VUV AND EUV IRRADIATION OF CH_4 + NH_3 ICE MIXTURES

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Motivation

Motivation

- *CN^- formation mechanisms*
  - Different results from 2 groups by electron irradiation at 10-15 K
  - We try to study the mechanism by VUV and EUV photons

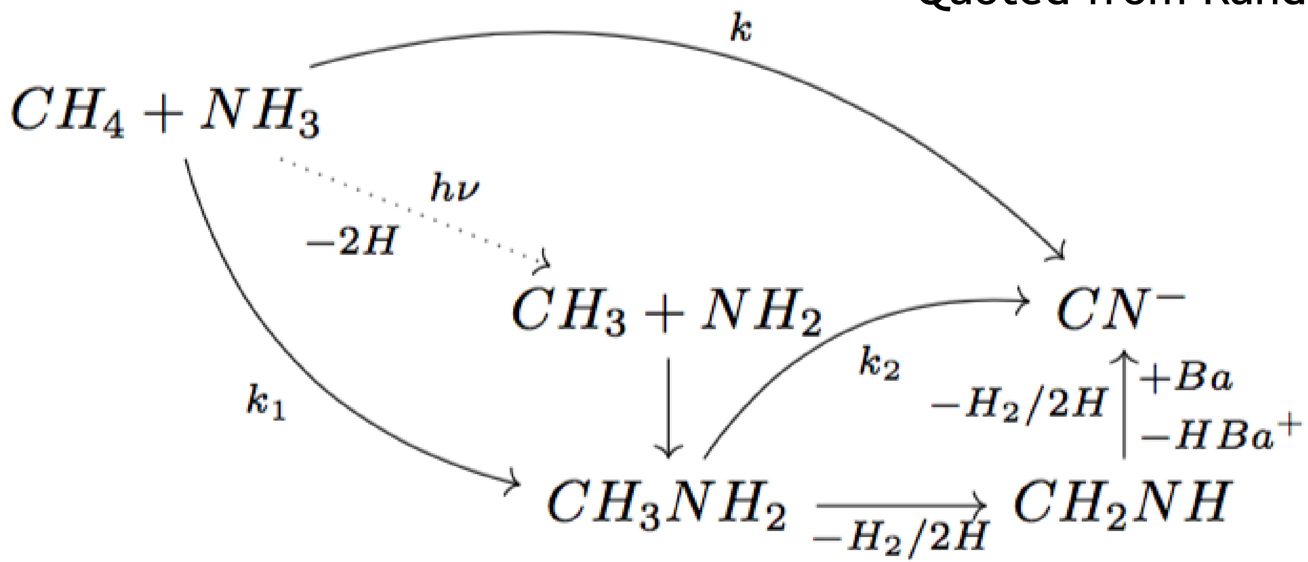
- *The following constituents are used to simulate Surface of Charon*
  - NH_3 : Infra-red spectra shows ammonia on Organa Crater
  - CH_4 : Surface temperatures at different latitudes
  - We try to study different relative ratios of CH_4 and NH_3 ice mixtures

Production mechanism of CN^-

Enthalpy of CH_3NH_2 formation

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

Quoted from Kundu et al. (2017)



Quoted from Kim and Kaiser (2011)

Production of CN^-

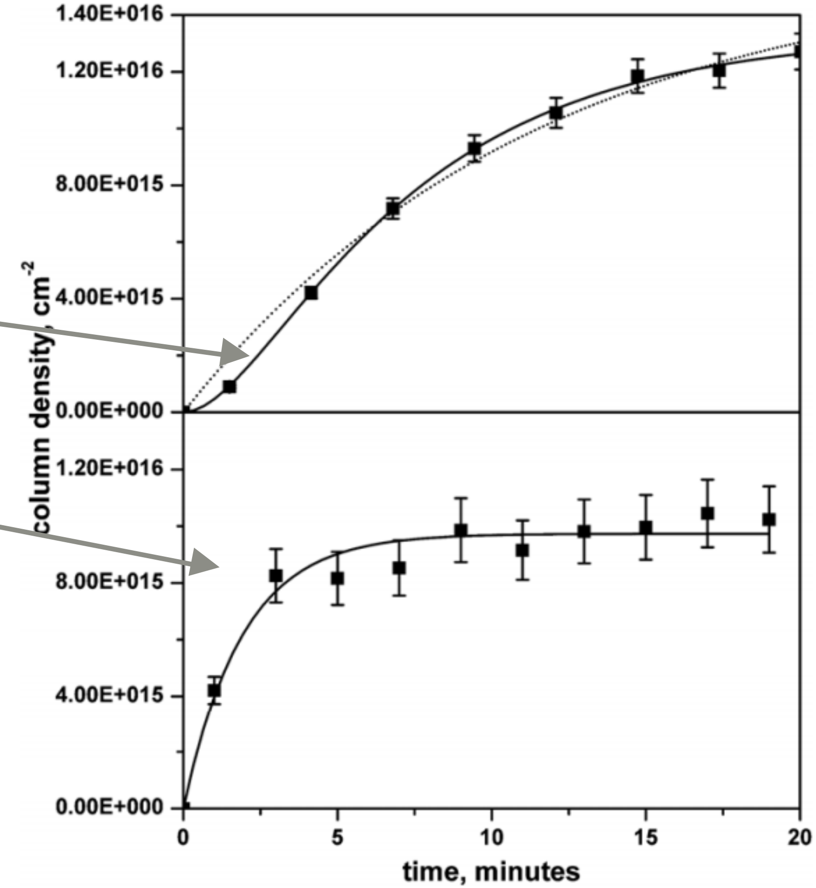
- 2 steps/1 step?

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^-

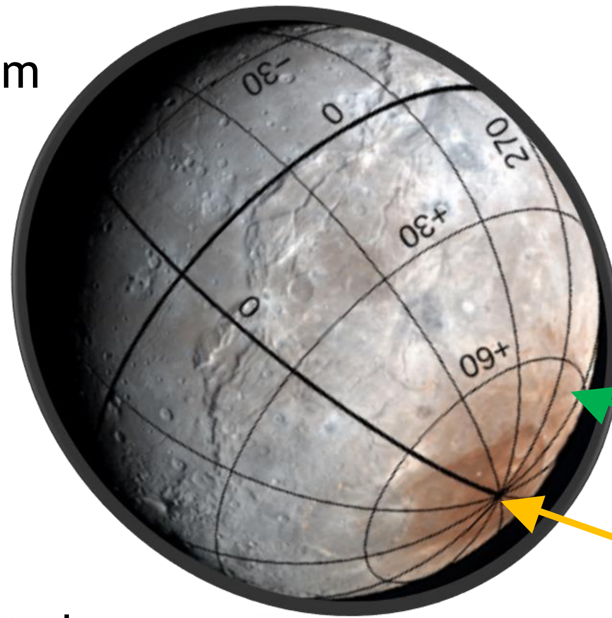
Attempts to detect CH_3NH_2:

- 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 EUV and VUV photons?

What astrophysical environments are we demonstrating?

Charon in Pluto system



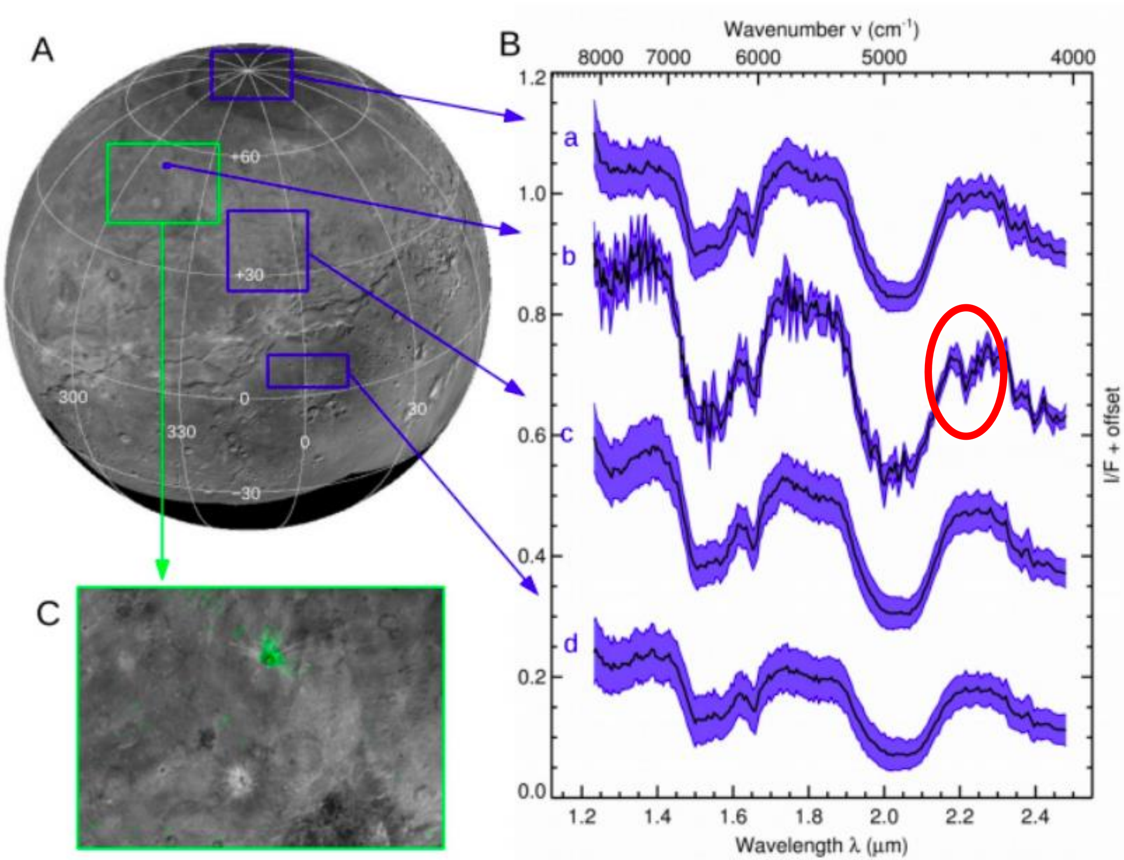
VUV and EUV irradiation

$NH_3 + CH_4 \longrightarrow CN^-$

Quoted from Grundy et al. (2017)

Ammonia on Organa Crater

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

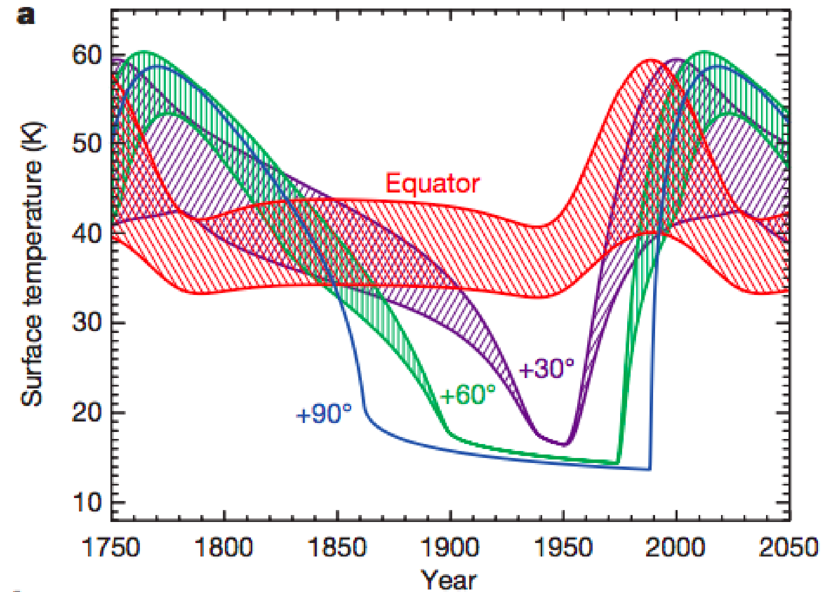


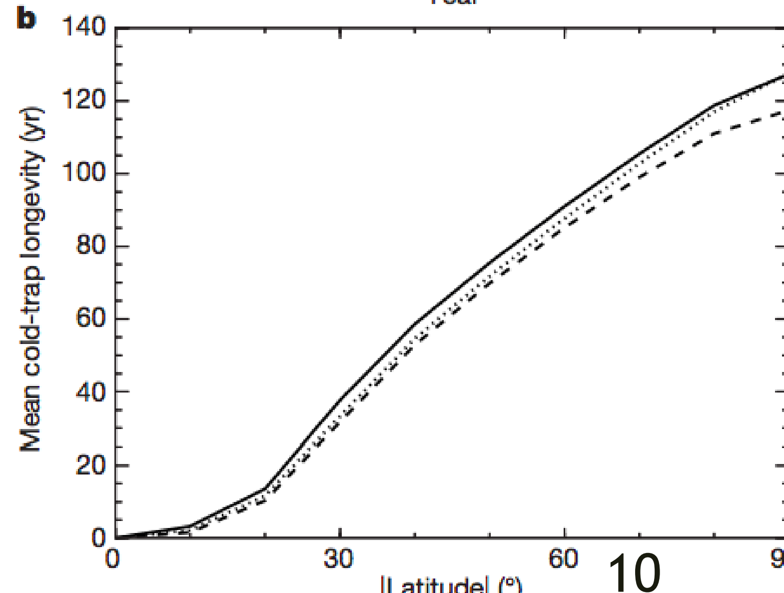
from Grundy et al. (2016)

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)





Short Summary

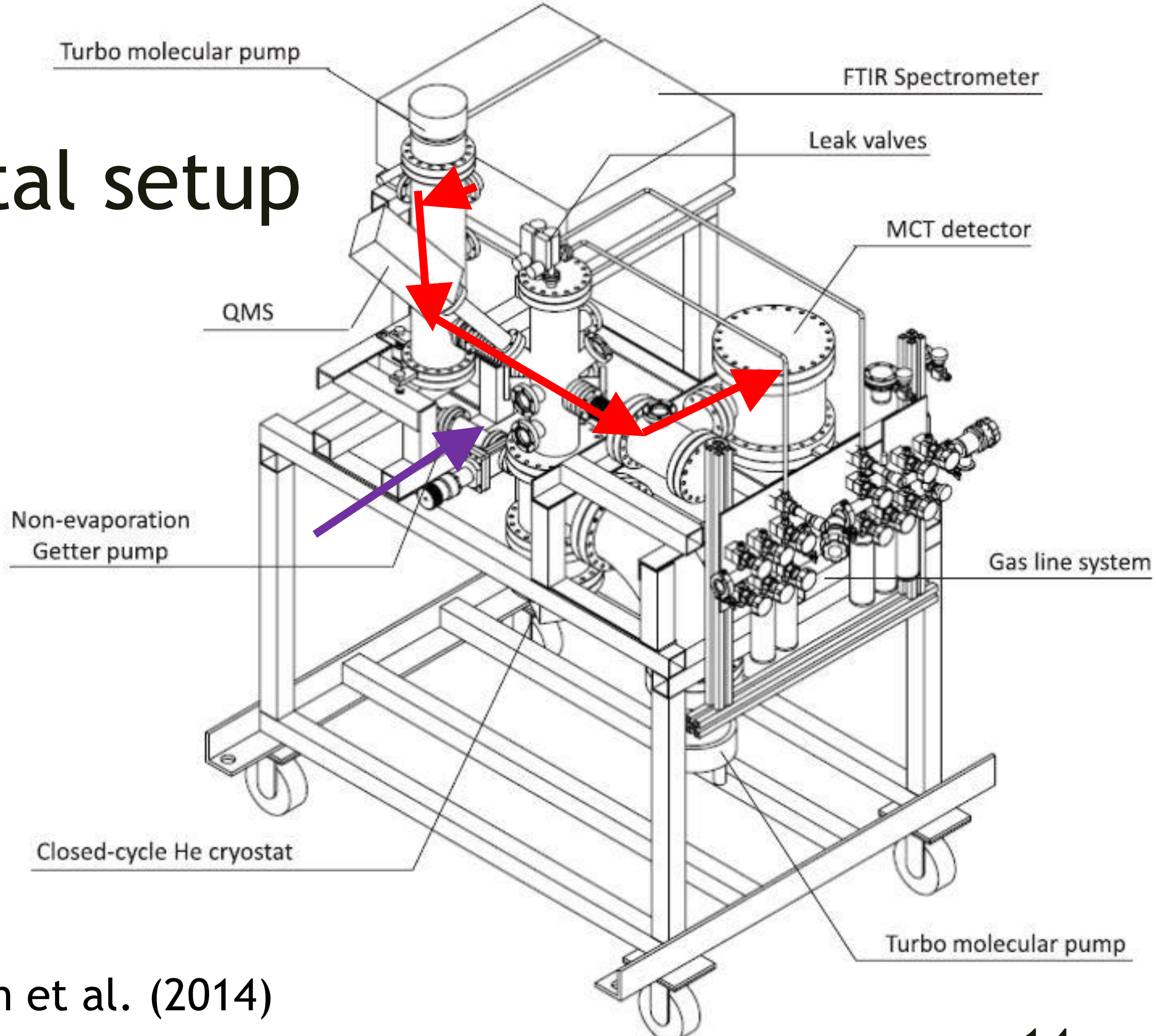
- 1. To compare with previous studies
  - *Kim and Kaiser (CH_4:NH_3 3:1) and Kundy et al. (2017) (CH_4:NH_3 3:2)*
  - *We perform experiment of CH_4+NH_3 = 3:2*
  - *Confirm the mechanism of CN^-*
- 2. To simulate the surface of Charon
  - *Experiment: CH_4:NH_3 =1:5, 1:10, 1:20*
  - *Variation of photon sources: from VUV to EUV*

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	--	--

Experimental setup



IR path

VUV/EUV path

Quoted from Chen et al. (2014)

Experimental Protocol

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

↓

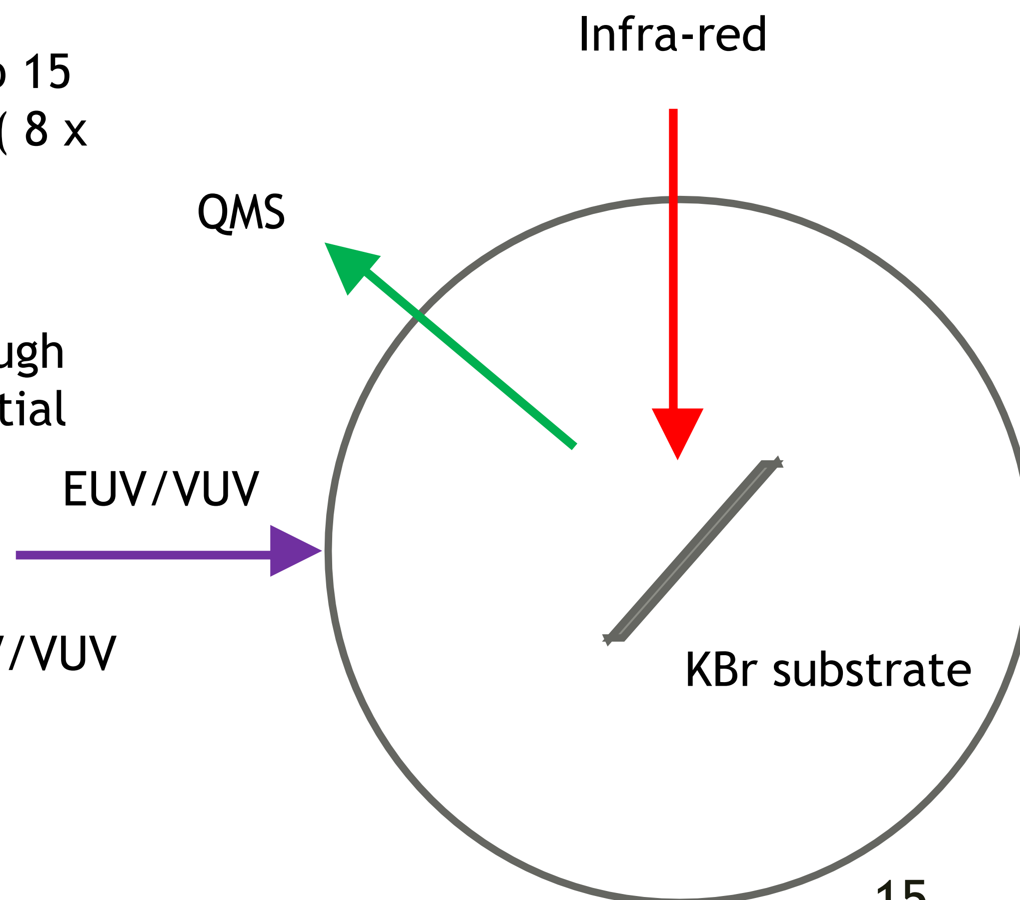
Deposit the ice mixtures through leak valve, with different partial pressures of CH_4 and NH_3

↓

Irradiate the samples by EUV/VUV

↓

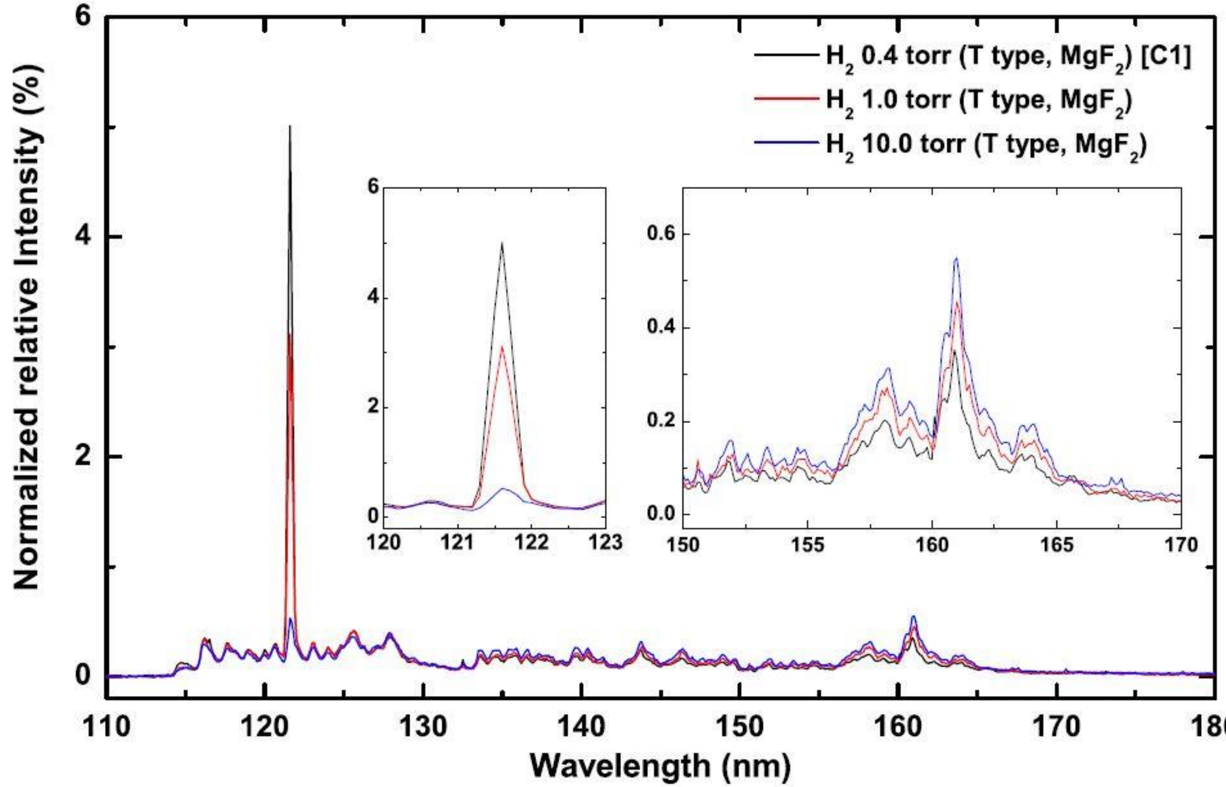
Warm-up with 1 K/min



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

Transmittance $T(v)$ is defined by:

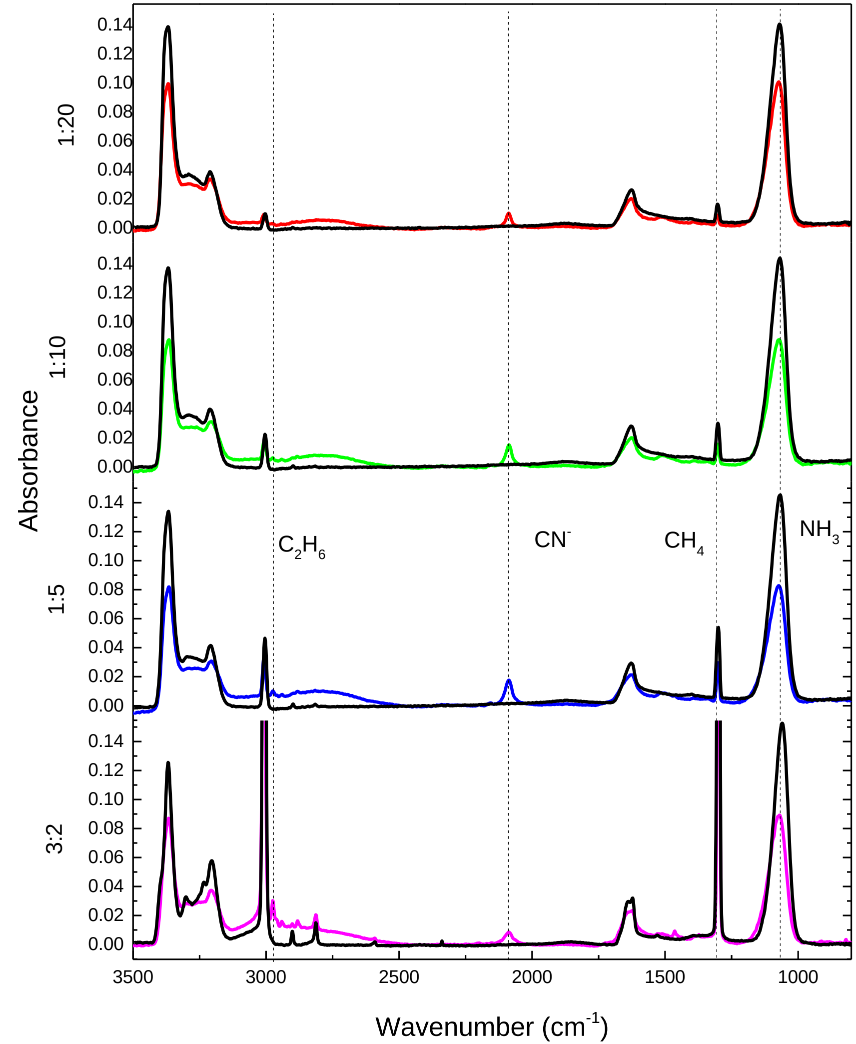
- $T(v) = \frac{I(v)}{I_o(v)}$

Absorbance $\tau(v)$ *is defined by:*

- $\tau(v) = -lnT = -\ln\left(\frac{I(v)}{I_o(v)}\right) = nl\sigma(v)$
  - *where n is number density (molecules cm^{-3}), l is the path length (cm) and $\sigma(v)$ is the cross-section (cm^2 molecules $^{-1}$)*

Column density N *is defined by:*

- $N = \frac{\int \tau(v)dv}{A(v)}$
  - *where N is column density (molecules cm^{-2}), $A(v)$ 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⁻

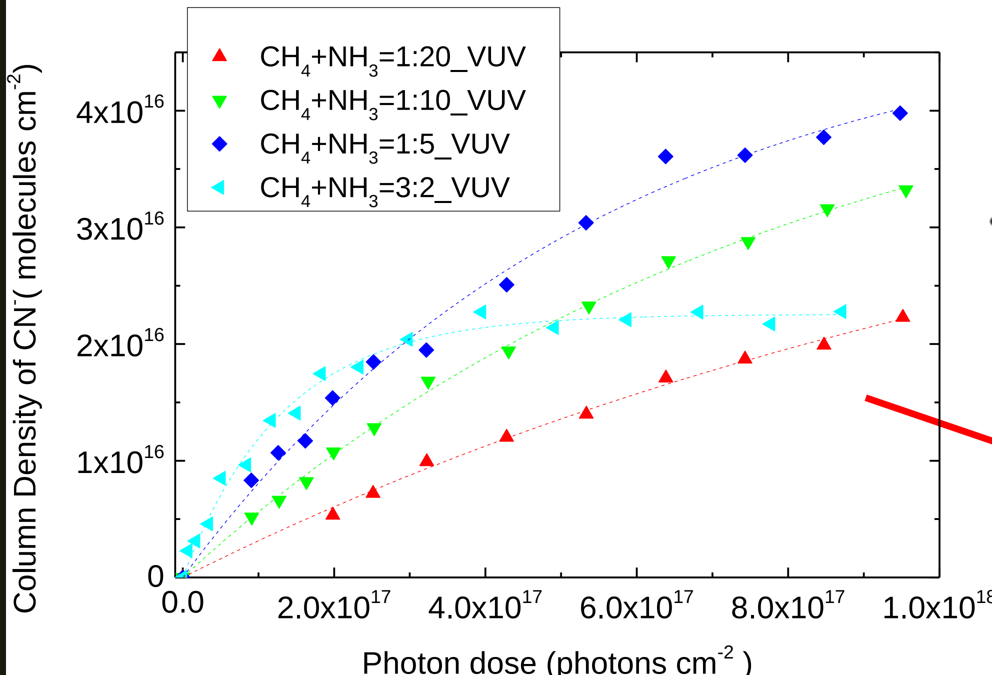
- $[CN^-] = \left(1 + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} - \frac{k_2 e^{-k_1 t}}{k_2 - k_1}\right)[A]_o$

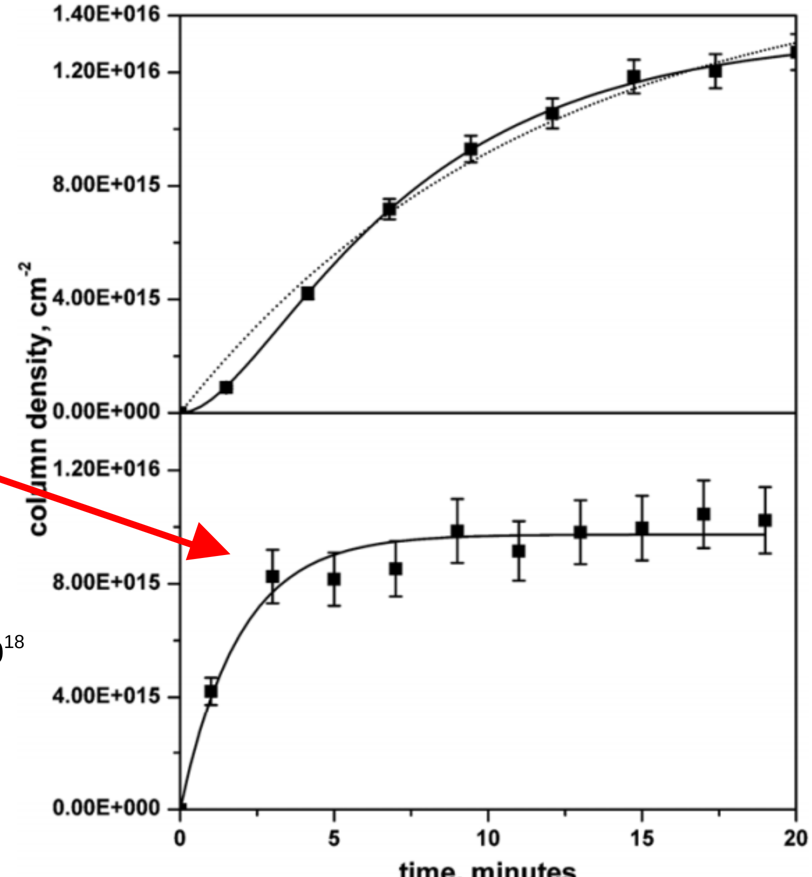
Table 3.5: The fitting results of CN^- by equation 2.10

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 ($\times 10^{-3}$ s^{-1})	k_2 ($\times 10^{-3}$ 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_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.

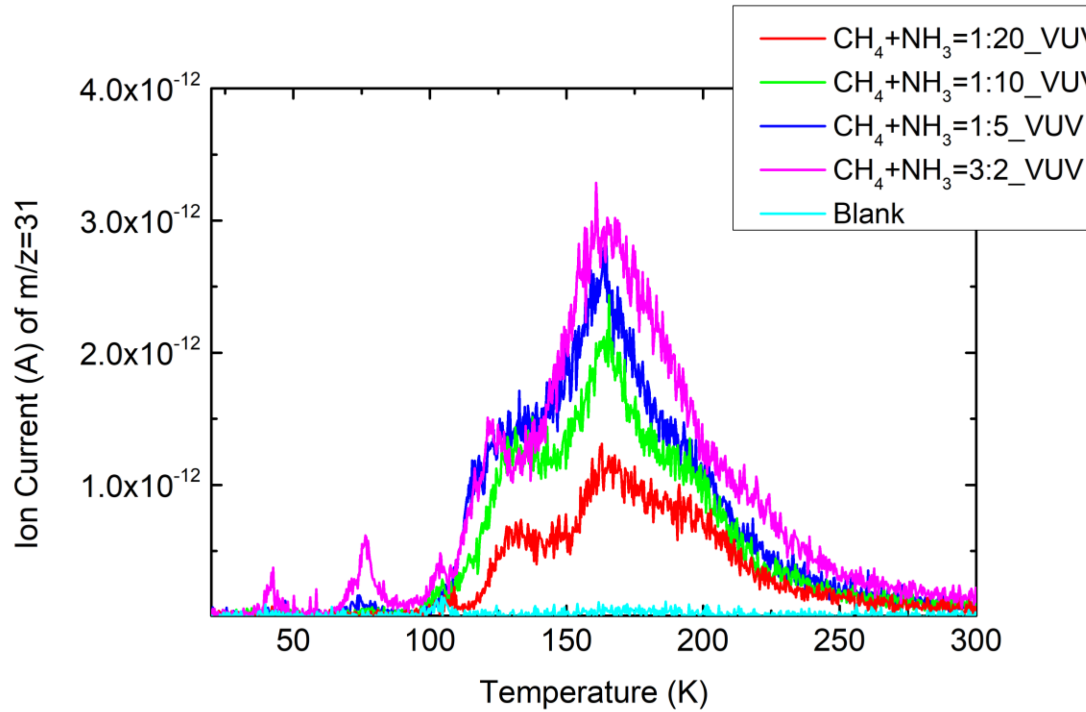
1. Production of CN^-





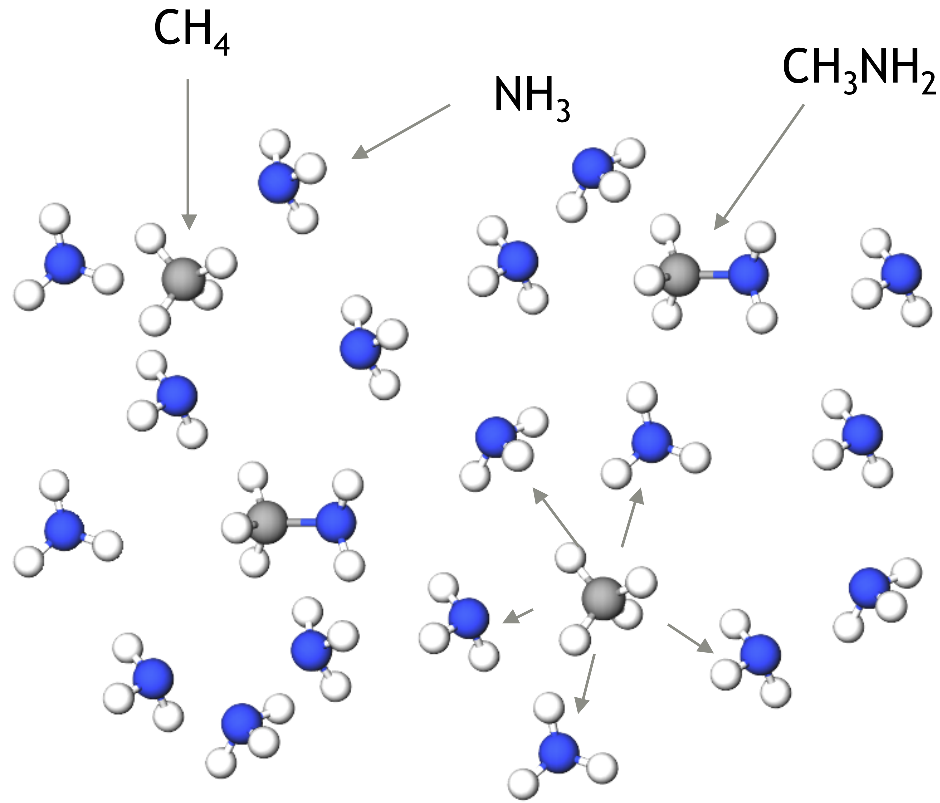
1. Production of CN^-

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



2. The scenario for NH_3 dominating ice mixtures

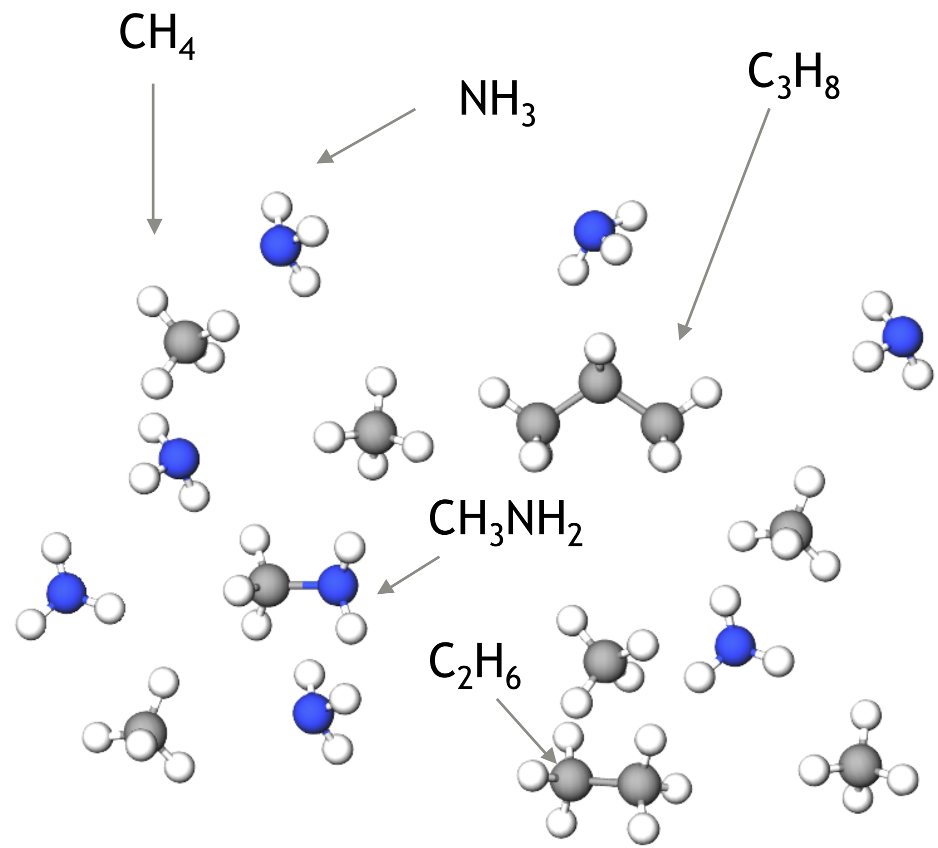
Once CH_4 becomes CH_3 radical, it can easily forms CH_3NH_2 and hence become CN^-.



A diagram of CH_4: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)

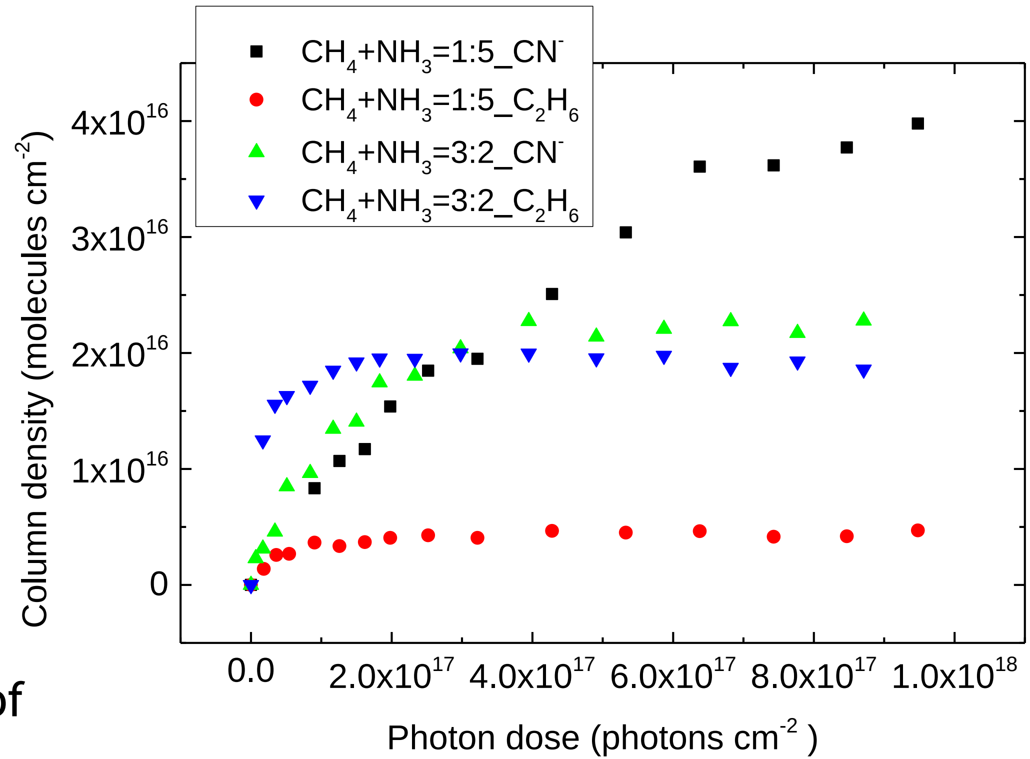


A diagram of CH_4+NH_3 = 3:2

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

$CH_4:NH_3$	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.



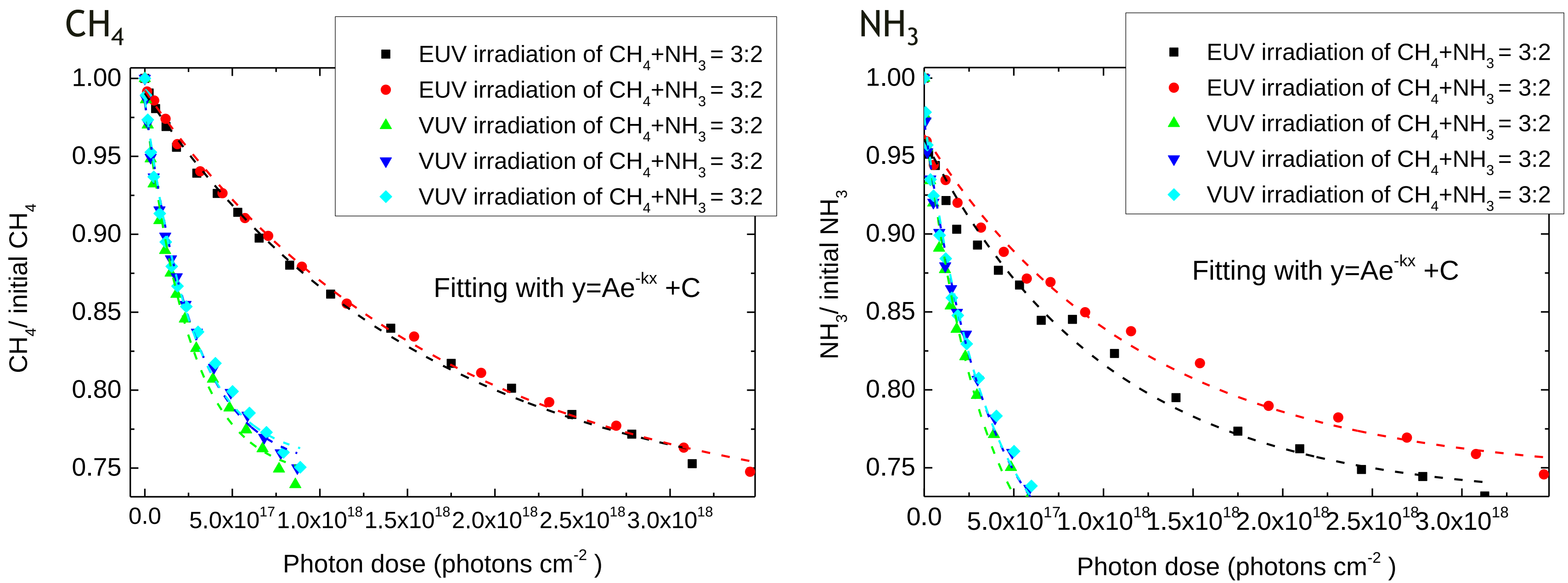
3. Energy needed for forming radicals by EUV (40.1 eV) and VUV (9.27 eV)

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))

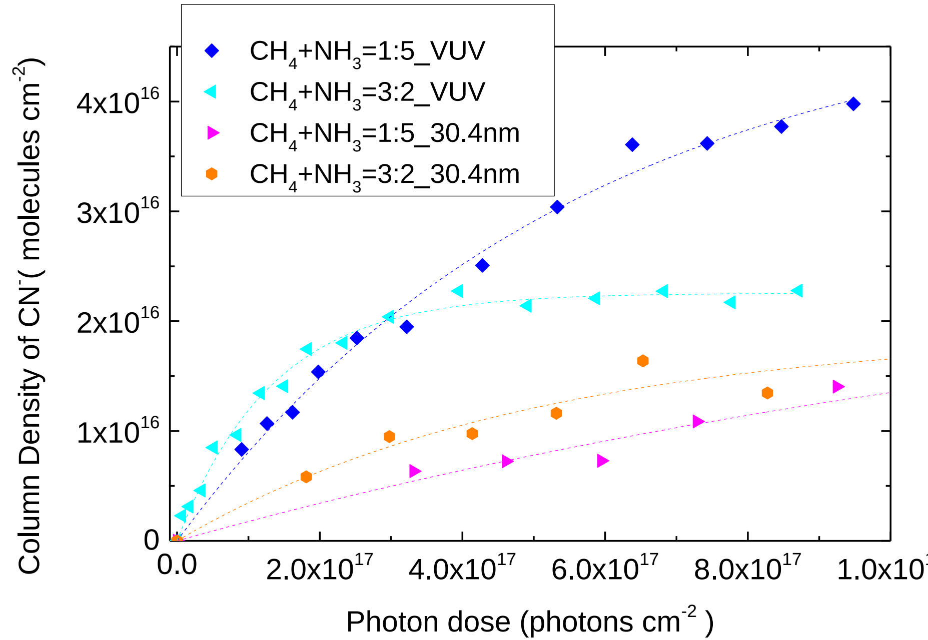
3. Destruction cross-section of EUV (40.1 eV) and VUV (9.27 eV)

- 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 x 10^9 eV cm^{-2} s^{-1} (Grundy et al. 2016)

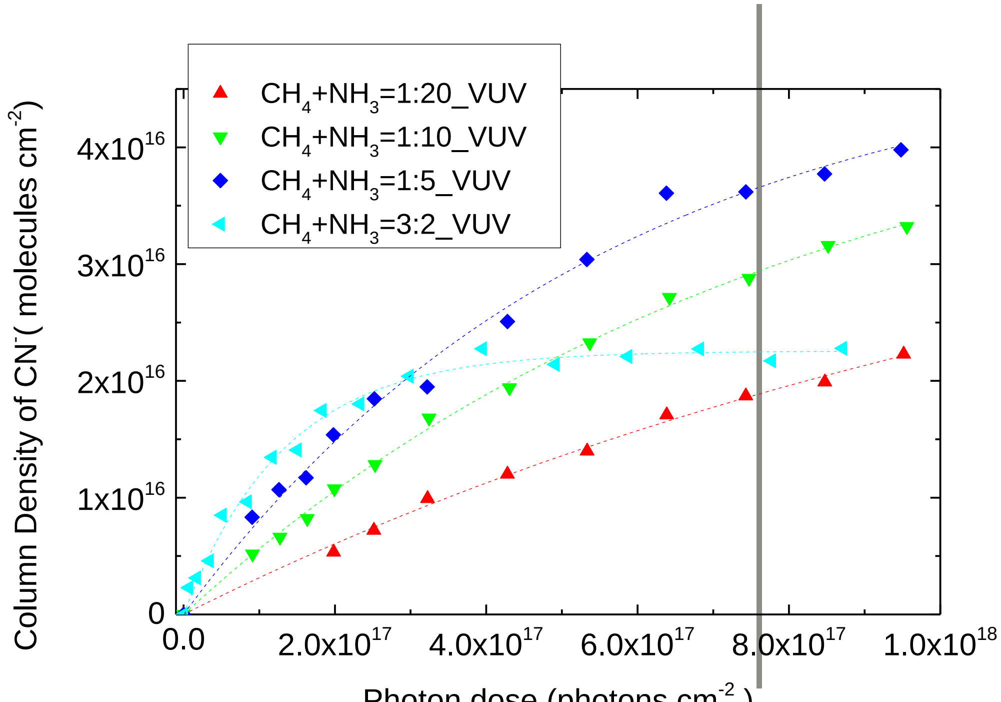
→photon dose: 7.64 x 10^{17} photons cm^{-2}

- CH_4 deposition rate:

(Hoey et al. 2017)

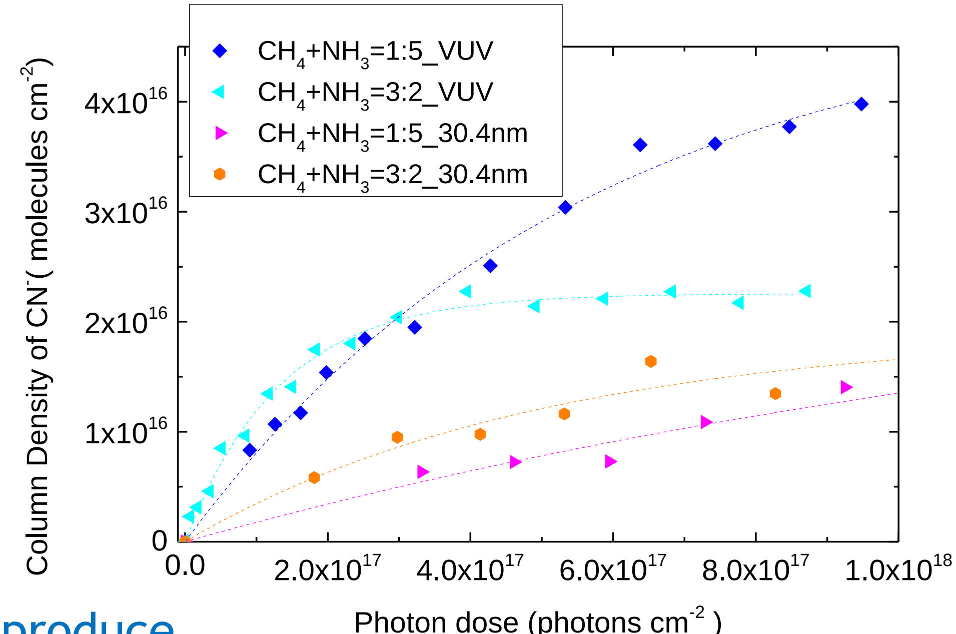
→ ~110-150 ML in 130 earth years

CH_4+NH_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-a exposure: 1.9 x 10^9 eV cm^{-2} s^{-1}*
  - *EUV exposure: 8.7 x 10^7 eV cm^{-2} 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