VUV AND EUV IRRADIATION OF $CH_4 + NH_3$ ICE MIXTURES

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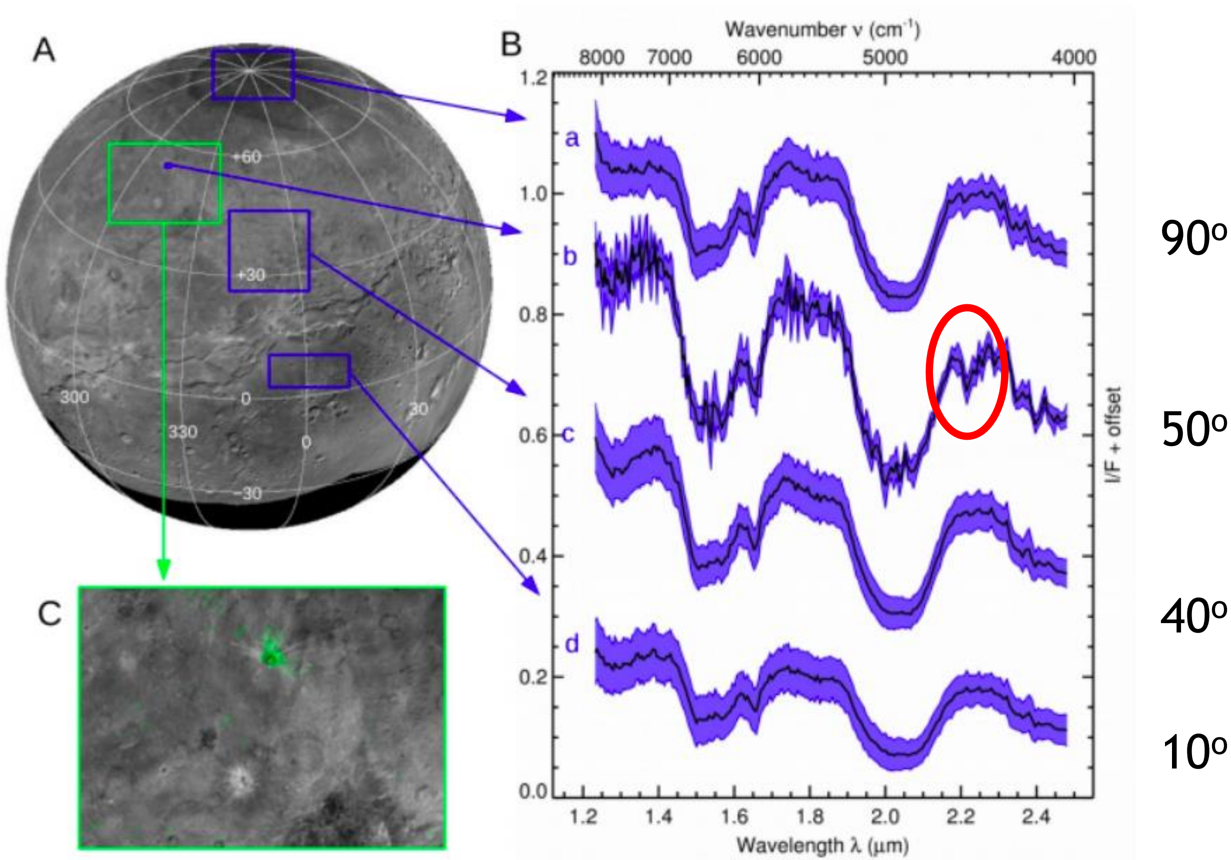
Contents

Motivation

Ammonia on Organa Crater

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

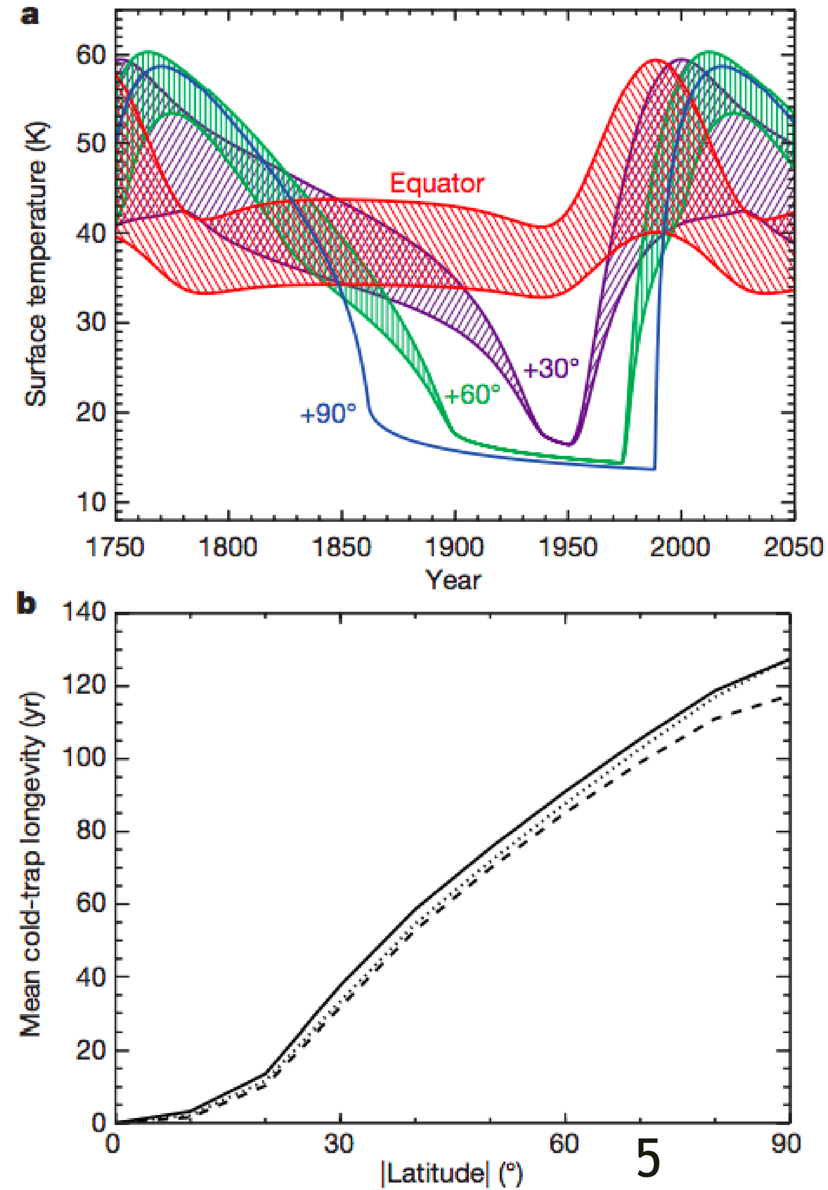


from Grundy et al. (2016)

Surface temperatures at different latitudes

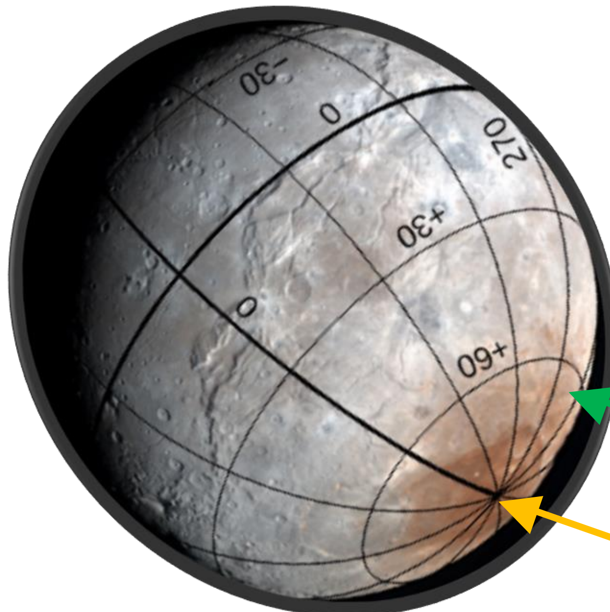
- Thermal model from Grundy et al. (2016) shows the pole position is below 25 K for 130 years
- Methane can condense on those positions where the temperature is below 25 K.

Quoted from Grundy et al. (2016)



What astrophysical environments are we demonstrating?

Charon in Pluto system



VUV and EUV irradiation

$NH_3 + CH_4 \longrightarrow CN^-$

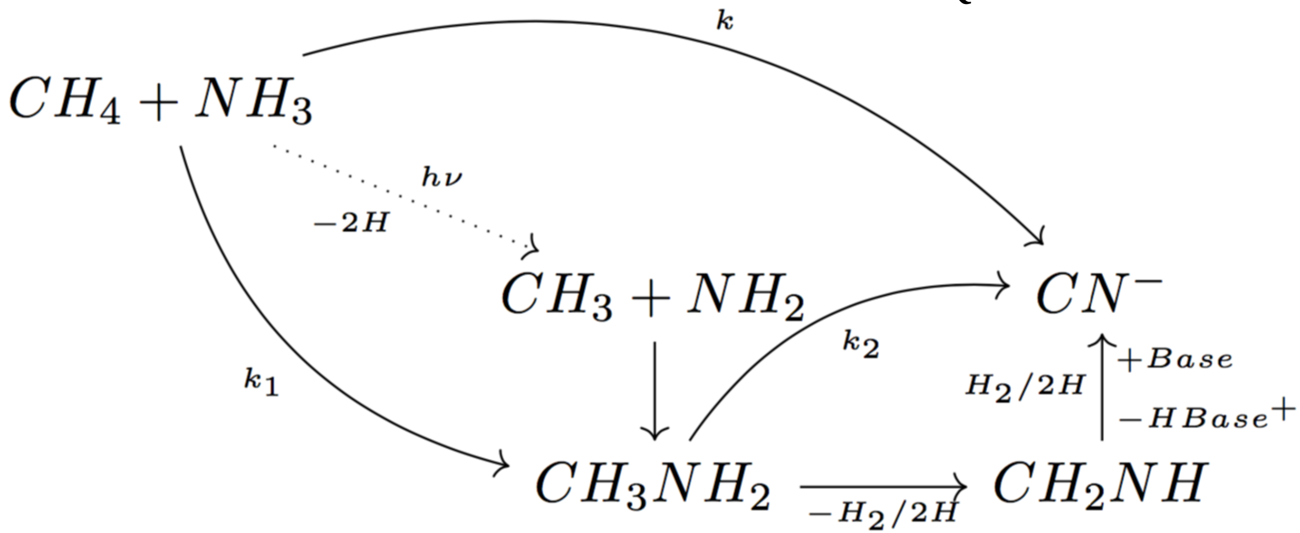
Quoted from Grundy et al. (2017)

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^-

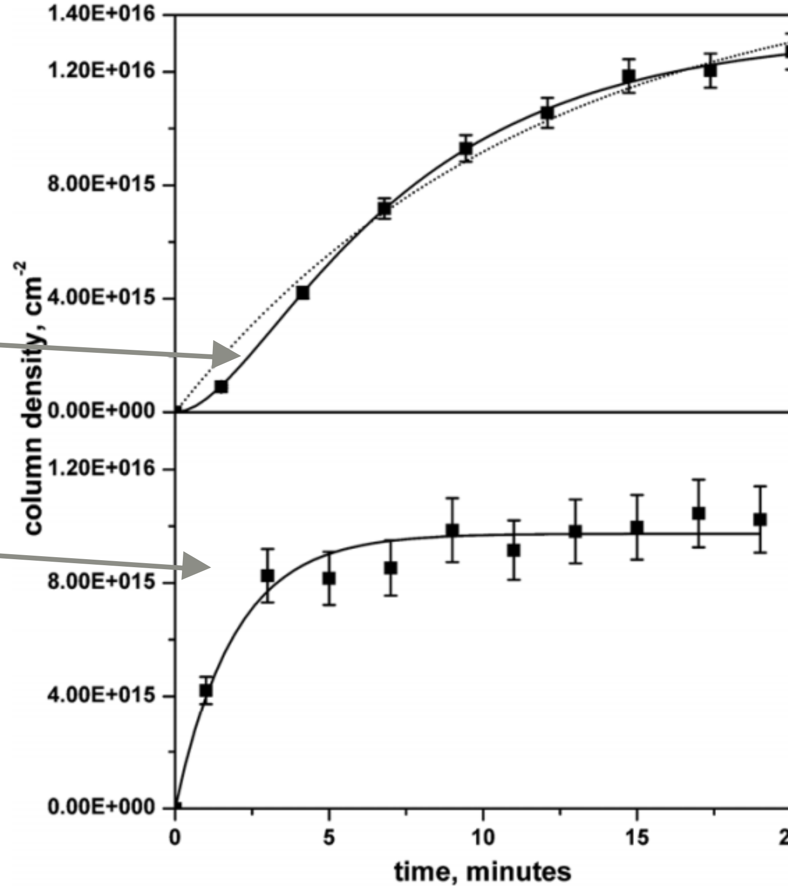
- 2 steps/1 step?

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^-

- 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 (CH_4:NH_3 3:1) (5 keV e^-)
  - Kundy et al. (CH_4:NH_3 3:2) (1-90 eV e^-)
  - We perform (CH_4: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

  CH_4:NH_3 1:5, 1:10, 1:20

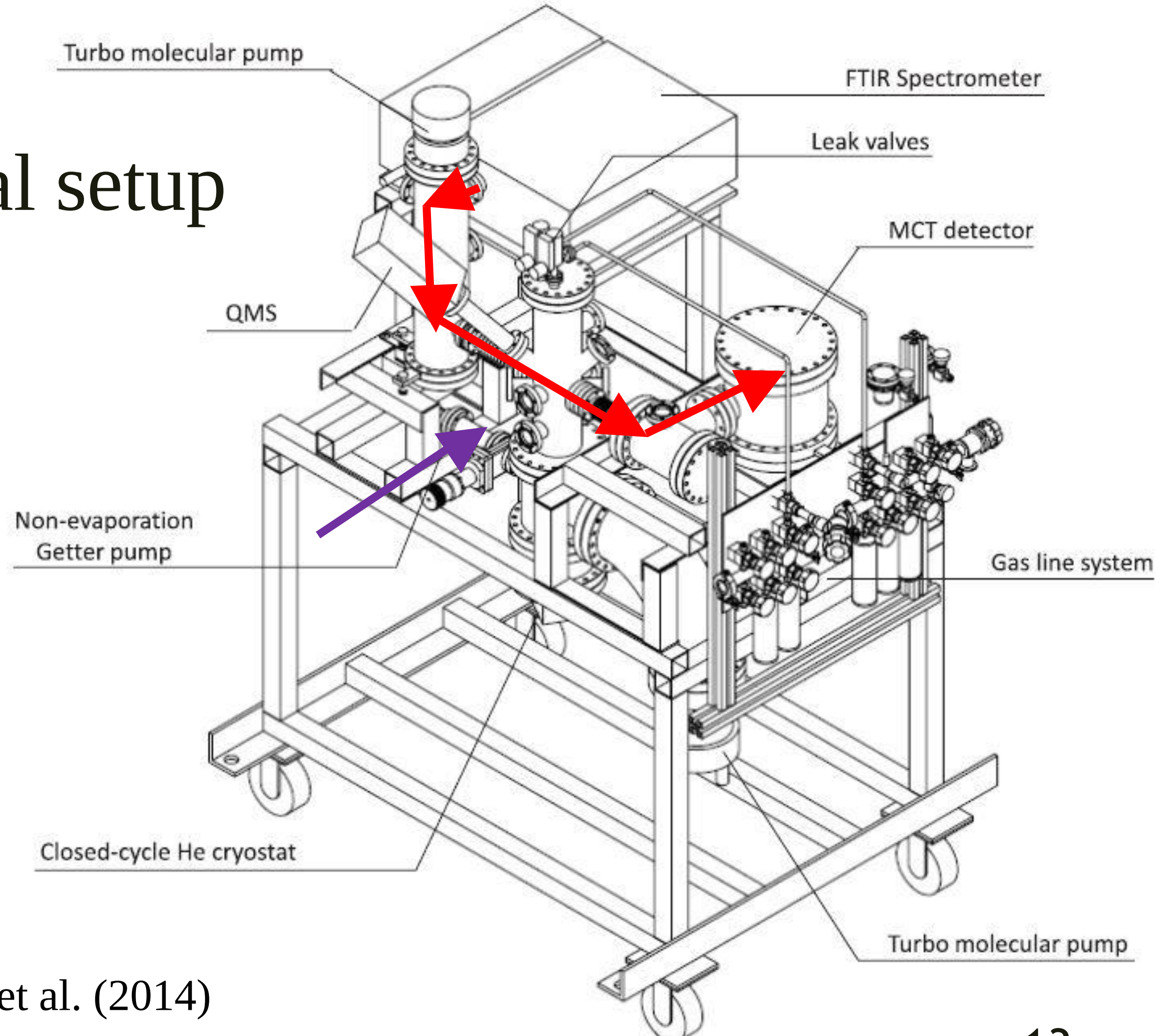
Methodology

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	--	--

Different initial amount of CH_4 correspond to different ratio of CH_4:NH_3 ice mixtures

Experimental setup



IR path

VUV/EUV path

Quoted from Chen et al. (2014)

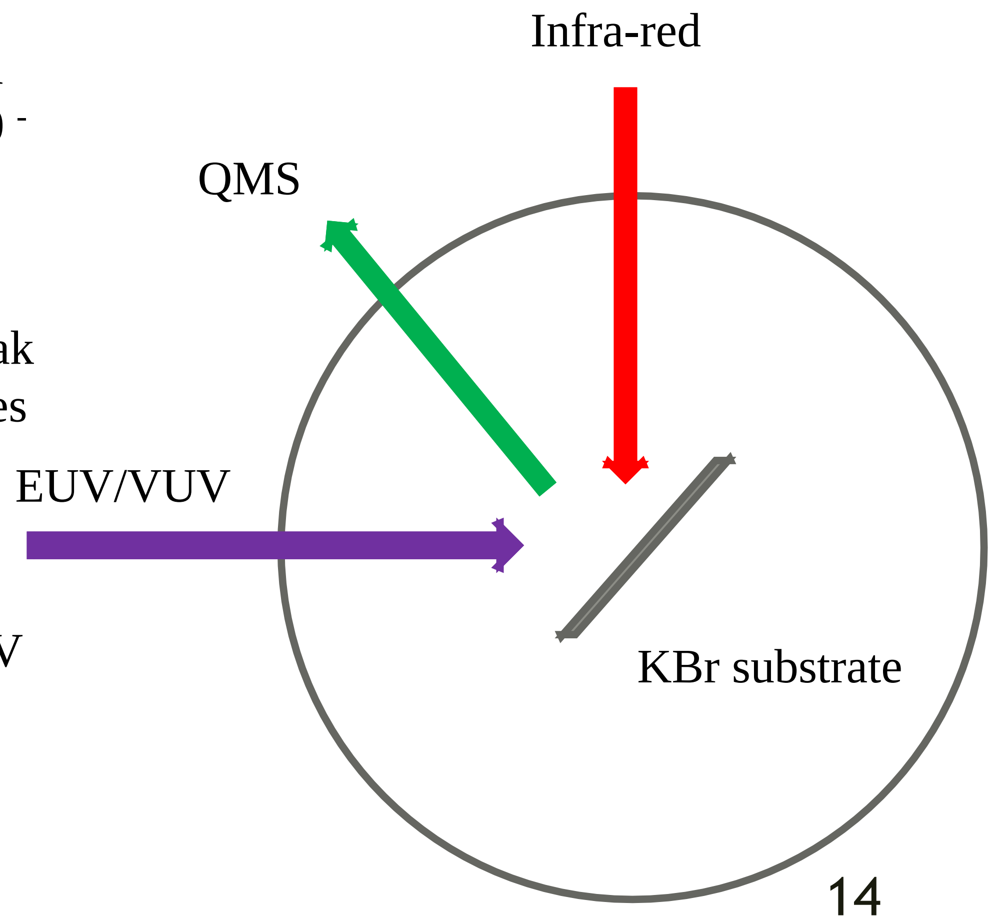
Experimental Procedure

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

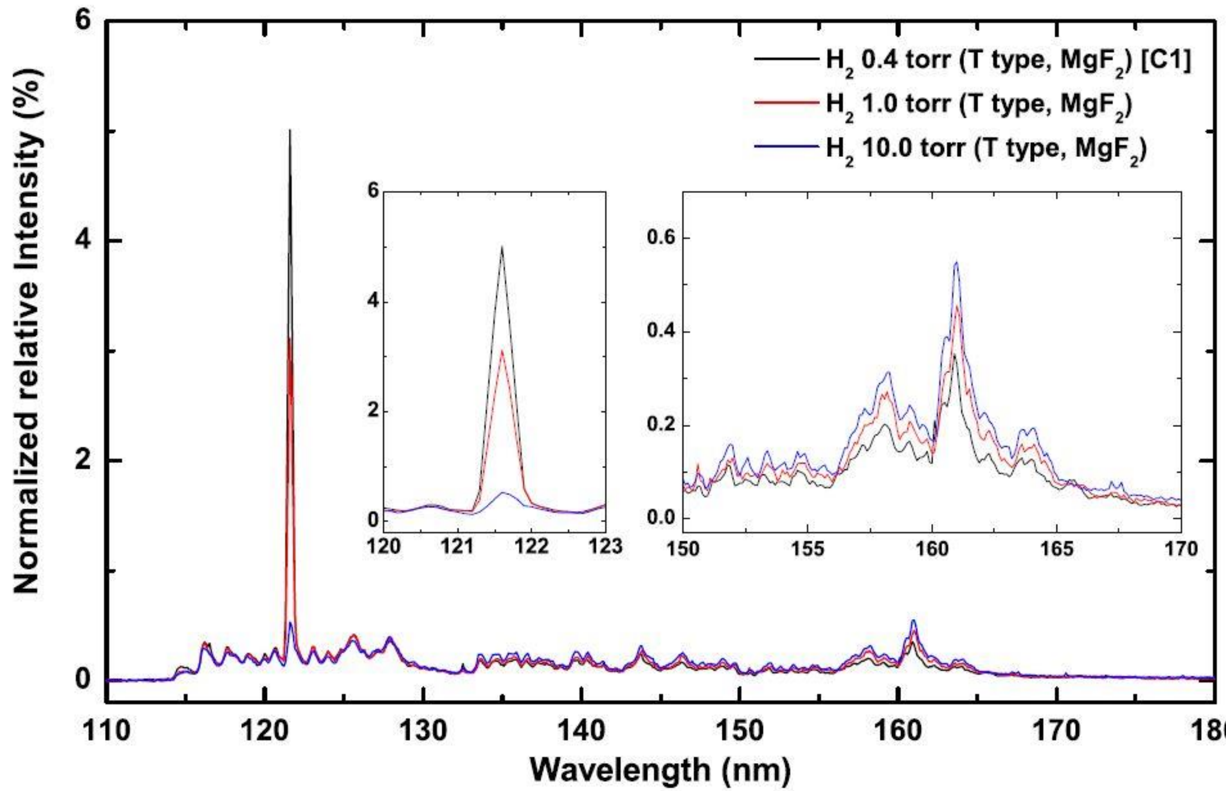
Warm-up with 1 K/min



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 τ(v) :

- $\tau(v) = -lnT = -\ln\left(\frac{I(v)}{I_o(v)}\right) = nl\sigma(v)$

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

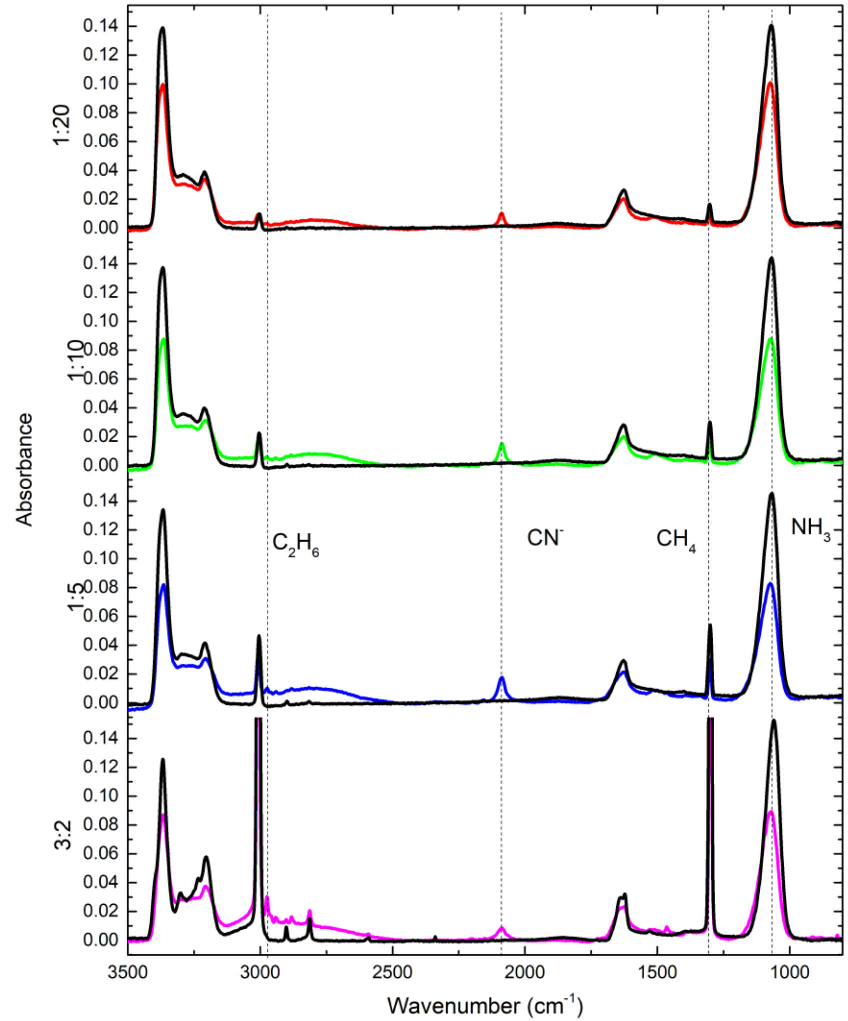
l: path length (cm)

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

Column density N:

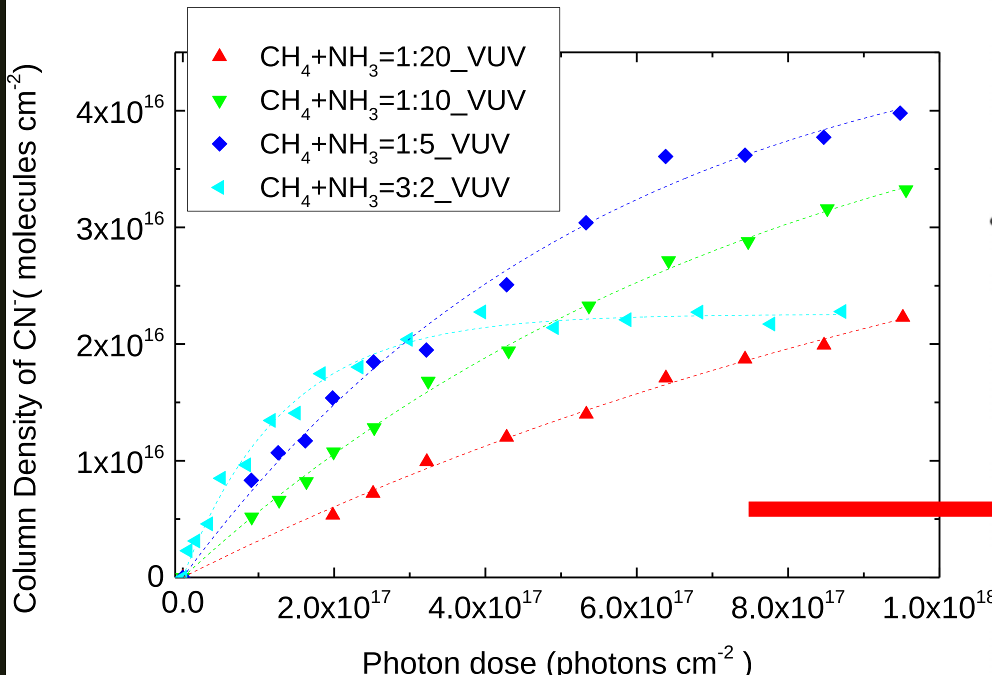
- $N = \frac{\int \tau(v)dv}{A(v)}$

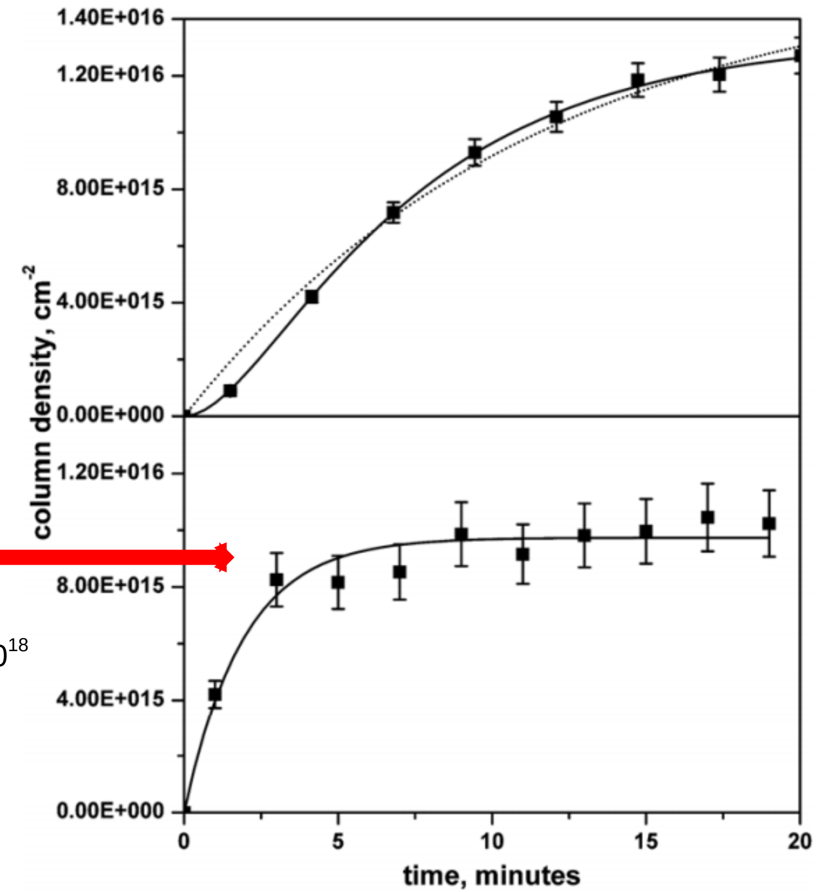
$A(v)$: absorption strength (A-value) (cm $molecule^{-1}$)



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^-

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

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

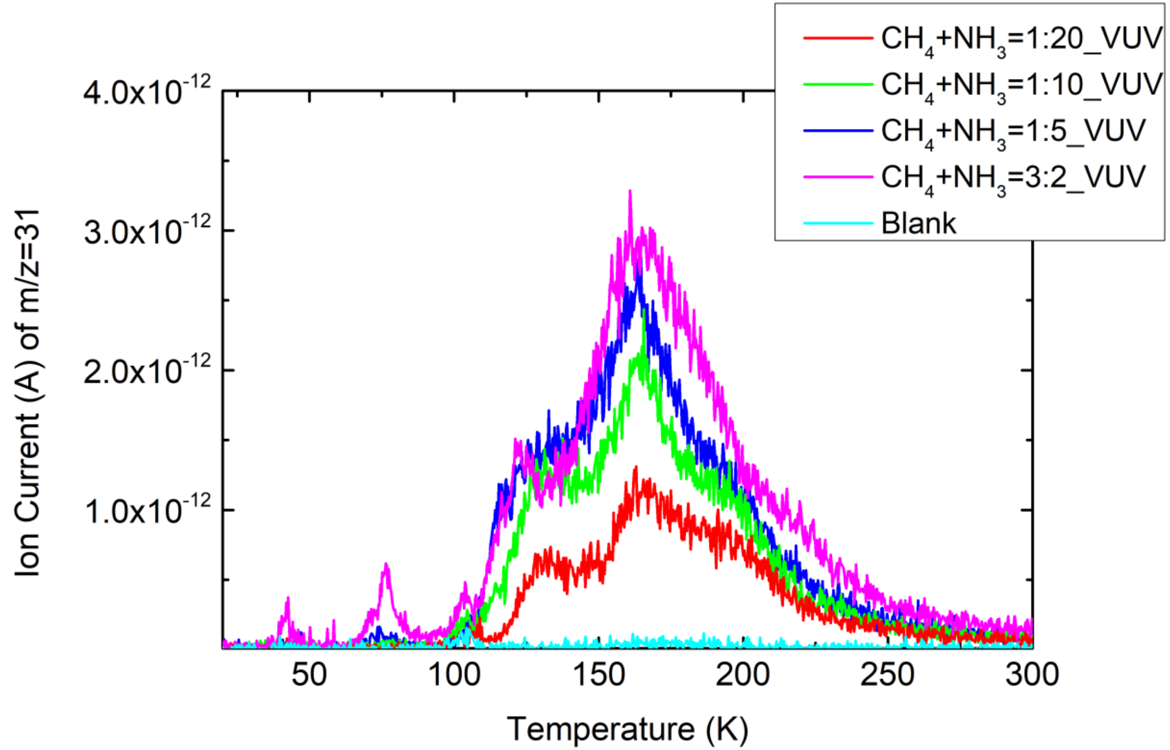
VUV experiments with CH_4+NH_3 ice mixtures			
Ratio	A ($\times 10^{16}$ molecules cm^{-2})	k_1 ($\times 10^{-18}$ $photon^{-1}$)	k_2 ($photon^{-1}$)
1:20	4.75 ± 0.40	0.70 ± 0.09	>1
1:10	4.51 ± 0.18	1.33 ± 0.13	>1
1:5	4.61 ± 0.18	1.93 ± 0.19	>1
3:2	2.24 ± 0.03	8.21 ± 0.70	>1
Quotated from Kim and Kaiser[2]			
Ratio	A($\times 10^{16}$ 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^-

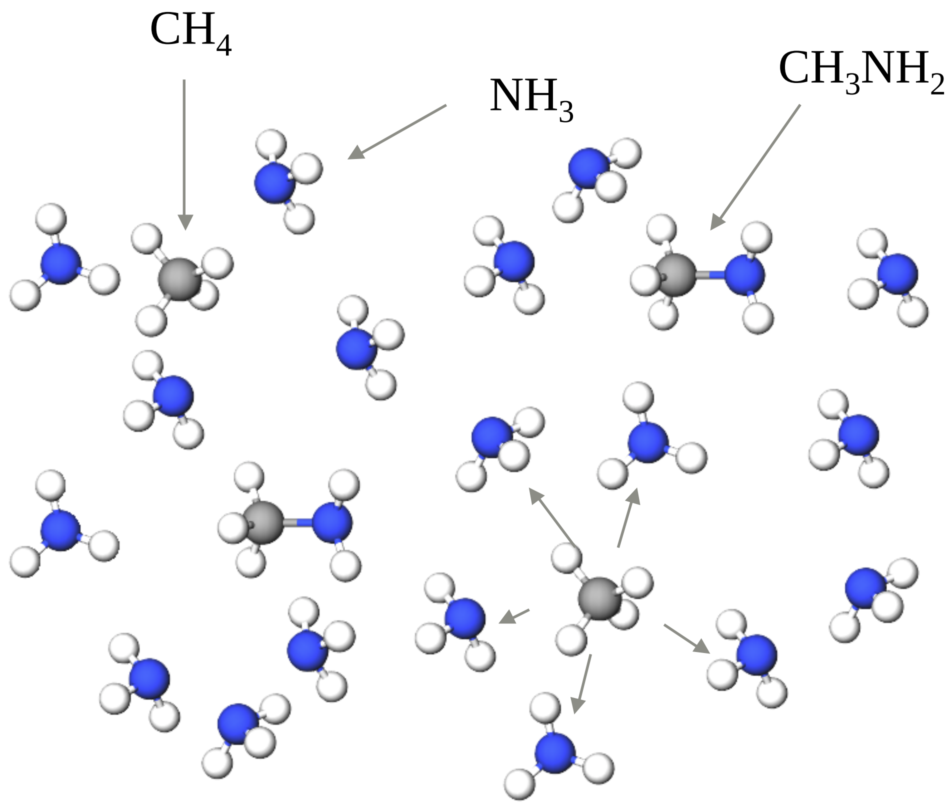
Methylamine (CH_3NH_2) with m/z=31 is detected by QMS

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$^-$.

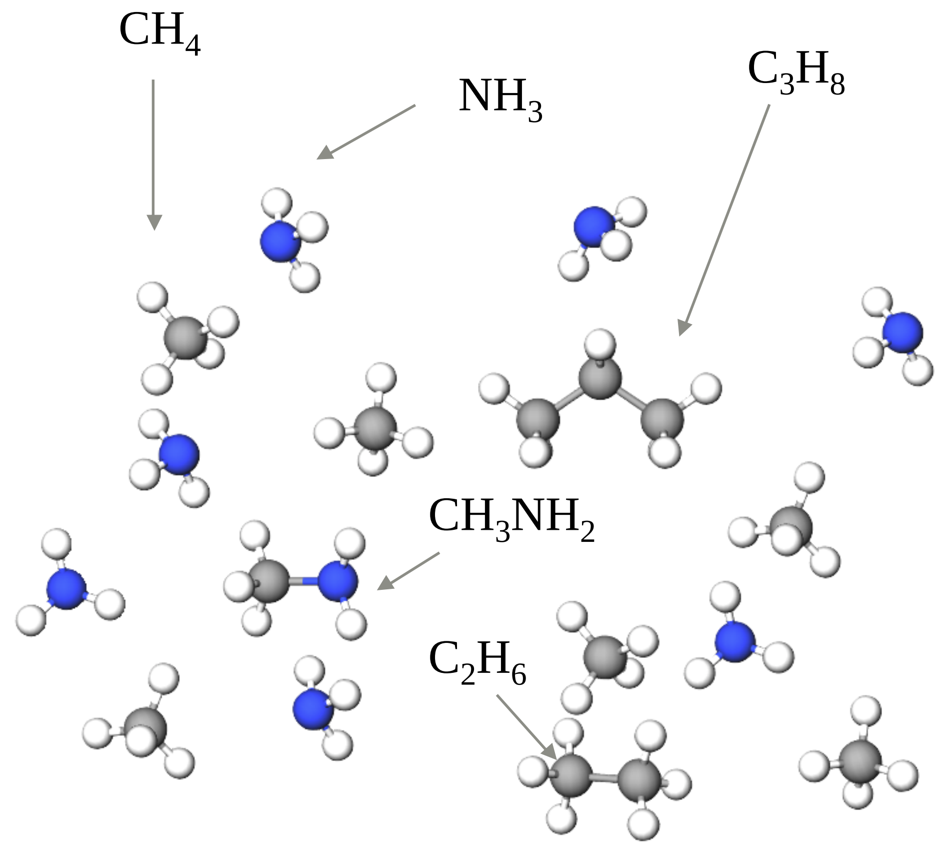


A diagram of CH_4:NH_3 = 1:5

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)

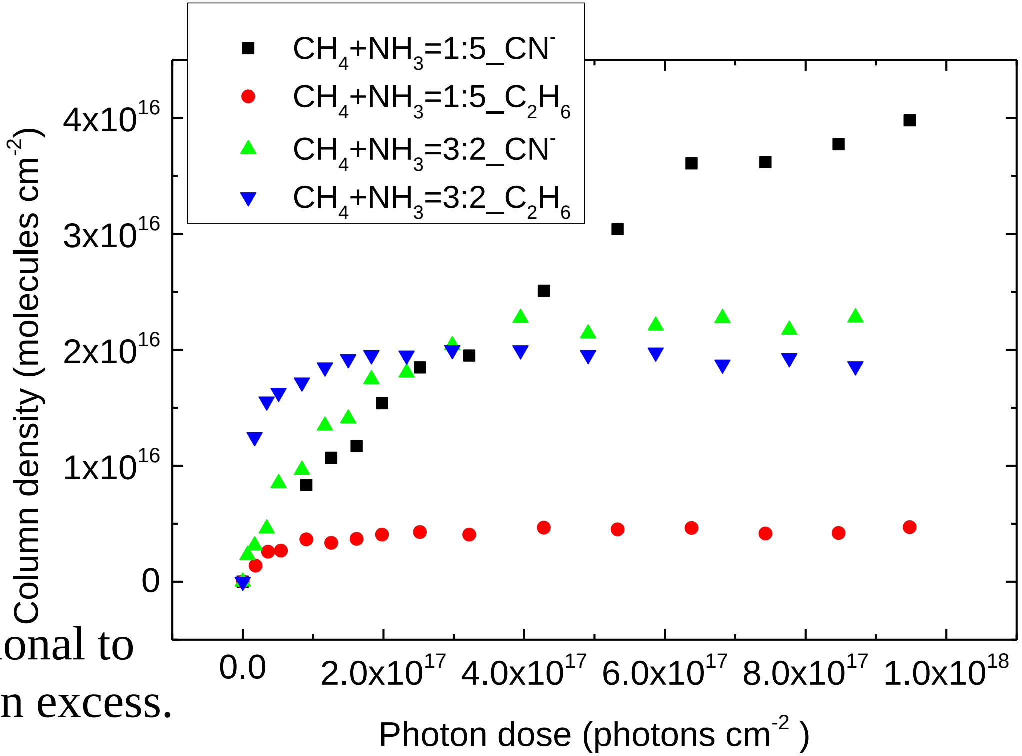
C_2H_6 can form easier than NH_3 dominating case



A diagram of CH_4+NH_3 = 3:2

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

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

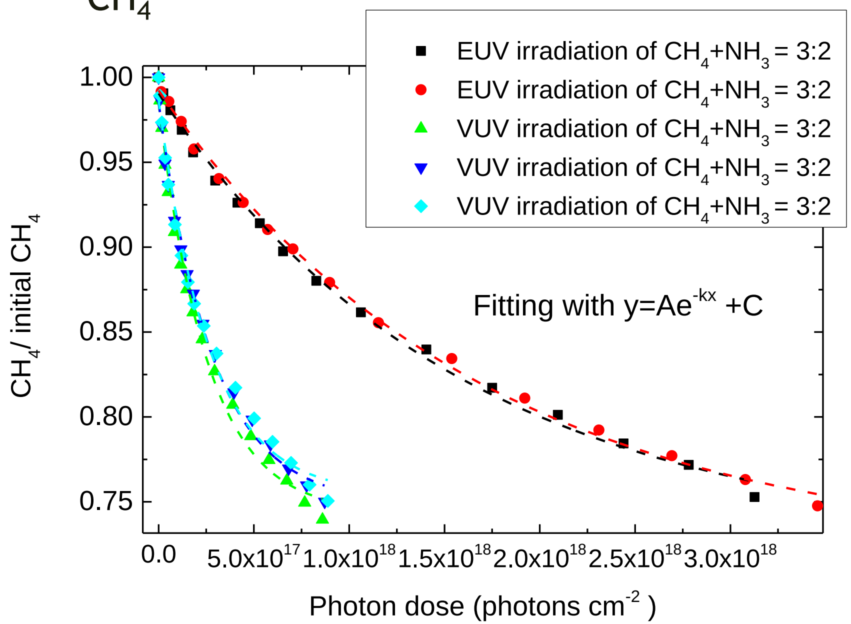


Concentration of CN^- is not proportional to initial amount of CH_4 when CH_4 is in excess.

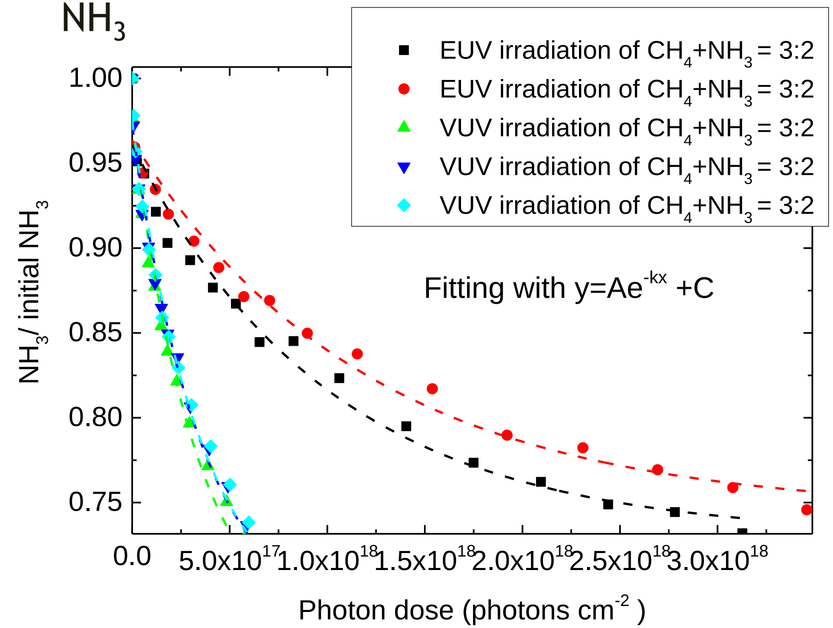
3. Rate constant of reactants by EUV (40.1 eV) and VUV (9.27 eV)

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

CH_4

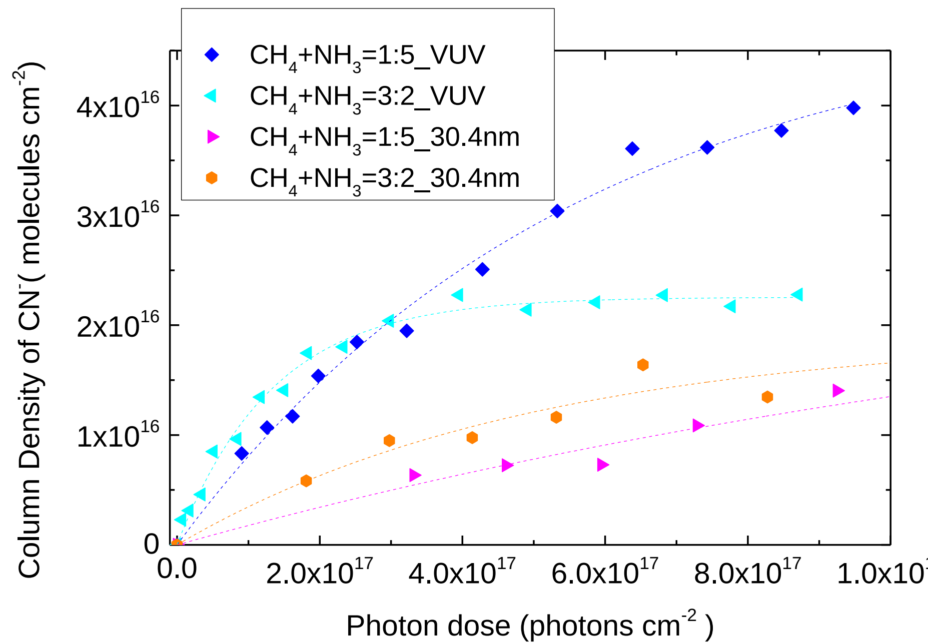


NH_3



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)

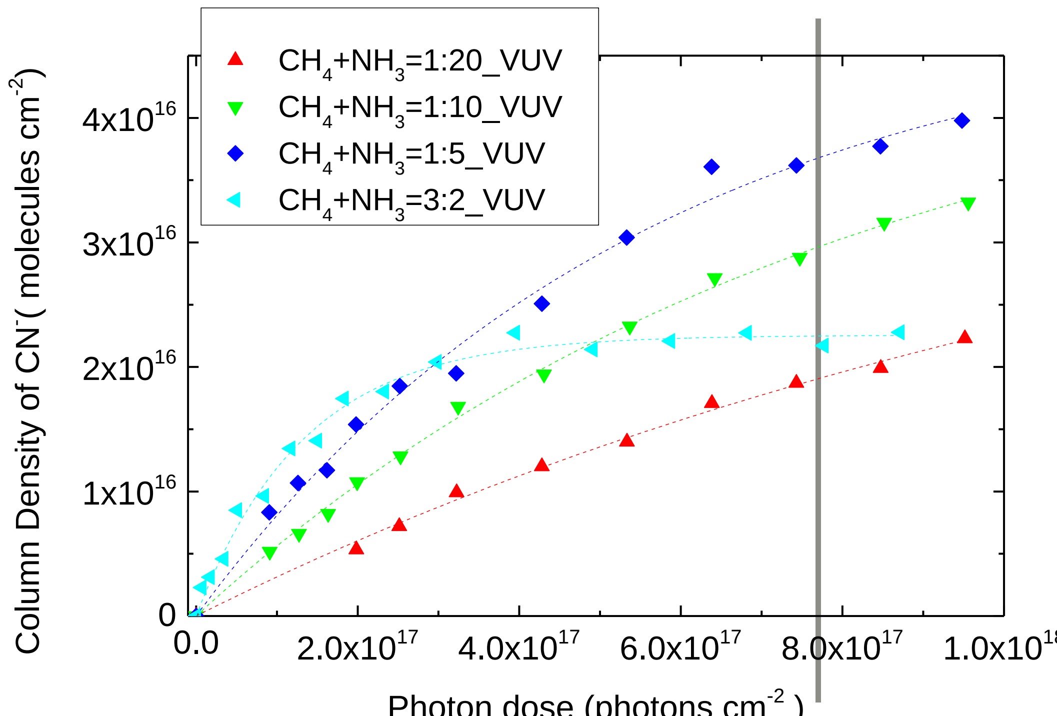
Ly-α flux: 1.9 x 10^9 eV cm^{-2} s^{-1} (Grundy et al. 2016)

→photon dose after 1 Pluto winter
7.64 x 10^{17} photons cm^{-2}

CH_4 after winter ~173 ML

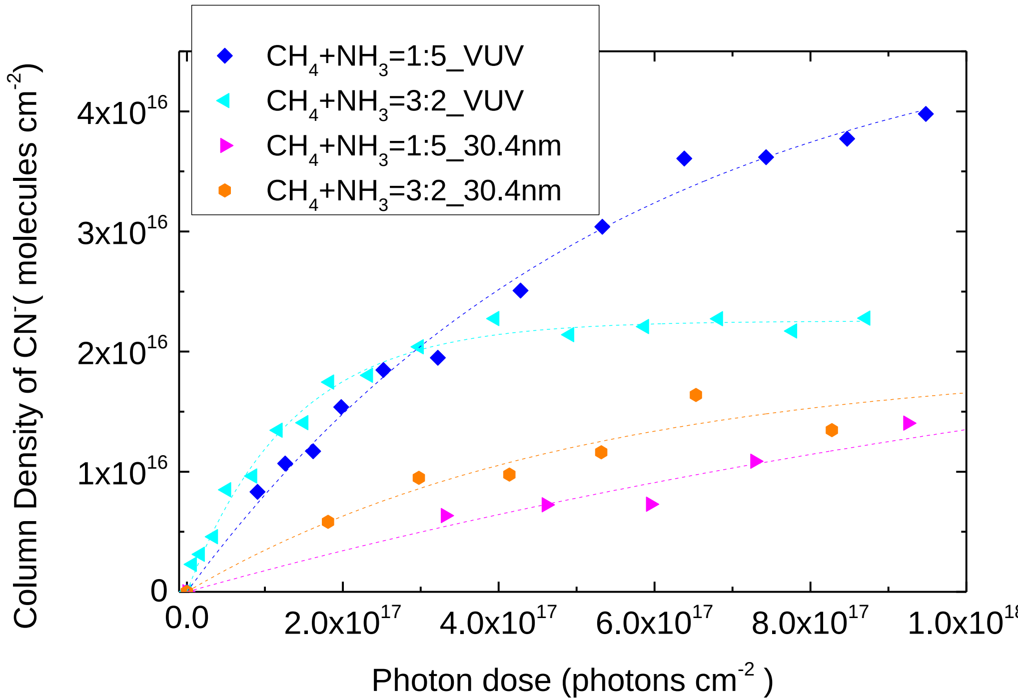
Assume the column density of NH_3 is 600 ML

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: 1.9×10^9 eV cm^{-2} s^{-1}
  - EUV flux: 8.7×10^7 eV cm^{-2} 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