 + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} - \frac{k_2 e^{-k_1 t}}{k_2 - k_1}\right) [A]_o$

Ratio of CH_4+NH_3	A ($\times 10^{16}$ molecules cm^{-2})	k_1 ($\times 10^{-18}$ 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

1. Production of CN^-

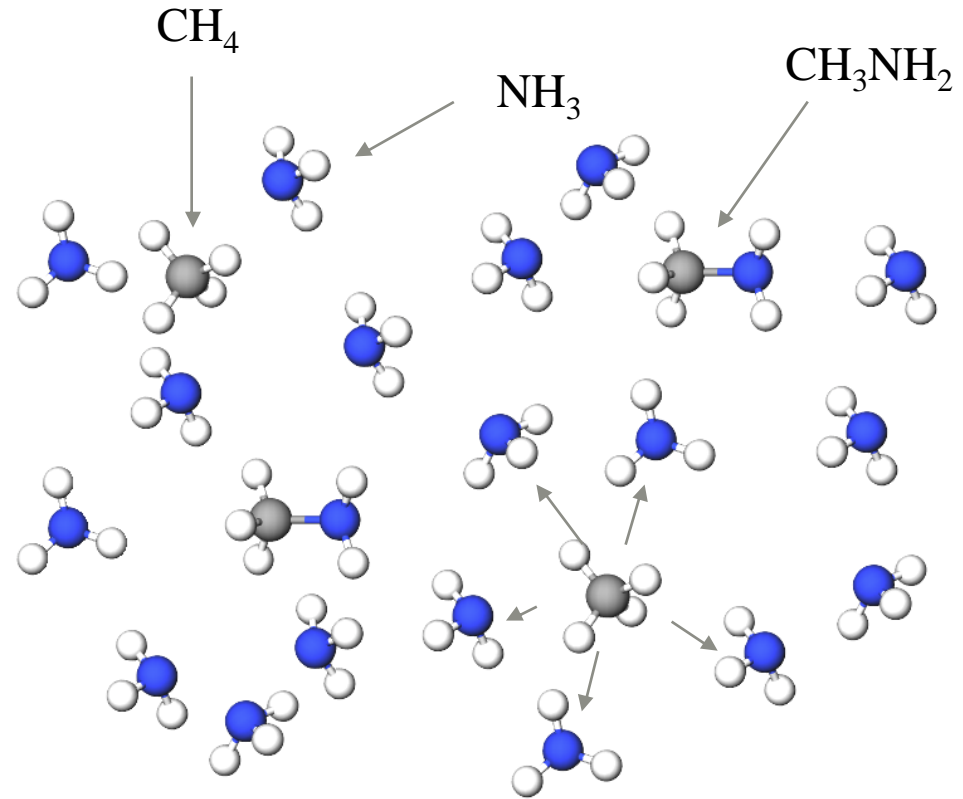
Methylamine
(CH_3NH_2) with
 $m/z=31$ is detected
by QMS

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^- .

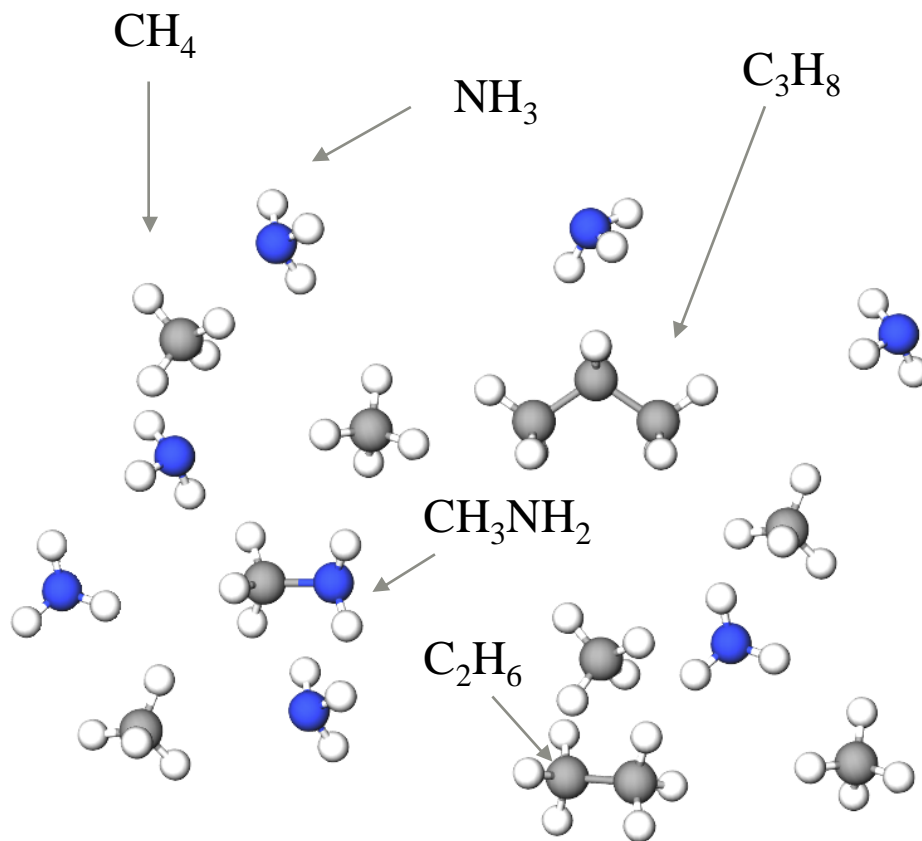


A diagram of $\text{CH}_4:\text{NH}_3 = 1:5$

2. The scenario for CH₄ dominating ice mixtures

CH₃NH₂ (formed by CH₃ + NH₂) has a competing relationship with C₂H₆ (formed by 2 CH₃) and C₃H₈ (formed by CH₂ + C₂H₆ or C₂H₄ + CH₄)

C₂H₆ can form easier than NH₃ dominating case

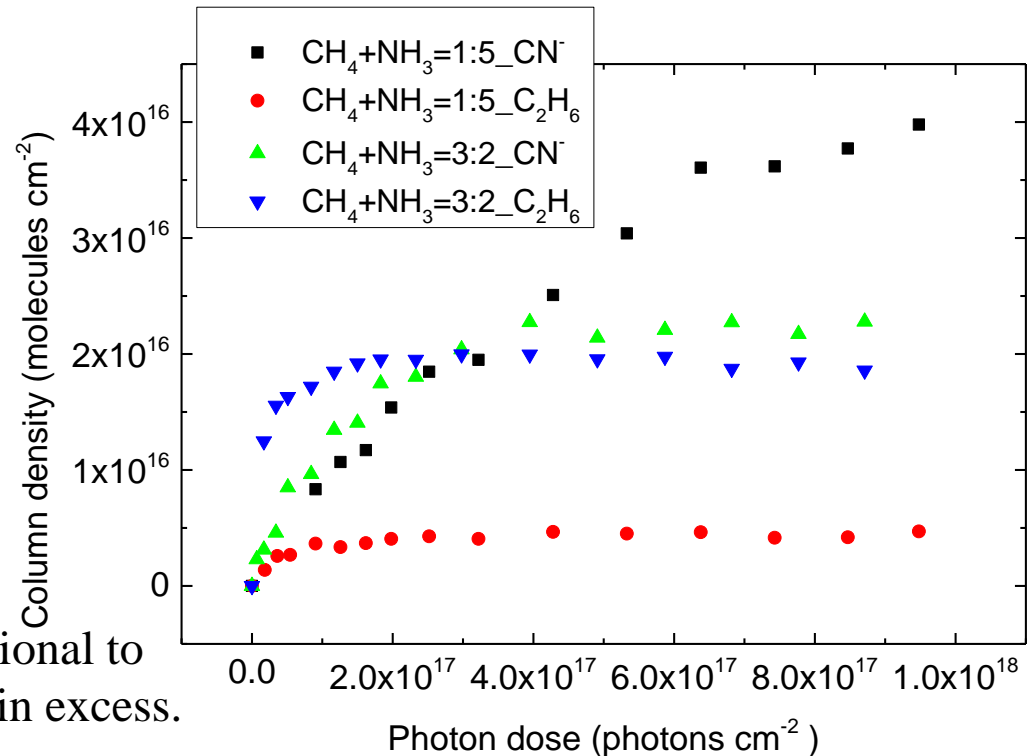


A diagram of CH₄+NH₃ = 3:2

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

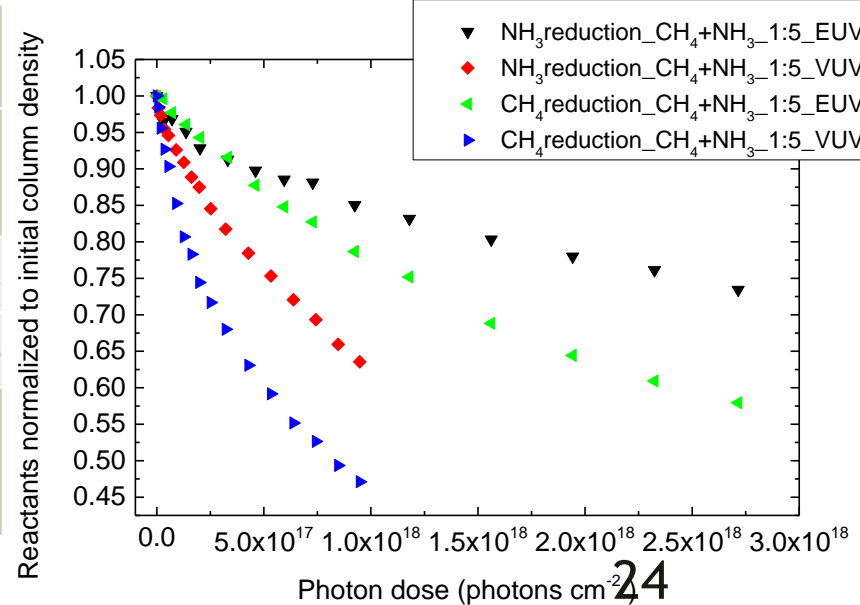
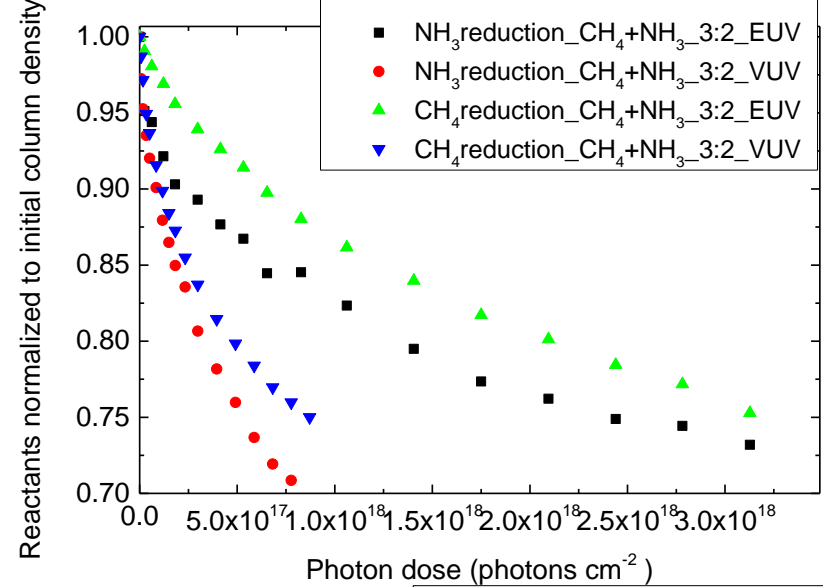
Concentration of CN^- is not proportional to initial amount of CH_4 when CH_4 is in excess.



3. Decay rate of reactants by EUV (40.1 eV) and VUV (9.27 eV)

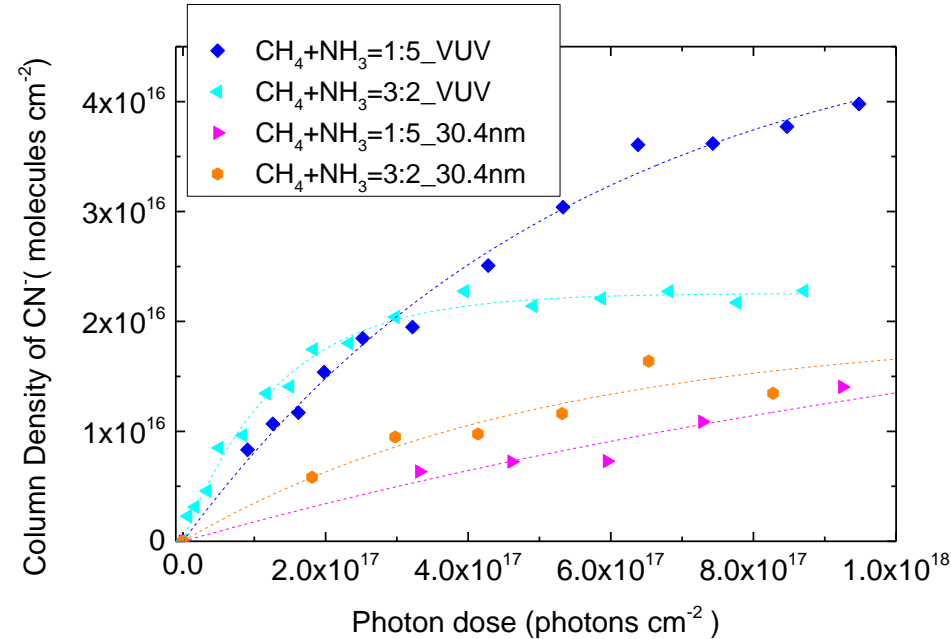
■ Fitting with $y = Ae^{-kx} + C$

Ratio of CH ₄ +NH ₃	3:2		1:5	
Decay rate k (photons ⁻¹ cm ²)	CH ₄ (x 10 ⁻¹⁸)	NH ₃ (x10 ⁻¹⁸)	CH ₄ (x 10 ⁻¹⁸)	NH ₃ (x10 ⁻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
Ratio of k (VUV to EUV)	6.06±0.07	3.18±0.12	5.52±0.07	2.07±0.13



3. Formation rate of CN^- by EUV (40.1 eV) and VUV (9.27 eV)

CN^- production rate k (photon $^{-1}\text{cm}^2$)	$\text{CH}_4 : \text{NH}_3$ 3:2 ($\times 10^{-18}$)	$\text{CH}_4 : \text{NH}_3$ 1:5 ($\times 10^{-18}$)
VUV (MDHL)	8.21 ± 0.70	1.93 ± 0.19
EUV (30.4nm)	1.92 ± 1.99	0.63 ± 0.37
Ratio of k (VUV to EUV)	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: $1.9 \times 10^9 \text{ eV cm}^{-2} \text{ s}^{-1}$

(Grundy et al. 2016)

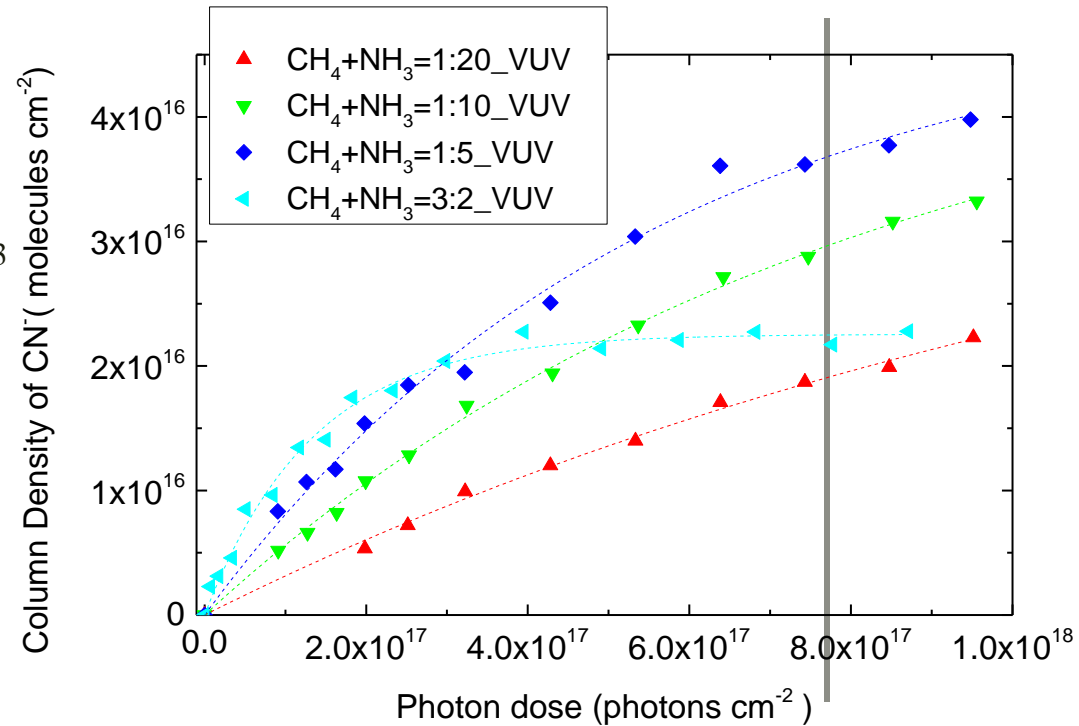
→ photon dose after 1 Pluto winter

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

CH₄ after winter ~173 ML

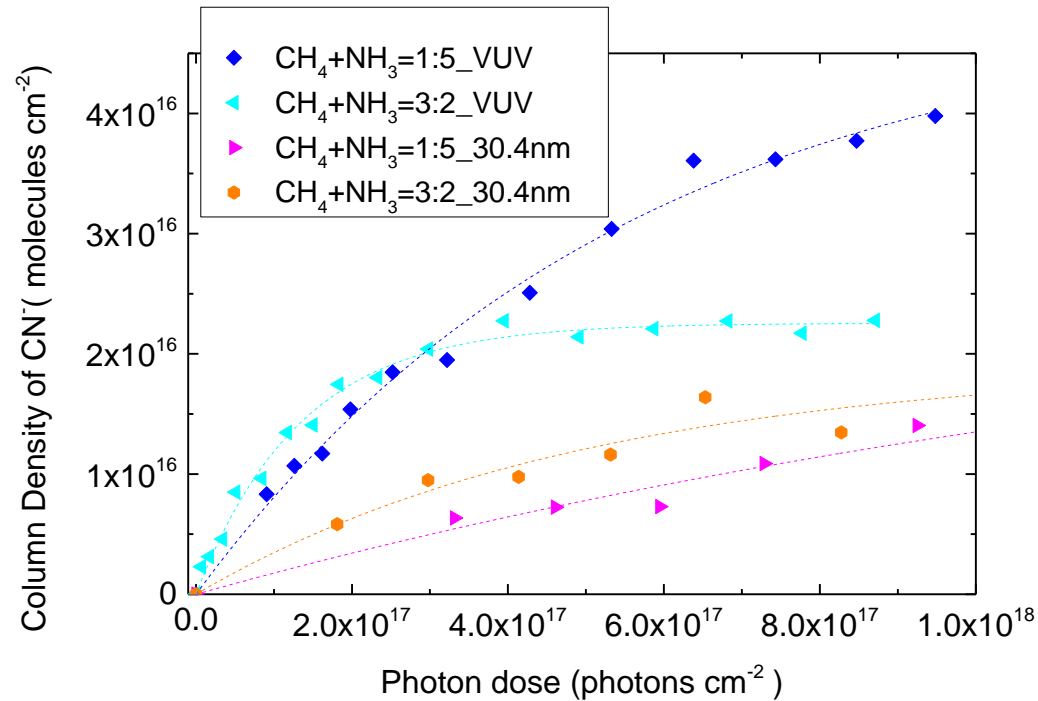
Assume the column density of NH₃ is 600 ML

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

