

國立中央大學

Physics Department

Master論文

VUV and EUV irradiation on  $\text{CH}_4+\text{NH}_3$   
ice mixtures

An implication of Tholin on Charon

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# VUV and EUV irradiation on $\text{CH}_4 + \text{NH}_3$ ice mixtures

## An implication of Tholin on Charon

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# VUV and EUV irradiation on $\text{CH}_4+\text{NH}_3$ ice mixtures

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# VUV and EUV irradiation on $\text{CH}_4 + \text{NH}_3$ ice mixtures

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# 1. Introduction

According to Hindu cosmological mythology, ancient people believe that a giant turtle bears the world on its back. Even after we stepped onto the moon at 1969, there are still plenty that we cannot explain. In the novel *Lord of the Rings*, the author named the path between hobbits as Mordor, which is also the name of the dark area on Pluto's moon, Charon. Recently, Mission New Horizons retrieved valuable data about Charon and Pluto. This thesis aims to explain the formation mechanisms of the red cap on the pole of Charon (fig. 1), especially during the long cold dark period, through observations in extreme ultra-violet (EUV) and vacuum ultra-violet (VUV) irradiation.

## Composition of Charon

The main composition on the surface of Charon is  $\text{H}_2\text{O}$ . According to Infrared (IR) spectroscopy, it is a mixture of 90 %  $\text{H}_2\text{O}$  and 10 % tholin at millimetre depth. The second most dominant component is ammonia hydrate, which can be observed by earth-based telescopes (brown 2000, cook 2007). In far IR spectrum taken by LEISA camera on the New Horizons, concentrated ammonia is found on Organa crater (fig 2.) and throughout Charon (fig 3.) (Grundy 2016a). The third component which forms the dark red cap (tholin?) is cold-trapped methane from Pluto's atmosphere ejecta (Hoey 2017). The presence of nitrogen and other ejecta from Pluto are neglected in this thesis because according to the model of Hoey et al. (2017) (fig.4), during New horizons' approach, 98 % of the arrived ejecta is  $\text{CH}_4$ . Charon's atmospheric pressure is further constrained by New Horizons to be below 0.3 nano bars, which is  $4 \times 10^{-13}$  torr for all 14 atoms and molecules including CO,  $\text{H}_2$ ,  $\text{CH}_4$ , Ne, Ar, etc. (fig. 5).  $\text{CH}_4$  remains undetectable when we convert the momentum of  $\text{CH}_4$  with 7 hops on the surface of Charon until deposited onto cold enough part is  $1 \times 10^{-11}$  Pa, which is  $7.5 \times 10^{-14}$  torr (Grundy



2016b).

#### VUV irradiation

Ly- $\alpha$  appears to be the largest source in the dark side of Charon, with attributions from both solar occultation (70 %) and resonance scattering by atomic hydrogen flow (30 %) in the solar system at flux  $3.5 \times 10^7$  photons  $\text{cm}^{-2} \text{s}^{-1}$  onto the winter pole of Charon (Grundy 2016b). The flux is 50 % larger than expected before Mission New Horizons (Gladstone 2015).  $\text{CH}_4$  deposits at temperature below 25 K at pressure  $7.4 \times 10^{-14}$  torr. The time for depositing  $\text{CH}_4$  is 2 times longer at the pole (130 earth years) than at 45 latitude according to the thermal model of Grundy et al. (2016b) (fig 6). In order to understand the formation of tholin at different latitudes of Charon, we performed VUV irradiation on  $\text{CH}_4+\text{NH}_3$  and  $\text{CH}_4+\text{NH}_3+\text{H}_2\text{O}$  experiments with different ratios (including 3:2, 1:5, 1:10 and 1:20 for  $\text{CH}_4+\text{NH}_3$  and 5:3:4, 1:5:5 and 1:10:10 for  $\text{CH}_4+\text{NH}_3+\text{H}_2\text{O}$  ice mixtures) to simulate the conditions at different latitudes on Charon with base pressure  $3 \times 10^{-10}$  torr, simulating atmosphere on Charon at 15 K, which corresponds to temperature on Charon at winter times (Grundy 2016b) in interstellar processing system (IPS) (Chen 2014).

#### EUV irradiation

Apart from VUV irradiation, EUV irradiation also took part. VUV irradiation is believed to be the main process to convert  $\text{CH}_4$  into heavier molecules which remained on the surface of Charon until the temperature of Charon become 60 K, at which methane evaporates from the ice. The ice is then further processed by EUV, solar wind, coronal mass ejections and interstellar pickup ions, etc to produce the tholin on Charon (Grundy 2016b). The EUV irradiation ( $>12.4$  eV) is  $8.7 \times 10^7 \text{ eV cm}^{-2} \text{s}^{-1}$  at mean heliocentric distance 39 A.U. whereas VUV irradiation (Ly- $\alpha$ ) is  $1.9 \times 10^9 \text{ eV cm}^{-2} \text{s}^{-1}$ . In order to investigate the effectiveness of EUV to VUV irradiation, we kept temperature of  $\text{CH}_4+\text{NH}_3$  (3:2 & 1:5) and  $\text{CH}_4+\text{NH}_3+\text{H}_2\text{O}$  (5:3:4) ice mixtures at 15 K and use the monochromatic 30.4 nm (He II) light provided by High flux beamline at National Synchrotron Radiation Research Centre (NSRRC) in Taiwan to irradiate the ice mixtures.



H<sub>2</sub>O involved?

We compared the conditions of CH<sub>4</sub>+NH<sub>3</sub> and CH<sub>4</sub>+NH<sub>3</sub>+H<sub>2</sub>O because tholin on Titan is believed to be formed by CH<sub>4</sub>+N<sub>2</sub> and a similar colour was observed on Charon. Charon is different from Titan as H<sub>2</sub>O dominates on Charon. What are the differences between tholin formed by CH<sub>4</sub>+NH<sub>3</sub> and CH<sub>4</sub>+N<sub>2</sub>? What role does H<sub>2</sub>O play on Charon in the formation of tholin? Is it just diluting the formation or new compounds are formed?

In this thesis, we will introduce the formation reaction mechanisms of CH<sub>4</sub>+NH<sub>3</sub> ice mixtures in EUV and VUV irradiation (section 3), the formation reaction mechanisms of CH<sub>4</sub>+NH<sub>3</sub>+H<sub>2</sub>O ice mixtures in EUV and VUV irradiation (section 4), and the residues of these mixtures and a brief comparison with tholin on Titan will be made (section 5). With these results, we will have a better understanding about Charon and some astrophysical implications will be presented (section 6).





## 2. Methods

### 2.1 Laboratory Astrophysics

To study the chemical reactivity in astrophysical environment experimentally, we conducted our experiments in Interstellar photoprocessing system (IPS) (Chen et al. 2014), an ultrahigh vacuum chamber with base pressure  $3 \times 10^{-10}$  torr and 14 K, corresponds to a density of  $10^6 \text{ cm}^{-3}$ , similar to dense cloud interiors. The system will be introduced in detail in section 2.1.1. To simulate the irradiation in interstellar environments, we use a micro-wave discharge hydrogen lamp (MDHL) and monochromatic extreme-ultraviolet irradiation (EUV) 30.4 nm to irradiate our ice mixtures, and they will be introduced in section 2.1.2 and 2.1.3 respectively. The experimental protocols will be elaborated in section 2.2. In order to better understand the physics behind, some basic theories of Infrared spectroscopy and concepts of chemical kinetics used in data analysis are included in section 2.3 and 2.4 respectively. To demonstrate the ice mixtures in KBOs, we used different configurations of ice mixtures that refers to different sections in chapter 3 and chapter 4.

#### 2.1.1 Experimental simulations by IPS system

We conducted our astrophysical simulations studied in chapter 3 to 4 in Interstellar Photo Processing System (IPS) (figure 2.1). IPS consists in three systems: the main chamber, where our experiments take places; the detection system, where we collect our data; and a gasline system, where we prepare our samples.

The main system consists of an ultrahigh vacuum chamber equipped with a closed-cycle helium cryostat (CTI-M350). It is pumped by a turbo molecular pump (KTKT FF – 160/620ZE, capacity  $600 \text{ liters s}^{-1}$ ), which is backed up by a scroll pump, and a non –evaporation get-

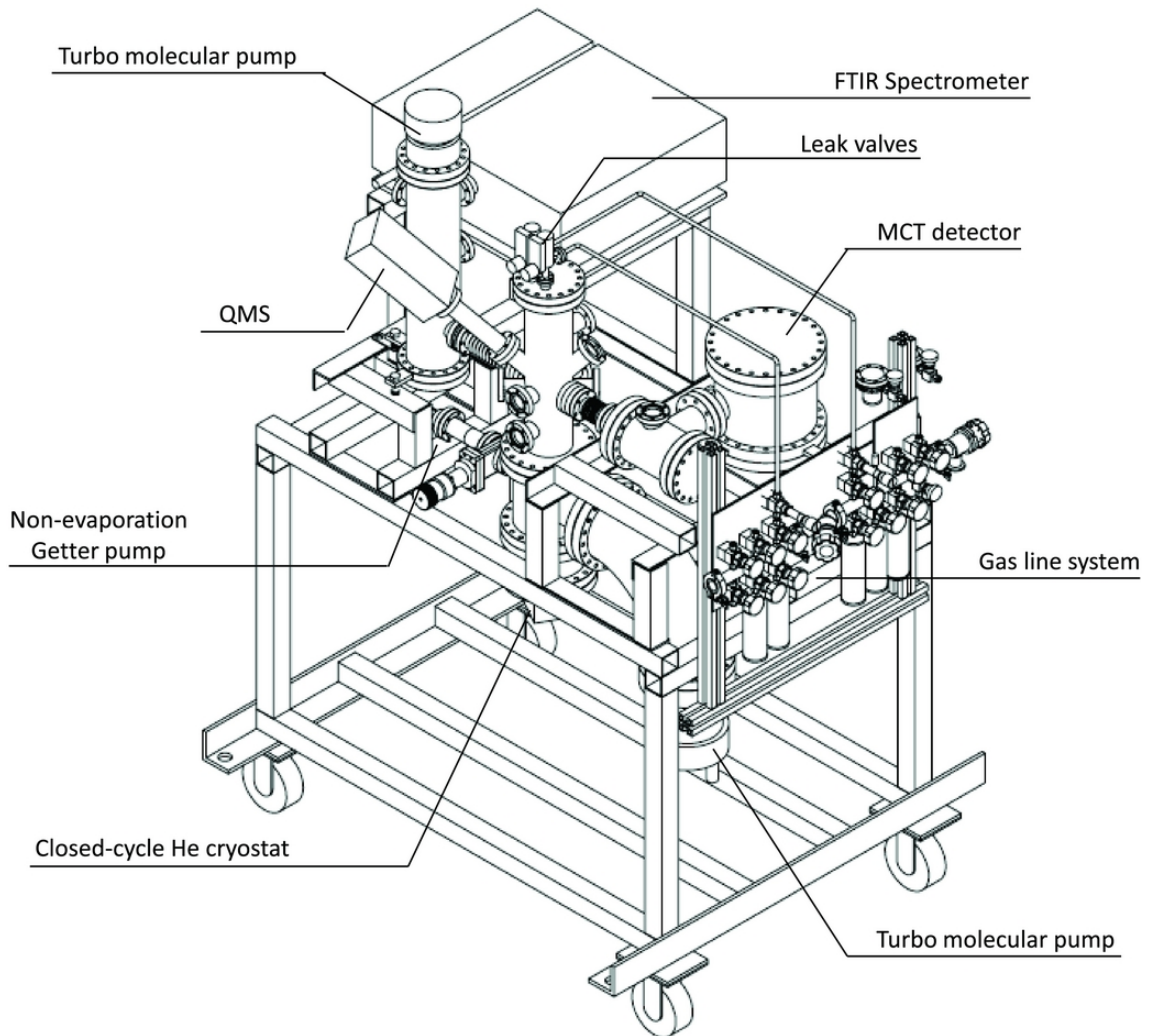


Figure 2.1: The schematic diagram of IPS system, mechanical pumps are not shown for clarity. (Quoted from Chen et al. 2014)



ter pump. The getter pump is a powerful tool to adsorb residue gases inside the main chamber, with a larger surface area,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{N}_2$  are adsorbed to obtain a better base pressure. After baking, the base pressure of our main chamber can reach  $1 \times 10^{-10}$  torr at 14 K, monitored by a Granville-Phillips 370 Stabil-Ion gauge. This pressure can be used to demonstrate the dense cloud interior environments and star forming region. The substrate we have chosen is KBr, which can allow infra-red photons with 700 to 4000  $\text{cm}^{-1}$  to penetrate. It is mounted by substrate holder made of oxygen-free copper, on the first stage of cold finger mounted on the tip of cryostat. Two silicon diodes and also a heater were placed onto the cold finger and one of the silicon diodes is near the substrate holder. They were connected to a temperature controller and PID system to achieve a warmup rate of 1K/min with an accuracy of 0.1 K.

The detection system consists in a mid-infrared Fourier transform spectrometer (mid-FTIR) (ABB FTLA2000-104) and a Quadrupole Mass Spectrometer (QMS). To prevent absorption bands of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  gas in the atmosphere, the IR beam path was built inside vacuum, pumped by dry pump. The main chamber and the IR path are separated by ZnSe windows, which can allow infra-red penetration from 0.5 – 20  $\mu\text{m}$  with absorption less than 0.07 %. In this study, the infrared spectra are obtained with resolution of 4  $\text{cm}^{-1}$  and averaged over 32 scans. The angle between the IR beam path and the substrate holder is 45 degrees. The QMS (MKS Microvision 2) consists of a controller and mechanical part sealed by a mounting flange in ultrahigh vacuum. It is mounted 10 cm from the substrate and run with a resolution 0.5 a.m.u. The Ionizer release 70 eV electron by filament and ionize incoming molecules to positive charged ions between anode grid and repeller. The ions were accelerated by focus plate and enters ion filter, which consists of four circular rods, with a combination of A.C and D.C. potential to sieve whole bandpass ions at millisecond timescale. The selected ions enter ion detector and are detected by either faraday cup and continuous dynode electron multiplier (CDEM) which can secondary multiply weak signals.

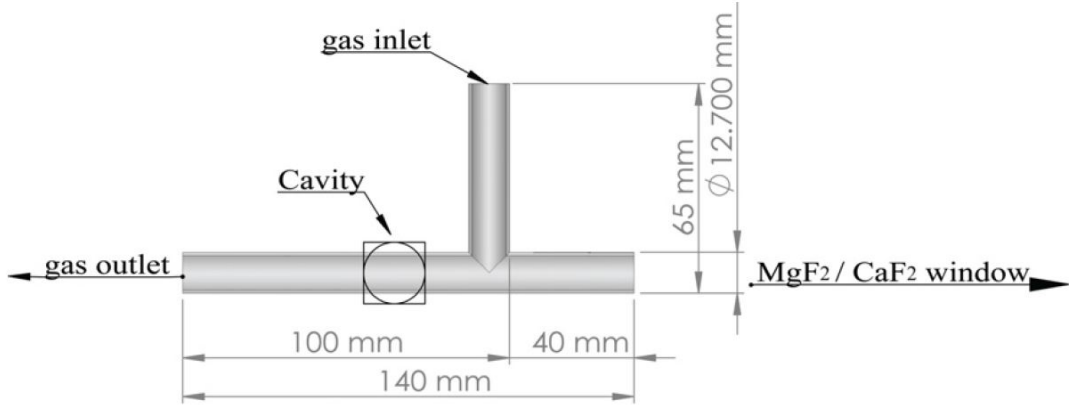


Figure 2.2: The cross-section of MDHL (T-type geometry) (Quoted from Chen et al. 2014).

The samples are prepared in situ in our gasline system. It contains four stainless steel bottles with the same volume, which is used to determine relative proportion of the gas mixtures by their partial pressures. The ammonia gas 99.99 % and methane 99.999 % are mixed with partial pressure measured by a Baratron with 0 - 100 torr range with a 0.25

### 2.1.2 Vacuum-UV source

In order to simulate the photoprocessing of vacuum ultraviolet (VUV) irradiation onto the interstellar ices and ices on planetary bodies, including KBOs, the ice mixtures are irradiated with a T-type Microwave-Discharged Hydrogen-flow lamp (MDHL). The molecular hydrogen with pressure 0.4 torr flows through the lamp with a support of a mechanical pump. Using a 2.4 GHz microwave generator and high voltage discharge, a low pressure plasma is produced in the Evenson cavity. Figure 2.2 shows a cross-section of T-type quartz tube; the middle part of the T-type quartz tube is being tunned by a ceramic rod that is called Evenson cavity. In order to measure the photon flux in situ, we use an 88 % transmittance nickel mesh with its photoelectric efficiency being obtained by high-flux beamline in National Synchrotron and a SXUV 100 photodiode calibrated by NIST. A  $\text{MgF}_2$  window is placed between the lamp and the sample holder to prevent penetration of VUV photons with wavelength shorter than 114nm, leads to a cut off at 114nm. Figure 2.3 shows a VUV emission spectrum of a MDHL. It consists in  $\text{Ly-}\alpha$  (121.6nm) and  $\text{H}_2$  molecular emission in 110-180 nm



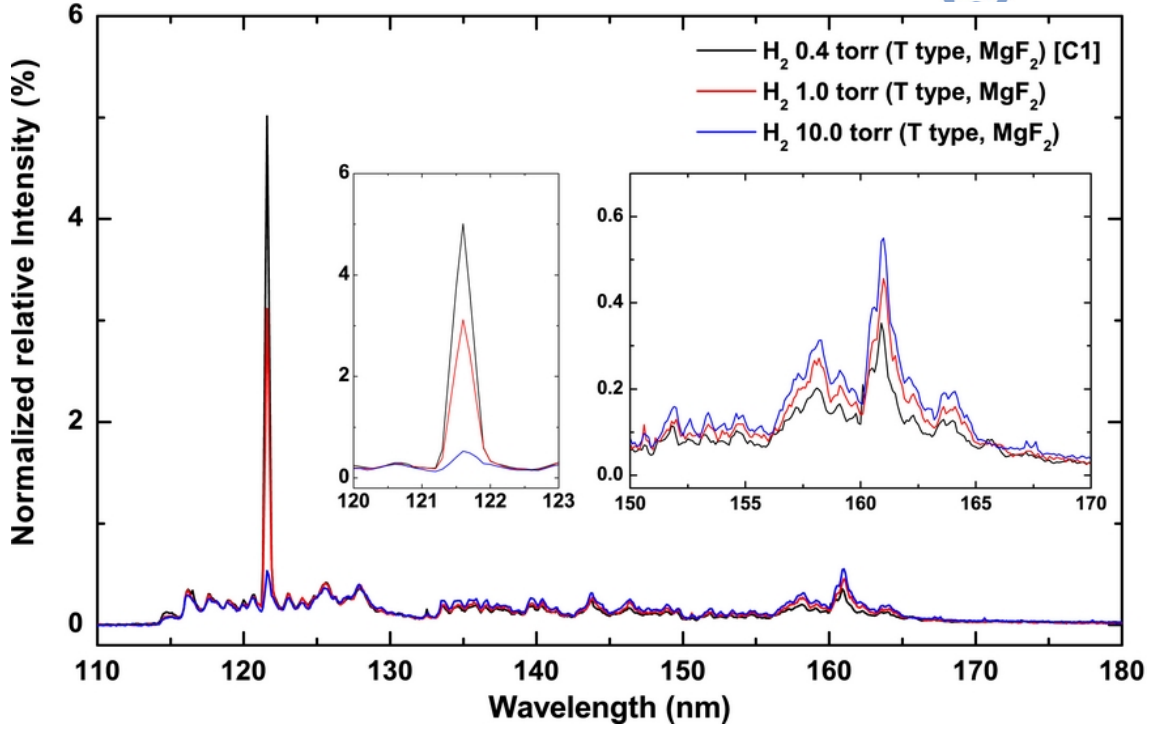


Figure 2.3: VUV spectra of MDHL (T-type geometry, 110-180 nm) with different  $H_2$  pressure inside the lamp (Quoted from Chen et al. 2014).

range. Chen et al. (2014) showed that the spectral characteristics of the VUV light emitted in this range depends on the gas type (mixture of  $H_2$  with He or Ar etc), pressure of  $H_2$  and lamp geometry. Throughout those configurations stated there, we adopted 0.4 torr molecular hydrogen and T-type MDHL that produces VUV irradiation at 114-170 nm with 19.1 % of Ly- $\alpha$  and a mean photon energy of 9.27 eV. The photon flux is  $6.4 \times 10^{13}$  photons  $cm^{-2}s^{-1}$  at sample position.

### 2.1.3 Extreme EUV source

To simulate the solar EUV irradiation reflected by IPM on both Charon and interstellar ices, we use the HF-CGM high – flux beam line of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. It provides a continuum EUV to VUV photons from 4 to 40 eV. The continuum is separated into monochromatic He II line (30.4nm) with a six-meter cylindrical grating monochrometer with an incident angle of 70 degrees. With the help of a movable entrance slit and movable curved exit slit, the energy resolving power can reach around  $3 \times 10^4$  at 40 eV for grating 1600 l/mm with both slits movable and set opening to



10  $\mu\text{m}$  (Hsieh 1998). Similar to VUV irradiation provided by MDHL, the light intensity was monitored by the same nickel mesh with photoelectric efficiency obtained by SXUV 100 photodiode calibrated by NIST. With the known photoelectric efficiency, the flux of monochromatic 30.4nm is measured to be  $2.15 \times 10^{14}$  photons  $\text{s}^{-1}\text{cm}^{-2}$  with a spot size of 1 cm

## 2.2 Experimental Protocol

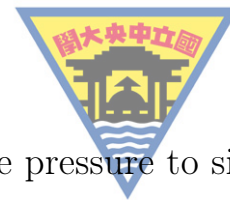
In this section, we will briefly introduce the procedures of how we performed our experiments. It is divided into four parts, preparation and cooling, deposition, irradiation and warmup.

### Preparation of experiments and cooling

Before any of experiment is done, we bake our system at 100 oC for 48 hours to reduce the contamination of water and residue gases as much as possible. It was cooled to room temperature that the background pressure can reach routinely at  $1 \times 10^{-10}$  torr. The gasline were connected with the regulators of the gas tanks and bake to 100 °C and pumped by molecularturbo pump for two days before any experiment were done. Also, The water sample has been freeze thaw several times by liquid nitrogen until there is no pressure increase recorded by baratron when water is freezed. Before cooling the substrate to cryogenic temperature, we took an IR spectrum and started the monitoring of residue gases by QMS in order to compare the residue molecules and to verify any possible contaminations in the main chamber. We then start the cooling process thanks to the closed-cycle He cryostat.

### Deposition

The gas mixtures are pre-mixed in our gasline system introduced in section 2.1.1. We used a leak valve to condense the gas from the stainless steel bottles onto pre-cooled KBr substrate at 14 K, which monitored by Fourier transformed Infra-red spectroscopy (FTIR) and Quadrupole mass spectrometer (QMS) during deposition. The pressure of deposition is fixed to  $1 \times 10^{-8}$  torr that the deposition rate is  $4 \times 10^{16}$  molecules  $\text{cm}^{-2}\text{min}^{-1}$ . After deposition, we placed the ice mixture at 14 K for 60 minutes and to allow pumping of residue gas, until



pressure of the main chamber reduce back to its base pressure to simulate the interstellar environment before irradiation.

### Photon Irradiation

The total irradiation time is 270 to 450 minutes depend on experiment configurations; with time intervals varies from 2 to 30 minutes. After each irradiation, we waited for 10 minutes allowing pumping out of the photodesorpted gas molecules. During irradiation, the photon flux is monitored by a nickel mesh. After Irradiation, we place the sample for 30 minutes to observe if any thermal reaction was conducted.

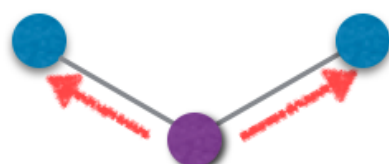
### Warmup

We use 1 K/min to warmup the substrate to 300 K to demonstrate effects of a new born star nearby an interstellar cloud. During warmup, we record the QMS from 1 to 100 a.m.u. to observe if there are low quantity of higher mass product formed during irradiation.

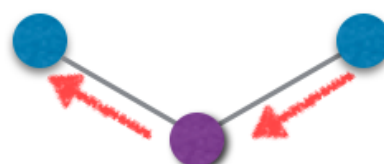
## 2.3 Infra-red spectroscopy and the Beer's Law

We used infra-red spectroscopy extensively in chapter 3 and 4, it is a powerful tool in studying molecular interactions during irradiation and warmup. We choose infra-red rather than Ramen spectroscopy because infra-red has lower energy that it would not change the structure of the ice mixture nor breaking any of the bonds. With different vibration modes, the energy absorbed by molecules are quantized. With the energy of absorption bands in infra-red spectrum, we may identify the functional group of the species. To simply classify, molecules can have, from less energetic, translational, rotational and vibrational motions. Generally, vibrational motions can be divided into stretching and bending. Stretching needs more energy than bending. For stretching, there exist Symmetric and Asymmetric stretching, while bending can be divided into In-plane Scissoring, rocking and out of plane Wagging and Twisting (Figure 2.4).

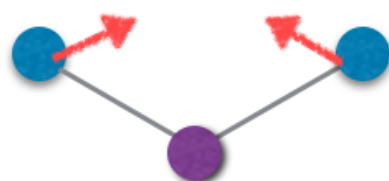
By Beer's Law, we may calculate the column density of the molecule



Symmetric ↵



Asymmetric ↵



In-plane Scissoring ↵



In-plane Rocking ↵



Out of plane Wagging ↵



Out of plane Twisting ↵

- indicate motion out of the page ↵
- indicate motion into the page ↵

Figure 2.4: Different vibrational modes of a three atom molecule.



with its functional groups, which are used to plot figures in chapter 3 and 4. Beer Lambert's Law suggest that when light passes through a medium, amount of light absorbed is proportional to density and path length of the medium. Assume the known intensity beam  $I_0(\nu)$  passes through the medium and beam intensity become  $I(\nu)$ . The transmittance  $T(\nu)$  is defined by equation 2.1.

$$T(\nu) = \frac{I(\nu)}{I_0(\nu)} \quad (2.1)$$

Also, the absorbance  $a(\nu)$  is defined by equation 2.2.

$$a(\nu) = -\ln T(\nu) = -\ln \frac{I(\nu)}{I_0(\nu)} = nl\sigma(\nu) \quad (2.2)$$

where  $n$  is number density (molecules/cm<sup>3</sup>),  $l$  is the path length (cm),  $\sigma(\nu)$  is the cross-section (cm<sup>2</sup>/molecule) of corresponding frequency  $\nu$ . This equation is known as Lambert Beer's Law.

As the ice mixture in our thesis are at 14K, the peaks of absorbance are often a broadband due to coupling between neighbor molecules. Therefore, we can integrate the whole band of the peak equation 2.2 with respect to frequency and use the absorbance strength ( $A$  value) in literatures to calculate the column densities  $N$  of the ices by equation 2.3.

$$N = \frac{\int a(\nu)d\nu}{A(\nu)} \quad (2.3)$$

where  $N$  is the column density (molecule cm<sup>-2</sup>),  $A(\nu)$  is the absorbance strength (cm molecule<sup>-1</sup>).

## 2.4 Reaction Rate Laws

In this section, we will introduce rate reaction of a consecutive reaction and the concept of pseudo first order which we used to fit our reaction product against irradiation time. The rate of a chemical reaction is the relation between change in concentration of a substance per unit of time. i.e. For a balanced chemical reaction,  $A \rightarrow 2B$ , the rate of



reaction is  $-\frac{\Delta[A]}{\Delta t}$ . The formation rate of B is 2 times destruction rate of A.

When there are two reactants, with balanced equation  $2A + B \rightarrow 2C$ . The reaction is a third order overall, second order in A and first order in B. rate  $= k[A]^2[B]$ .

To determine the order of a reaction, we can only determine it experimentally. One way is method of initial rates. By changing concentration of initial reactants, and find out the initial reaction rate, we may find out the relation between two reactants and the rate. i.e. rate  $= k[A]^x[B]^y$ . For a reaction with only one reactant  $[R]$ , we may use the relation between time and reactant concentration to plot graphs to find out the order of reaction. For a zero order reaction, the rate is not depending on any reactant that it is a constant. The rate  $= -\frac{\Delta[R]}{\Delta t} = k[R]^0$ . By calculus,  $[R]_0 - [R]_t = kt$ .

For a first order reaction, rate  $= -\frac{\Delta[R]}{\Delta t} = k[R]$ . By calculus,  $\ln[R]_t = -kt + \ln[R]_0$ .

For a second order reaction, rate  $= -\frac{\Delta[R]}{\Delta t} = k[R]^2$ . By calculus,  $\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$ .

Hence, if we get a straight line in a plot between time as x-axis, and the concentration of reactant as y axis, it is a zeroth order reaction, similarly, in first order reactions, we get straight line in plots between  $\ln[R]$  as y axis and t in x axis.

In a reaction with one reactant in excess, the rate of reaction is called pseudo first order reaction where pseudo means pretended. For  $A+B \rightarrow C$ , rate  $= k[A][B]$ . As  $[B]_0 \gg [A]_0$ , change of  $[B]$  is negligible that  $[B] \sim [B]_0$ . Therefore,  $[B]$  is assumed to be a constant and included in the rate constant k.

For a consecutive reaction, where  $A \rightarrow B \rightarrow C$  that the produced product will not convert back as reactant. A simple example is radioactive decay. At  $t = 0$ ,  $[A] = [A]_0$ ,  $[B] = 0$ ,  $[C] = 0$  and at all times,  $[A] + [B] + [C] = [A]_0$ . The rate equations are as follows:

$$-\frac{\Delta[A]}{\Delta t} = k_1[A] \quad (2.4)$$



$$-\frac{\Delta[B]}{\Delta t} = k_1[A] - k_2[B] \quad (2.5)$$

$$-\frac{\Delta[C]}{\Delta t} = k_2[B] \quad (2.6)$$

By equation 2.4, we get

$$[A] = [A]_0 e^{-k_1 t} \quad (2.7)$$

By substituting equation 2.7 into equation 2.5, we get

$$-\frac{\Delta[B]}{\Delta t} + k_2[B] = k_1[A]_0 e^{-k_1 t} \quad (2.8)$$

After solving the differential equation 2.8, we get

$$[B] = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0 \quad (2.9)$$

Finally, since  $[C] = [A]_0 - [B] - [A]$ , by equation 2.7 and 2.9, we get

$$[C] = \left( 1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right) [A]_0 \quad (2.10)$$







### 3. Results and Discussions

According to the New Horizons team (0, ),  $\text{CH}_4$  from Pluto may accumulate by cold-trapping, onto surface of Charon. The amount of  $\text{CH}_4$  varies throughout the surface of Charon because it depends on duration of temperature below 25 K. The duration depends on diurnal motion and thermal inertia of Charon. With a tilted axis of 112 degrees to the ecliptic, higher concentration of  $\text{CH}_4$  will accumulate at the pole (see chapter 1 for details). Therefore, we investigate different concentrations of  $\text{CH}_4 + \text{NH}_3$  ice mixtures and answer several questions: Will different concentration of  $\text{CH}_4$  mix with high concentration of ammonia observed on crater position and throughout the surface of Charon (Grundy et al. 2016) have structure difference in accumulation of tholin? Are there variations of photo-products when concentration of  $\text{CH}_4$  differ during warm-up? Since both EUV and VUV irradiation irradiates onto Charon, are there any differences when we change the photon source from VUV to EUV to irradiate the ice mixtures?

The main source to irradiate the dark side of Charon is  $\text{Ly } \alpha$  reflected by interplanetary medium (Grundy 2016). Other sources such as the energetic ions in solar wind, consists of mainly  $\text{H}^+$ ,  $\text{He}^+$ ,  $\text{He}^{++}$  and  $\text{O}^{2+}$  etc are originated from solar corona or IPM. These ions would also reflect solar irradiation to the dark side of Charon. Among these irradiations, we picked He II irradiation because He II is 3 – 20 times more intense than He I during a solar flare. As it varies, it is difficult to estimate the dose onto Charon. Besides, electronic flux is also present in solar wind but it is one order of magnitude lower than proton flux. The flux for energetic electrons observed at the 1 A. U. position is available (<http://www.swpc.noaa.gov/products/goes-electron-flux>). Although electron flux is much less important than  $\text{Ly } \alpha$ , and their flux



varies, we also compare the electron irradiation experiment done by Kim and Kaiser (2011) on  $\text{CH}_4+\text{NH}_3$  ice mixtures in this chapter.

When Charon is shine by direct sun light, the surface temperature increases and deliver the heat to the poles by conduction. From the model of Grundy et al. (2016), the surface temperature of the pole area would increase to 60 K that the heating rate depends on the thermal conductivity of Charon. To demonstrate the heating process, we warmup our ice mixture with a heating rate 1 K/min and monitor the ice by both QMS and scanning IR spectra with 5 K intervals. We will look into whether there are new species formed during warmup and monitor the gas phase desorption.

Finally, in this chapter, after we focus on the concentration effect of  $\text{CH}_4$  on photo-products, photon energy effects, species detected during warmup phases, we present the residues accumulated by irradiating  $\text{CH}_4+\text{NH}_3$  ice mixtures with different ratios. Since both tholin formed on Titan and Charon has similar colour, we also compare the IR spectra of MDHL, NSRRC with different configurations with the residues on Titan with experiments done by Imanaka et al.

### 3.1 The infra-red spectrums and peaks identification

Before and after deposition, we scanned an IR spectrum and plotted the absorbance of the ice mixtures. Figure 3.1 is a plot of the absorbance of the  $\text{CH}_4+\text{NH}_3$  ice mixtures in different ratios of  $\text{CH}_4+\text{NH}_3$  ice mixtures, from top to bottom 1:20, 1:10, 1:5 and 3:2. We have labelled the peaks which we used to calculate the column densities by dotted lines throughout the graph. Main products we have detected are  $\text{C}_2\text{H}_6$ ,  $\text{CN}^-$  and  $\text{C}_3\text{H}_8$ . The peak positions with the references are listed in Table 3.1.

We integrated the area and divided by the absorption strength stated in table 3.2. Although we understand that there is an average error in absorption strengths of no more than 10 % when the pure ice is diluted in  $\text{N}_2$  and  $\text{H}_2\text{O}$  (Richey and Gerakines 2012). In our case,

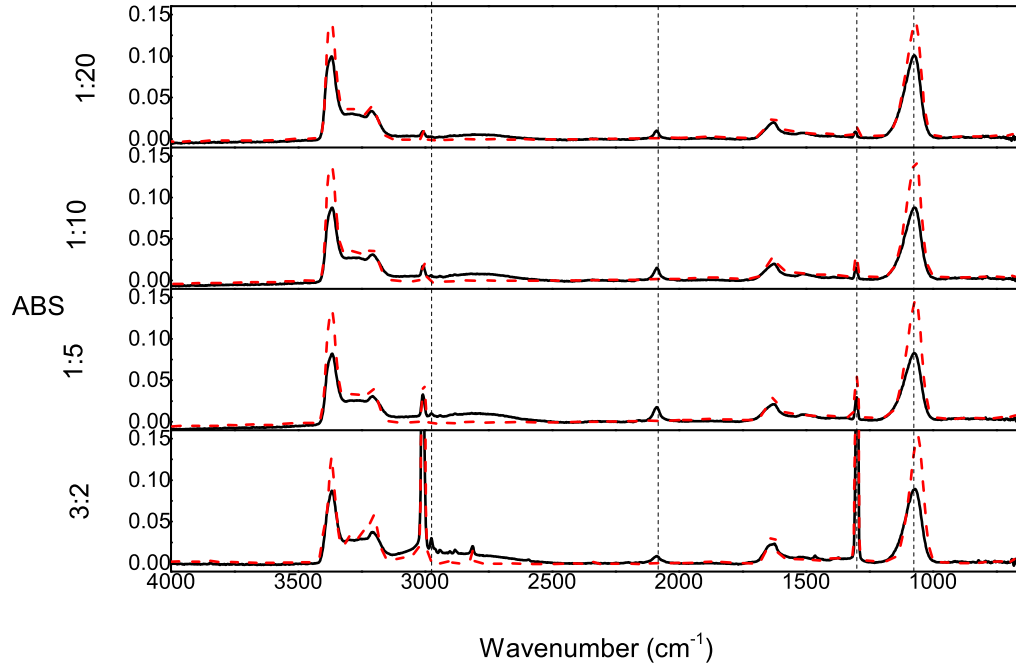


Figure 3.1: The the infra-red spectrum of  $\text{CH}_4 + \text{NH}_3$  ice mixtures before irradiation (dashed) and VUV irradiated ice mixtures provided by MDHL.

Table 3.1: The peak positions of identified substances after irradiation in different configurations of ice mixtures.

Literture assignments		$\text{CH}_4 + \text{NH}_3$ ratio (MDHL)				Ref.
Wavenumber ( $\text{cm}^{-1}$ )	Carrier	1:5 ( $\text{cm}^{-1}$ )	1:10 ( $\text{cm}^{-1}$ )	1:20 ( $\text{cm}^{-1}$ )	3:2 ( $\text{cm}^{-1}$ )	
3375	$\nu_3$ ( $\text{NH}_3$ )	3366	3366	3369	3367	1
3290	$2\nu_4$ ( $\text{NH}_3$ )	-	-	-	-	1
3210	$\nu_1$ ( $\text{NH}_3$ )	3207	3208	3210	3205	1
3011	$\nu_3$ ( $\text{CH}_4$ )	-	-	-	-	2
2972	$\nu_{10}$ ( $\text{C}_2\text{H}_6$ )	2975	-	-	2975	3
2960	$\text{C}_3\text{H}_8$	-	-	-	2960	7
2941	$\nu_8 + \nu_{11}$ ( $\text{C}_2\text{H}_6$ )	2940	-	-	2940	3
2904	$\nu_1$ ( $\text{CH}_4$ )	2901	-	-	2901	5
2879	$\nu_5$ ( $\text{C}_2\text{H}_6$ )	2882	2883	-	2882	3
2814	$\nu_2 + \nu_4$ ( $\text{CH}_4$ )	-	-	-	2815	5
2083	$\nu$ ( $\text{CN}^-$ )	2088	2087	2088	2088	2
1625	$\nu_4$ ( $\text{NH}_3$ )	1625	1625	1626	1631	1
1514	$\delta$ ( $\text{NH}_2$ )	1509	1507	1505	1511	6
1465-1440	deform $\text{CH}_2$ scissor	1461	-	-	1463	3,4
1390-1370	$\text{CH}_3$ sym deform	1394	1394	1394	1372	4
1298	$\nu_4$ ( $\text{CH}_4$ )	1301	1302	1305	1299	2
1075	$\nu_2$ ( $\text{NH}_3$ )	1073	1072	1072	1072	1
820	$\nu_{12}$ ( $\text{C}_2\text{H}_6$ )	-	-	-	820	3

Reference: 1. Bossa et al 2008 2. Moore and Hudson 2003 3. Kim et al. 2010 4. Socrates 2001 5. Bennet and Kaiser 2007 6. Zheng et al. 2008 7. Hudson and Moore 2004



absorption strengths changes after  $\text{CH}_4$  and  $\text{NH}_3$  are mixed. For example, according to d' Hendecourt and Allamandola (1986), the band of  $\text{NH}_3$  located at  $1070 \text{ cm}^{-1}$  would not change much (from  $1.1 \times 10^{-17}$  to  $1.2 \times 10^{-17}$ ) when excess water is added to pure  $\text{NH}_3$  and therefore, we may use the same absorption strength throughout our discussion to give a brief concept on what is the column density of the species and how is the absorption area changes when concentrations of ice mixtures and photon energy are changed. For the case of  $\text{CN}^-$ , we know that  $\text{CN}^-$  has a bond order =3 by its molecular orbitals which is different from CN stretching (bond order 2.5) which is very sensitive to the matrix environment. As an example, by Borget et al. (2012), the CN stretch in amino acetonitrile change by factor of 2 between the pure molecule itself and in a mixture of amino acetonitrile and  $\text{H}_2\text{O}$  (1:3). Here, we adopt the absorption strengths stated in Table 3.2 and neglect the error in absorption strengths.

Table 3.2: The strength of absorbance adopted in this thesis measured in literatures of pure ice samples

Wavenumber ( $\text{cm}^{-1}$ )	Assignment	Vibration	FWHM	A value ( $\times 10^{-17}$ )	Reference
2976	$\text{C}_2\text{H}_6$	- $\text{CH}_3$	-	1.05	2
2960	$\text{C}_3\text{H}_8$	- $\text{CH}_2$ -	-	2.58	2
2086	$\text{CN}^-$	CN	-	1.8	3
1297	$\text{CH}_4$	CH deformation	8	0.61	1
1070	$\text{NH}_3$	"umbrella mode"	68	1.7	1

Reference: 1. d'Hendecourt and Allamandola (1986) 2. Moore and Hudson (1998) 3. Noble et al. (2013)

## 3.2 Reaction mechanisms

### 3.2.1 $\text{C}_2\text{H}_6$

The assignment of  $\text{C}_2\text{H}_6$  is confirmed by several bands listed in table 3.1. Figure 3.2 is a partial of figure 3.1. The absorption peak located at  $2075 \text{ cm}^{-1}$  is the strongest vibration of  $\text{C}_2\text{H}_6$ . The formation mechanism of  $\text{C}_2\text{H}_6$  in astrophysical environment is proposed by Bennet et al. (2006), that the main route to form  $\text{C}_2\text{H}_6$  is by a combination of 2  $\text{CH}_3$  radicals (equation 3.1 and 3.2):



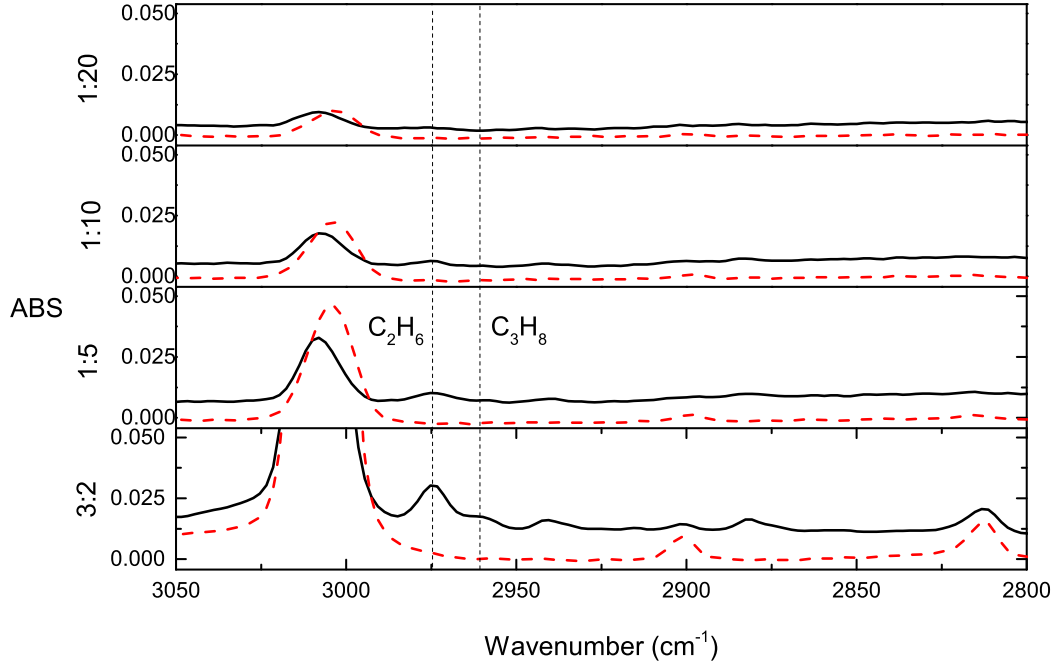


Figure 3.2: The the infra-red spectrum of  $\text{CH}_4 + \text{NH}_3$  ice mixtures of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  before irradiation (dashed) and VUV irradiated ice mixtures provided by MDHL.



The energy required to produce 1  $\text{CH}_3$  radical from  $\text{CH}_4$  is 4.42 eV. 2  $\text{CH}_3$  radicals recombine to form  $\text{C}_2\text{H}_6$  releases 3.74 eV. Therefore, equation 3.2 is a no-barrier exothermic process. However,  $\text{C}_2\text{H}_6$  is not detected in  $\text{CH}_4 + \text{NH}_3 = 1:20$  ice mixtures. Figure 3.3 shows the temporal formation column density of  $\text{C}_2\text{H}_6$  in different configurations of irradiated ice mixtures. As the formation only depends on  $\text{CH}_4$ , we may use first order kinetics equation to fit the column density versus photon dose.

$$[A] = [A]_0(1 - e^{-k_1 t}) \quad (3.3)$$

to fit the formation of  $\text{C}_2\text{H}_6$ . The fitting results are shown in table 3.3.

Table 3.3: The fitting results of  $\text{C}_2\text{H}_6$  by  $[\text{C}_2\text{H}_6] = [\text{C}_2\text{H}_6]_0(1 - e^{-k_1 t})$

Ratio of $\text{CH}_4 + \text{NH}_3$	A ( $\times 10^{15}$ molecules $\text{cm}^{-2}$ )	k ( $\times 10^{-17}$ photon $^{-1}$ )
1:10	$2.90 \pm 1.25$	$0.92 \pm 0.15$
1:5	$4.16 \pm 0.28$	$2.28 \pm 0.28$
3:2	$19.2 \pm 0.15$	$5.28 \pm 0.25$

From table 3.3, production rate is also proportional to the initial

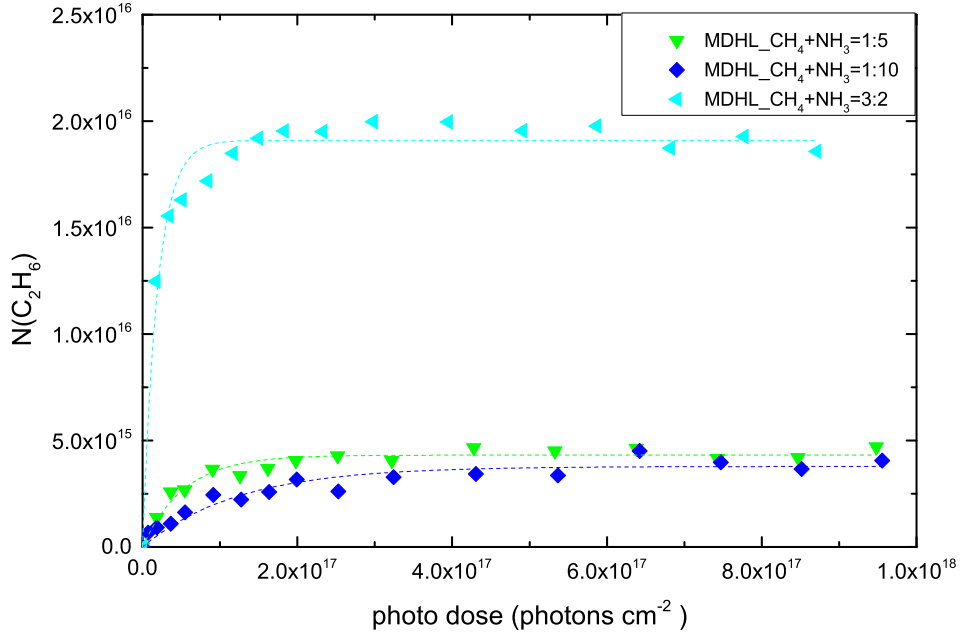


Figure 3.3: The column density of C<sub>2</sub>H<sub>6</sub> during CH<sub>4</sub> + NH<sub>3</sub> ice mixtures irradiated by MDHL.

CH<sub>4</sub> concentration.

### 3.2.2 C<sub>3</sub>H<sub>8</sub>

The peak positioned at 2960 cm<sup>-1</sup> belongs to -CH<sub>2</sub>- so we assigned that as C<sub>3</sub>H<sub>8</sub>, as the shortest carbon chain. The signal to noise ratio in CH<sub>4</sub>+NH<sub>3</sub> = 1:10 is poor that we can not quantize the amount of C<sub>3</sub>H<sub>8</sub> (figure 3.2).

It is a secondary product formed by a combination of either C<sub>2</sub>H<sub>6</sub> + CH<sub>2</sub> (equation 3.4) or C<sub>2</sub>H<sub>4</sub> + CH<sub>4</sub> (equation 3.5).



By modern peak fitting method, we deconvoluted the overlapped C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> into two gaussians.

### 3.2.3 CN<sup>-</sup>

From infra-red absorption spectrum (figure 3.4) and their positions, we assigned the peak 2086 cm<sup>-1</sup> to CN<sup>-</sup> but not a combination of HCN and CN<sup>-</sup>. The assignment is based on a absence in CN bending mode at

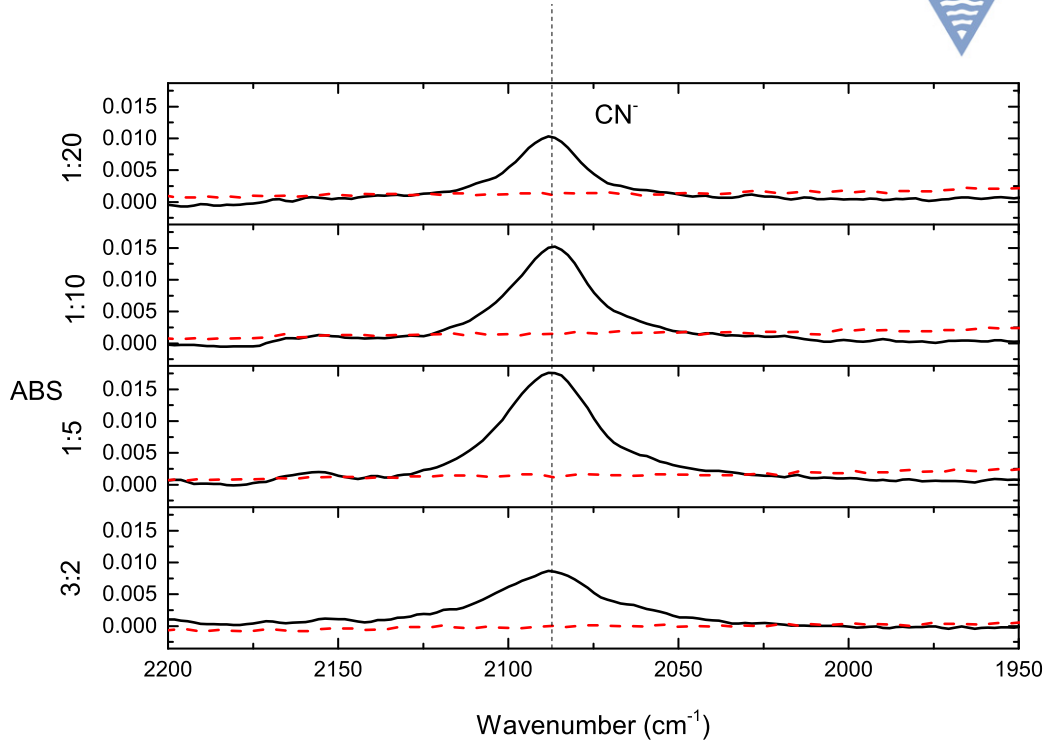


Figure 3.4: The the infra-red spectrum of  $\text{CH}_4 + \text{NH}_3$  ice mixtures of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  before irradiation (dashed) and VUV irradiated ice mixtures provided by MDHL.

$848 \text{ cm}^{-1}$ . In the case  $\text{CH}_4 + \text{NH}_3 = 3:2$ , we may observe a peak located at  $820 \text{ cm}^{-1}$ , which is with a FWHM half of HCN and it is eliminated at 50 K during the warm-up phase. Since 50 K is the desorbing temperature of  $\text{C}_2\text{H}_6$  and the peak position is the close to  $\nu_{12}$  mode of  $\text{C}_2\text{H}_6$ , we believe that the  $820 \text{ cm}^{-1}$  peak is contributed by  $\text{C}_2\text{H}_6$ . Therefore, we may assign our peak located at  $2086 \text{ cm}^{-1}$  as purely  $\text{CN}^-$ .

The formation mechanism of  $\text{CN}^-$  at low temperature was first suggested by Kim and Kaiser (2011) to be two step reaction mechanism with methylamine as intermediate.  $\text{CH}_4$  and  $\text{NH}_3$  irradiated by photon to become  $\text{CH}_3$  and  $\text{NH}_2$  radical (figure ??, followed by propagation and recombination of radicals becoming  $\text{CH}_3\text{NH}_2$  and dehydrogenation and acid-base reaction to form  $\text{CN}^-$ . Although Kim and Kaiser used 1.5keV electron as energy source to simulate the cosmic ray induced photochemistry, this formation mechanism also applies in our photon irradiation experiments because we can also detect the methylamine

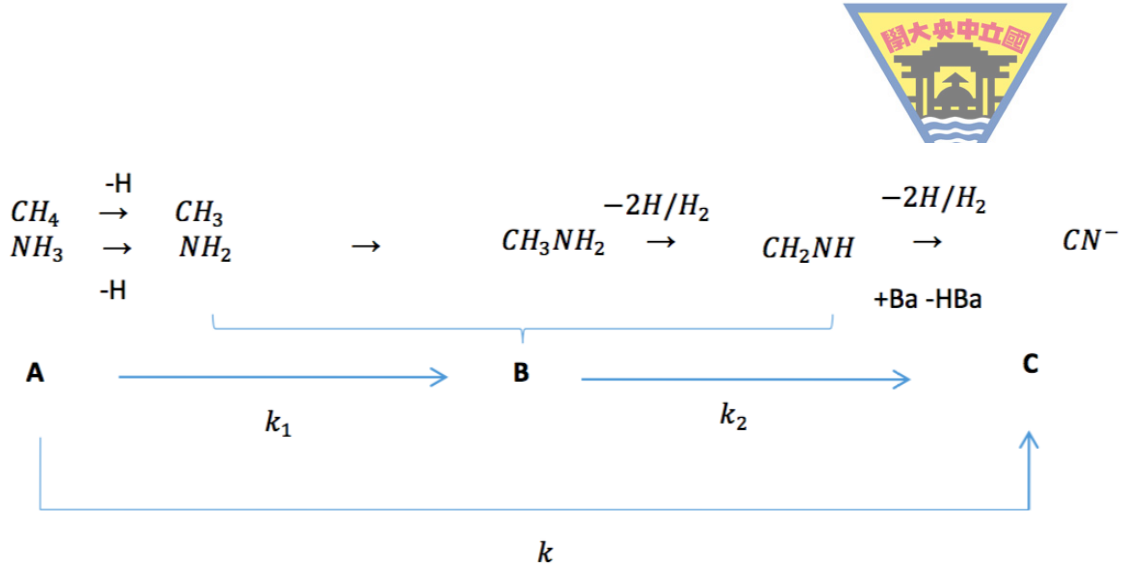


Figure 3.5: The formation mechanism of  $\text{CN}^-$  proposed by Kim and Kaiser(2011).

during our warm-up phase. The ion fragment with  $m/z=31$  is assigned as  $\text{CH}_3\text{NH}_2^+$  and detectable in all ratios of our  $\text{CH}_4+\text{NH}_3$  experiments (figure ??).

By the deviation performed in section 2.4, we have a rate equation for consecutive reactions 2.10. With one of the reactant larger than another, we applied the pseudo first order assumption. With equation 2.10, we fitted the formation of  $\text{CN}^-$  (figure 3.7) and found that one of the rate constant is always larger than the other in all of the ratios. The fitting results are averaged by more than two experiments and are shown in table 3.6. The results of Kim and Kaiser is also listed into the table, they could observe a two-step reaction mechanism in production of  $\text{CN}^-$  in  $\text{CH}_4+\text{NH}_3$  (3:1) experiments with electron current  $0.1 \mu\text{A}$ . However, when they increased the electron flux to  $1 \mu\text{A}$  for irradiation  $\text{C}_n\text{H}_{2n+2}(n=1-6)$  and  $\text{NH}_3$  ice mixtures, they also observed a one-step reaction mechanism.

Table 3.4: The fitting results of  $\text{CN}^-$  by equation 2.10

Ratio of $\text{CH}_4+\text{NH}_3$	A ( $\times 10^{16}$ molecules $\text{cm}^{-2}$ )	$k_1$ ( $\times 10^{-18}$ photon $^{-1}$ )	$k_2$ (photon $^{-1}$ )
1:20	$4.75 \pm 0.40$	$0.70 \pm 0.09$	$>1$
1:10	$4.51 \pm 0.18$	$1.33 \pm 0.13$	$>1$
1:5	$4.61 \pm 0.18$	$1.93 \pm 0.19$	$>1$
3:2	$2.24 \pm 0.03$	$8.21 \pm 0.70$	$>1$

represents the amount of  $\text{CN}^-$  we may obtain when irradiated the ice for infinitely long.



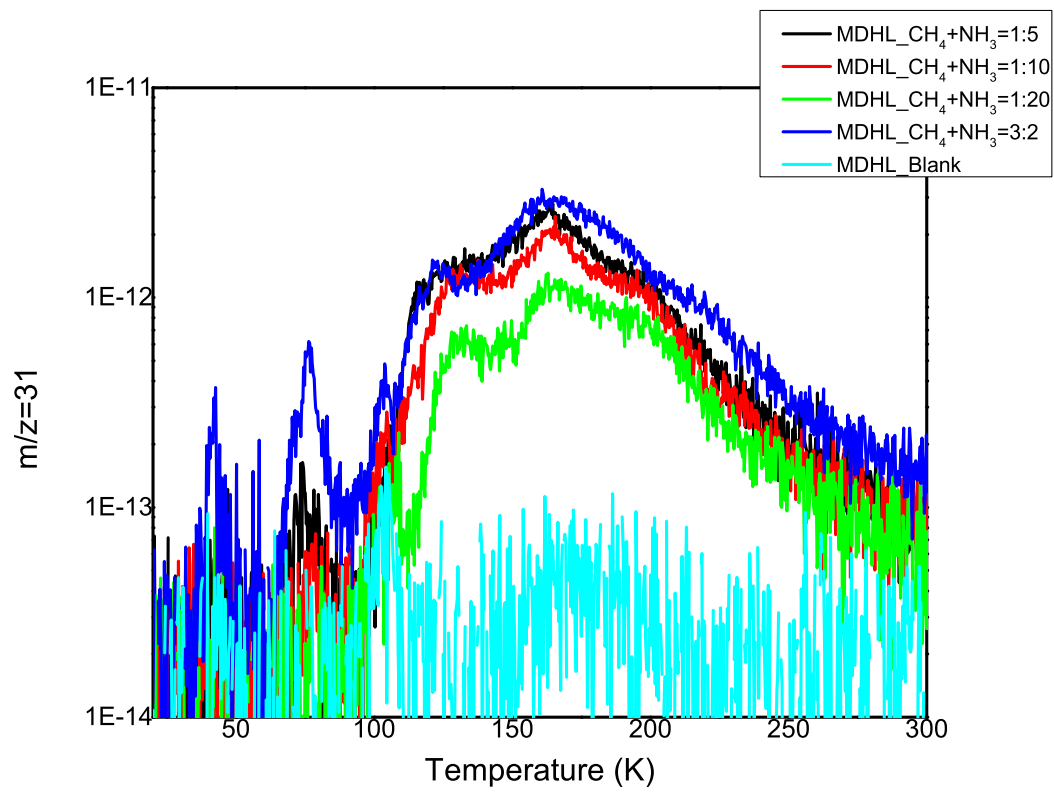


Figure 3.6: The  $m/z=31$  detected by QMS during warm-up with heating rate 1 K/min in different configurations of ice mixtures.

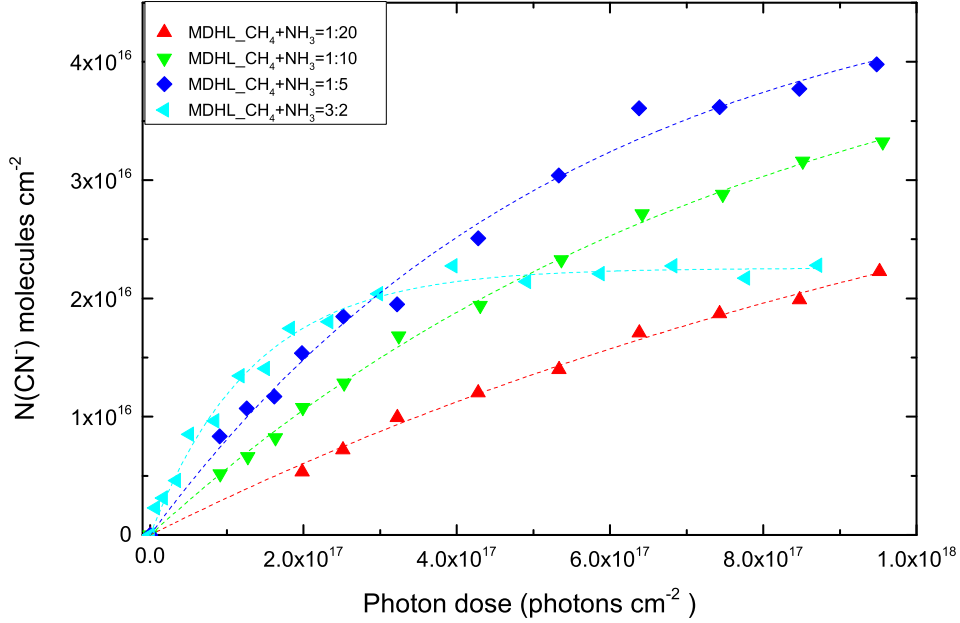


Figure 3.7: The column density of  $\text{CN}^-$  accumulated when different configurations of  $\text{CH}_4 + \text{NH}_3$  ice mixtures are irradiated by VUV photons provided by MDHL. The dotted lines are fits of column densities by equation 2.10.

### 3.3 The Concentration Effect in formation of Cyanide ions and Ethane

#### 3.3.1 Cyanide ion

From table 3.6, we may see that the rate  $k_1$  is proportional to the concentration of  $\text{CH}_4$ . The rate constant  $k_1$  increases when concentration of  $\text{CH}_4$  increases. Since  $\text{NH}_3$  is fixed in all of our experiments, more  $\text{CH}_4$  are evolved into  $\text{CH}_3$  radical formation when proportion of  $\text{CH}_4$  in the ice mixture increases. More abundant  $\text{CH}_3$  radicals in the ice mixtures would produce more  $\text{CH}_3\text{NH}_2$  intermediates.

In  $\text{CH}_4 + \text{NH}_3 = 3:2$  ice mixtures, A is half of the other ratios. The reduction is mainly because  $\text{CN}^-$  has a competing relationship with formation of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ .  $\text{NH}_2$  radicals competes with  $\text{CH}_2$ ,  $\text{CH}_3$  and  $\text{C}_2\text{H}_4$  radicals. With this competition, the intermediate  $\text{CH}_3\text{NH}_2$  is reduced. Therefore, in ratio 3:2  $\text{CH}_4 + \text{NH}_3$  ice mixture, the yield of  $\text{CN}^-$  is the least (table 3.6). Note that the formation yield of  $\text{C}_2\text{H}_6$  is the maximum in this ratio (table 3.3)

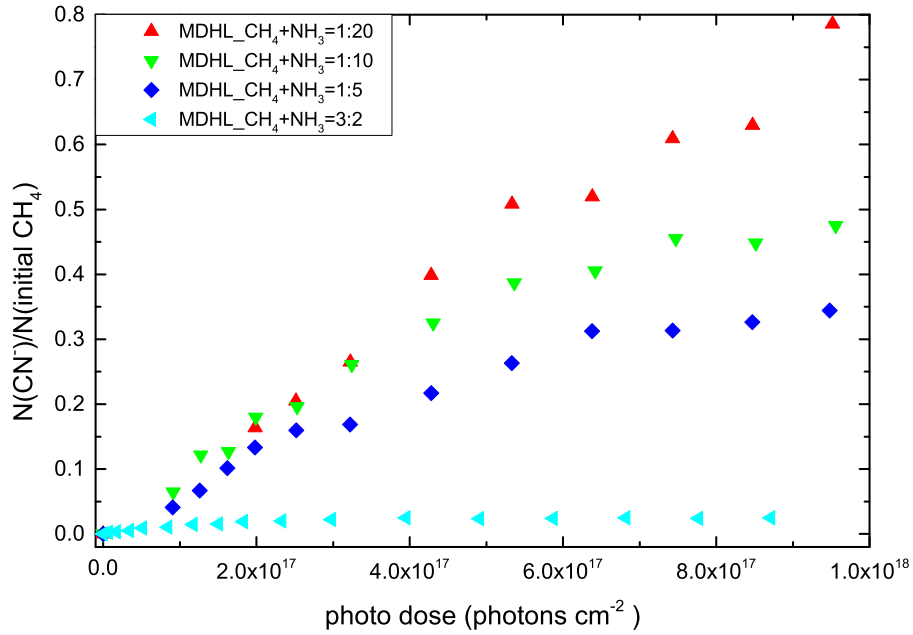


Figure 3.8: The column density of  $\text{CN}^-$  divided by initial  $\text{CH}_4$  accumulated when different configurations of  $\text{CH}_4 + \text{NH}_3$  ice mixtures are irradiated by VUV photons provided by MDHL.

Considering the normalized  $\text{CN}^-$  with respect to the initial  $\text{CH}_4$  (figure 3.8), the formation of  $\text{CN}^-$  is more effective in low  $\text{CH}_4$  concentration ice mixtures. The mobile  $\text{CH}_3$  radical is aggregated by excess  $\text{NH}_3$ . In this situation,  $\text{CH}_3$  radicals have less chance to meet another  $\text{CH}_3$  radical or  $\text{C}_2\text{H}_4$ . It is more likely to react with  $\text{NH}_2$  radicals so the formation of  $\text{CN}^-$  in low  $\text{CH}_4$  concentration ice mixtures are more efficient.

### 3.3.2 Ethane

Considering the case of ratio of  $\text{CN}^-$  divided by  $\text{C}_2\text{H}_6$ , the formation of  $\text{CN}^-$  in ice mixtures with diluted  $\text{CH}_4$  has more  $\text{CN}^-$  formed than  $\text{C}_2\text{H}_6$ . It is because ice mixtures with higher concentrations in  $\text{CH}_4$  is more effective for one  $\text{CH}_3$  radical to combine with another  $\text{CH}_3$  radical. On the contrast,  $\text{CH}_3$  radicals formed in the ice mixtures with diluted  $\text{CH}_4$  concentrations are aggregated by  $\text{NH}_3$ . Therefore,  $\text{CN}^-$  is less efficient to form in ice mixtures with excess  $\text{NH}_3$ .

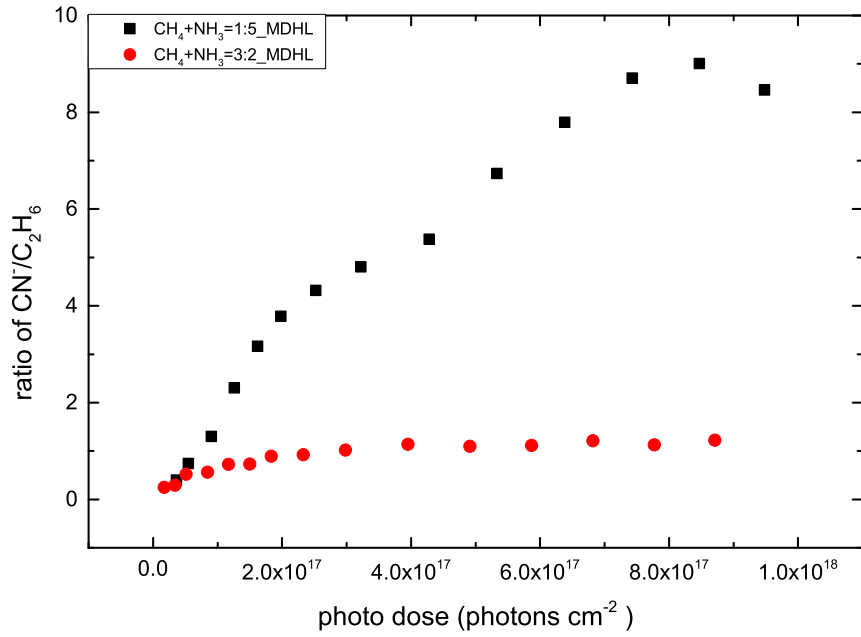


Figure 3.9: The column density of  $\text{CN}^-$  divided by  $\text{C}_2\text{H}_6$  accumulated when different configurations of  $\text{CH}_4 + \text{NH}_3$  ice mixtures are irradiated by VUV photons provided by MDHL.

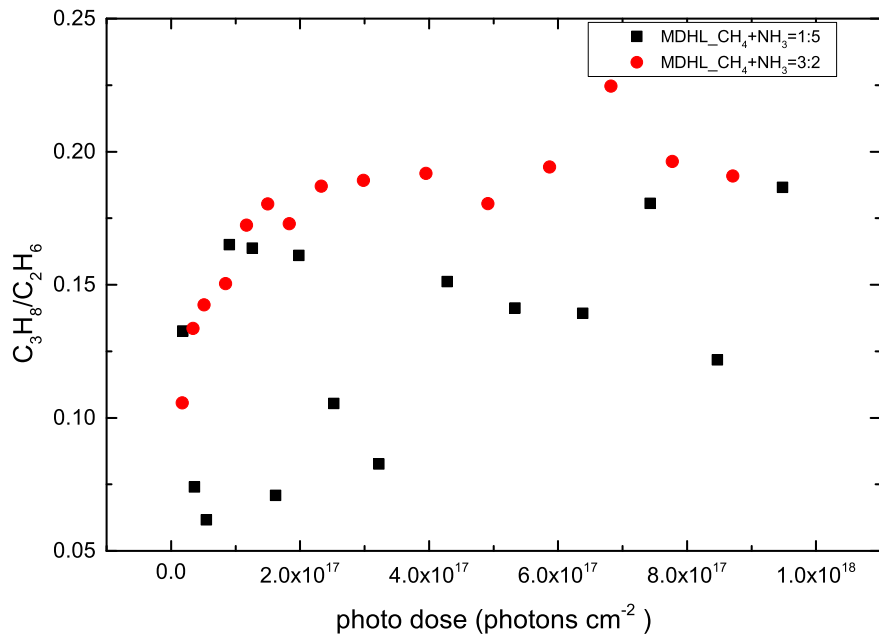


Figure 3.10: The column density of  $\text{C}_3\text{H}_8$  divided by  $\text{C}_2\text{H}_6$  accumulated when different configurations of  $\text{CH}_4 + \text{NH}_3$  ice mixtures are irradiated by VUV photons provided by MDHL.



### 3.3.3 Propane

$C_3H_8$  forms based on to the  $C_2H_6$  3.10 is the plot with column densities of  $C_2H_6$  divided by  $C_3H_8$ . We may see that the ratio in  $CH_4+NH_3 = 1:5$  experiment is around 6 where  $CH_4+NH_3 = 3:2$  is around 3. This shows that the amount of  $C_3H_8$  in  $CH_4+NH_3 = 3:2$  experiment is higher. It is rather difficult for  $C_3H_8$  to form in  $CH_4+NH_3 = 1:5$  experiments because  $NH_3$  aggregated them. The formation of  $C_3H_8$  in  $CH_4+NH_3 = 1:5$  and  $3:2$  experiments has given a reasonable explanation about why  $C_2H_6$  formation is most efficient in  $CH_4+NH_3 = 1:10$  experiments.

## 3.4 Cyanide ion produced by photon source and electron source

We study the ice mixtures of  $CH_3$  dominated ice mixtures and compare the efficiencies in CN

We calculated the percentage of photons absorbed by  $CH_4+NH_3$  ice mixtures in different configurations. Applying cross-sections measured by Cruz-Diaz et al. (2014) and the spectrum of our MDHL and substitute them into Beer's law. In  $CH_4+NH_3 = 3:2$  ice mixtures with ammonia fixed at 600 ML can absorb more than 99.9 % of light. Therefore, we may assume all the irradiated light is absorbed by the ice. For  $CH_4+NH_3 = 3:2$  ice mixture, around  $9 \times 10^{17}$  photons were irradiated in 270 minutes.

In Kim and Kaiser (2011) electron irradiation experiments, the energy transferred to  $CH_4 + NH_3$  ice mixtures is by linear electron transfer (LET) that  $1.3 \text{ eV molecule}^{-1}$  was absorbed by the ice in 90 minutes. They get flattened at 20 minutes' irradiation, with fluence of  $2.0 \times 10^{14}$  electrons  $\text{cm}^{-2}$ . While we got flattened at a dose of  $3 \times 10^{17}$  photons  $\text{cm}^{-2}$ . Considering the energy of their electron (1.5 keV) and energy of our photons, they got flattened at  $3 \times 10^{17} \text{ eV cm}^{-2}$  while we get flattened at  $27.81 \times 10^{17} \text{ eV cm}^{-2}$ . Comparing these energy doses, less electrons are needed to flatten the formation of  $CN^-$ .

Comparing our  $CN^-$  obtained after infinitely long exposure, 13 – 16 ML of  $CN^-$  was obtained by electron irradiation depending on which equation they choose to fit. In our MDHL experiments, we have 14.8 ML



of  $\text{CN}^-$ . However, Kim and Kaiser (2011) adopted the  $\text{CN}^-$  absorption coefficient measured by Georgieva and Velcheva (2006) to be  $3.7 \times 10^{-18} \text{ cm molecule}^{-1}$ , which is 4.86 times smaller. We do not adopt this absorption coefficient because it violates the carbon balance that number of  $\text{CN}^-$  produced will be larger than  $\text{CH}_4$  consumption. If we adopted the same absorption coefficient, the production yield of  $\text{CN}^-$  should be multiplied by 4.86. Therefore, our yield is 72 ML of  $\text{CN}^-$ . Regarding percentage of  $\text{NH}_3$  (limiting reactant), Kim and Kaiser has 5 - 6 % yield where we have 12 % yield if we adopted the same absorption coefficients. To conclude, electron irradiation has a smaller absorption cross-sections, the percentage of yield is also smaller than VUV irradiated ice mixtures with similar ice thicknesses.

### 3.5 Photon Energy Effect - EUV and VUV

According to Blanksby and Ellison, the dissociation energy for  $\text{CH}_4$ , becoming  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  and  $\text{C}$  are 4.55, 4.79, 4.39 and 3.51 eV respectively at 298 K. Whereas dissociation energy for  $\text{NH}_3$ , becoming  $\text{NH}_2$  is 4.67 eV at 298 K.

Considering our MDHL with average energy of 9.27 eV, all of the above fragments may exist rather in the form of radicals or combined with other radicals to form heavier molecules in our ice mixtures. It is not necessary to further increase the photon energy in order to get another new fragmentation pathway. However, the fragmentation of  $\text{CH}_4$  and  $\text{NH}_3$  depends on photon energy.

Several gaseous state measurements also presents this result. First, Gans et al. (2011) changed photon wavelengths from 121.6 nm to 118.2 nm to dissociate the  $\text{CH}_4$  molecules and ionize the fragments with the corresponding photon energy. Changing from 121.6 to 118.1 nm significantly changed the ionized fragmentation ratio from  $\text{CH}_3^+$  and  $\text{CH}_2^+$  1:1 to 1:2 using pulsed laser. This slightly change of photon energy, from 10.2 eV to 10.4 eV has a significant change in the fragmentation of  $\text{CH}_4$ .

Second, Tsai et al. used 30.4 nm to photo dissociate  $\text{CH}_4$  and test it by time - of - flight mass spectrometer yields  $\text{CH}_3^+$ :  $\text{CH}_2^+$ :  $\text{CH}^+$ :  $\text{C}^+$  = 1 :0.32: 0.118: 0.0237 (Tsai 1980). Since it is also a gaseous state experimental results, we cannot directly apply this fragmentation into

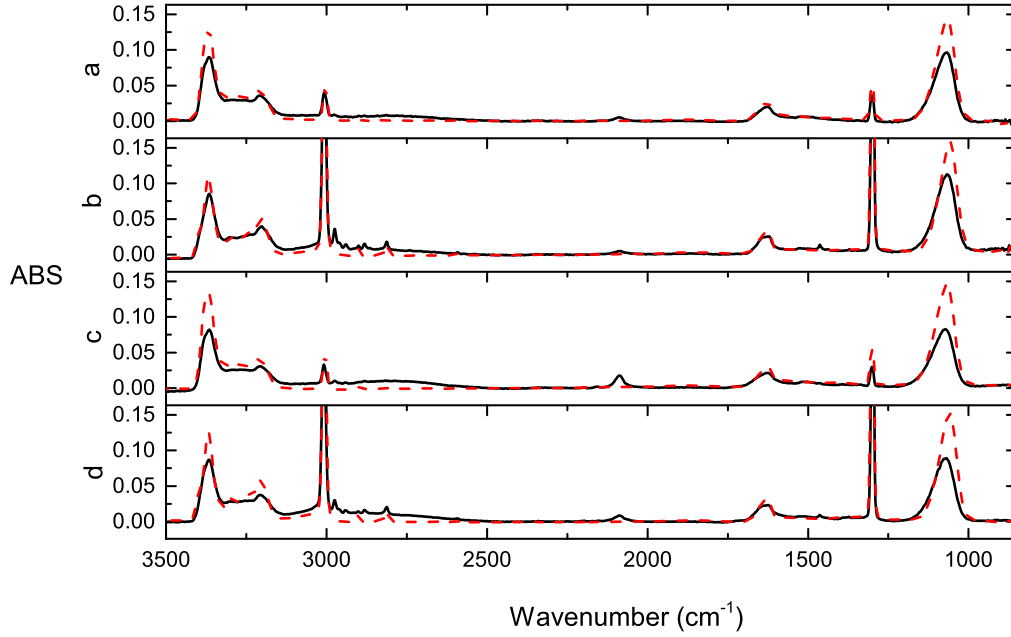


Figure 3.11: The the infra-red spectrum of  $\text{CH}_4 + \text{NH}_3$  ice mixtures before irradiation (dashed) and VUV and EUV (solid) irradiated ice mixtures provided by MDHL. (a) and (b) are EUV irradiated  $\text{CH}_4 + \text{NH}_3 = 1:5$  and  $3:2$  ice mixtures respectively, and (c) and (d) are VUV irradiated  $\text{CH}_4 + \text{NH}_3 = 1:5$  and  $3:2$  ice mixtures respectively.

our calculations. Note that the VUV absorption spectra of  $\text{CH}_4$  in solid phases is different from gaseous phases (Cruz-Diaz 2014), so the exact photo dissociation fragmentation ratios by 30.4 nm nor VUV irradiations in astronomical environments are still unknown.

Thirdly, a group also varies ratios of  $\text{CH}_4 + \text{NH}_3$  mixtures and irradiate with far UV irradiation at 134 nm (Bossard 1980). However, this group only used gas chromatography to analyse the final products and their reaction is carried in gas phase in room temperature. Although the photon energy of our MDHL is enough to dissociate both the  $\text{CH}_4$  and  $\text{NH}_3$  molecules, we further increase photon energy to He II 30.4 nm to examine whether there are differences in photo-products. It is worthwhile for us to perform experiment by EUV irradiation to see if the EUV irradiation can generate any new products on the surface of Charon, or any difference in yield. After investigation, we may answer several questions: Are there any differences in products or production yields? Would the formation mechanism change?



Table 3.5 shows the identified peaks of  $\text{CH}_4+\text{NH}_3$  ice mixtures irradiated by VUV and EUV (30.4 nm) irradiated in IR spectra (figure 3.11).

Table 3.5: The peak positions of identified substances after VUV and EUV irradiations in different configurations of ice mixtures.

Literture assignments		$\text{CH}_4+\text{NH}_3$ ratio (MDHL)		$\text{CH}_4+\text{NH}_3$ ratio (30.4 nm)		Ref.
Wavenumber ( $\text{cm}^{-1}$ )	Carrier	1:5 ( $\text{cm}^{-1}$ )	3:2 ( $\text{cm}^{-1}$ )	1:5 ( $\text{cm}^{-1}$ )	3:2 ( $\text{cm}^{-1}$ )	
3375	$\nu_3$ ( $\text{NH}_3$ )	3366	3367	3368	3368	1
3290	$2\nu_4$ ( $\text{NH}_3$ )	-	-	-	-	1
3210	$\nu_1$ ( $\text{NH}_3$ )	3207	3205	3209	3205	1
3011	$\nu_3$ ( $\text{CH}_4$ )	-	-	-	-	2
2972	$\nu_{10}$ ( $\text{C}_2\text{H}_6$ )	2975	2975 2977	2976		3
2960	$\text{C}_3\text{H}_8$	-	2960	-	2960	7
2941	$\nu_8 + \nu_{11}$ ( $\text{C}_2\text{H}_6$ )	2940	2940	-	2942	3
2904	$\nu_1$ ( $\text{CH}_4$ )	2901	2901	2901	2901	5
2879	$\nu_5$ ( $\text{C}_2\text{H}_6$ )	2882	2882	-	2884	3
2814	$\nu_2 + \nu_4$ ( $\text{CH}_4$ )	-	2815	-	2813	5
2083	$\nu$ ( $\text{CN}^-$ )	2088	2088	2090	2089	2
1625	$\nu_4$ ( $\text{NH}_3$ )	1625	1631	1627	1631	1
1514	$\delta$ ( $\text{NH}_2$ )	1509	1511	1509	1511	6
1465-1440	deform $\text{CH}_2$ scissor	1461	1463	-	1465	3,4
1390-1370	$\text{CH}_3$ sym deform	1394	1372	-	1372	4
1298	$\nu_4$ ( $\text{CH}_4$ )	1301	1299	1303	1301	2
1075	$\nu_2$ ( $\text{NH}_3$ )	1073	1072	1070	1068	1
820	$\nu_{12}$ ( $\text{C}_2\text{H}_6$ )	-	820	-	-	3

Reference: 1. Bossa et al 2008 2. Moore and Hudson 2003 3. Kim et al. 2010 4. Socrates 2001 5. Bennet and Kaiser 2007 6. Zheng et al. 2008 7. Hudson and Moore 2004

Considering the formation mechanisms of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ , equation (3.2 and 3.4), when changing the photon source from MDHL VUV irradiation to He II 30.4 nm monochromatic light to irradiate  $\text{CH}_4+\text{NH}_3$  (3:2) ice mixtures, the ratio of  $\text{C}_2\text{H}_6$  /  $\text{C}_3\text{H}_8$  of ice mixtures irradiated by VUV irradiation is lower than EUV irradiation provided by NSRRC (figure 3.2.1). There are two probable explanations. First, the fragmentation of  $\text{CH}_4$  is different with different photon energies. Therefore, less  $\text{C}_3\text{H}_8$  is produced with EUV photons. Second, the destruction of  $\text{CH}_4$  is much less efficient by EUV irradiation. Therefore, the  $\text{CH}_3$  radicals are not as rich as the ice mixture irradiated by VUV photons provided by the MDHL. As a result, we further irradiate our ice mixtures by EUV photons until the destruction of  $\text{CH}_4$  is similar to VUV irradiation experiments done with MDHL. We found that the second explanation is more persuasive because after  $\text{CH}_4$  destruction equals to VUV irradiation, the ratio of  $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$  of average of last 7 irradiations is 3.53 and



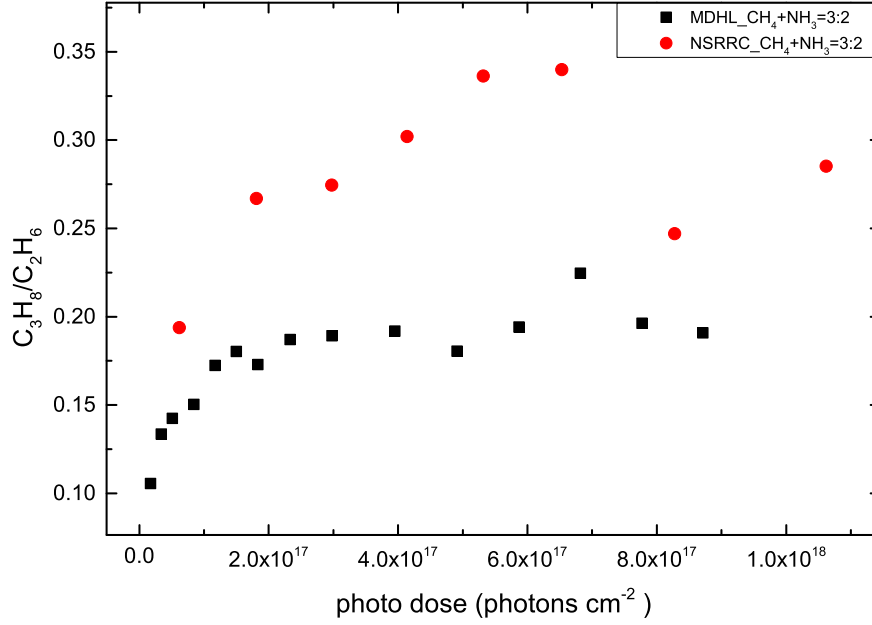


Figure 3.12: The column density of  $C_3H_8$  divided by  $C_2H_6$  accumulated when different configurations of  $CH_4 + NH_3$  ice mixtures are irradiated by VUV and EUV photons

3.66 in experiments done with 3 experiments with MDHL and 2 experiments in NSRRC respectively. From figure 3.2.2, The reduction of  $CH_4$  is 6.06 times slower in EUV experiments than VUV experiments while the reduction of  $NH_3$  is  $3.19 \pm 0.12$  times slower. Therefore, the destruction cross-section of  $CH_4$  and  $NH_3$  ice has a  $6.06 \pm 0.07$  and  $3.19 \pm 0.12$  times lower in 30.4 nm than in 121.6 nm.

Figure 3.12 shows the column density of  $C_2H_6$  divided by  $C_3H_8$  after  $CH_4 + NH_3 = 3:2$  ice mixtures are irradiated by VUV irradiation and He II monochromatic light.

From 3.12, we may observe that more  $C_3H_8$  is produced by 30.4nm photons than by VUV photons. Recall the formation mechanism of  $C_3H_8$  (equation 3.5),  $CH_2$  and  $C_2H_4$  radicals are essential in producing  $C_3H_8$ . This increase production in  $C_3H_8$  may be caused by the increase in  $CH_2$  radicals during fragmentation of  $CH_4$ . This result is similar to the findings of Gans et al. (2011), the ratio of  $CH_2$  radicals increases from 0.3 to 0.48 when photon energy increases from 121.6 nm to 118.2 nm in their pulsed laser experiments.

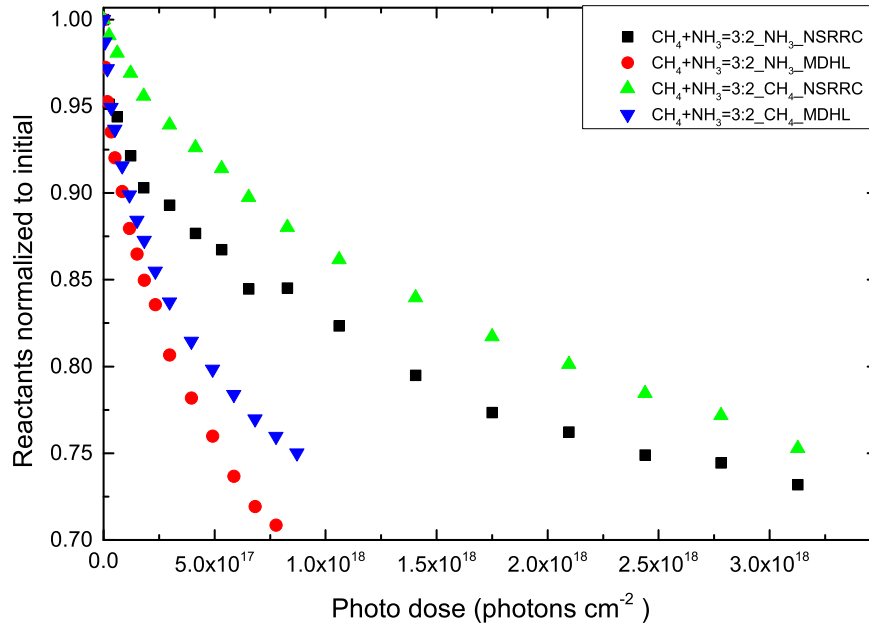


Figure 3.13: The normalized reduction of  $\text{CH}_4$  and  $\text{NH}_3$  in  $\text{CH}_4 + \text{NH}_3$  ice mixtures irradiated by VUV and EUV photons

Apart from  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ , are there any difference in  $\text{CN}^-$  production? Figure 3.14 shows the accumulated column densities of  $\text{CN}^-$  generated by irradiation of  $\text{CH}_4 + \text{NH}_3$  ice mixtures by MDHL and 30.4 nm monochromatic light. The fitting results are shown in Table 3.6. The rate constants forming  $\text{CN}^-$  is 3.06 to 4.13 times larger in  $\text{CH}_4 + \text{NH}_3 = 1:5$  and  $3:2$  irradiated by MDHL than irradiated by 30.4 nm monochromatic light respectively. From figure ??, the  $\text{CH}_4$  reduction in NSRRC is  $6.06 \pm 0.07$  times slower. With the rate constants of  $\text{CN}^-$  only 3.06 to 4.13 times smaller, the 6 times slower in  $\text{CH}_4$  reduction and 3 times slower in  $\text{CN}^-$  formation give rise to a similarity of reduced  $\text{NH}_3$  destruction cross-section and reduced rate in  $\text{CN}^-$  production in EUV irradiation experiments. Therefore, we may conclude that the reduction in  $\text{CN}^-$  formation rate by 30.4nm EUV irradiation is mainly due to the decreased  $\text{NH}_3$  destruction cross-sections.

### 3.6 Residues

The residues we studied are the accumulated residues onto the substrate. We do not understand are there any interaction between residues

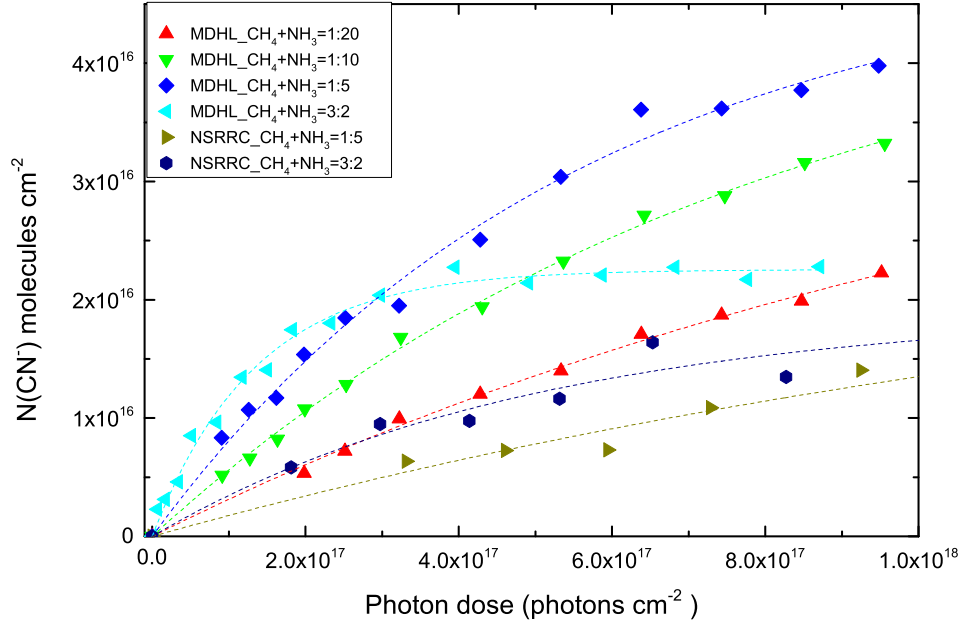


Figure 3.14: The column densities of  $\text{CN}^-$  generated by irradiation of  $\text{CH}_4+\text{NH}_3$  ice mixtures by MDHL and 30.4 nm monochromatic light.

Table 3.6: The fitting results of  $\text{CN}^-$  by equation 2.10

Light source	Ratio of $\text{CH}_4+\text{NH}_3$	A ( $\times 10^{16}$ molecules $\text{cm}^{-2}$ )	$k_1$ ( $\times 10^{-18}$ photon $^{-1}$ )	$k_2$ (photon $^{-1}$ )
VUV	1:5	$4.61 \pm 0.18$	$1.93 \pm 0.19$	$>1$
	3:2	$2.24 \pm 0.03$	$8.21 \pm 0.70$	$>1$
EUV	1:5	$2.89 \pm 1.29$	$0.63 \pm 0.37$	$>1$
	3:2	$2.24 \pm 0.03$	$1.92 \pm 1.99$	$>1$

Fitting result of figure ?? with pseudo first order equation  $[\text{CN}^-] = A(1 - e^{-kx})$ . These fitting results of MDHL experiments are an average of at least 2 experiments with the same circumstances. I



and the ice mixtures. However, we may know what is the change of residues when we change the ratio of the  $\text{CH}_4 + \text{NH}_3$  from  $\text{CH}_4$  dominating to  $\text{NH}_3$  dominating. Figure ?? is a comparison of  $\text{CH}_4 + \text{NH}_3 = 3:2$  after VUV experiments, residues accumulated after EUV exposure of  $\text{CH}_4 + \text{NH}_3 = 3:2$  ice mixtures and the plasma experiment done by Imanaka et al. (2004). The residues in ammonia dominated ice mixtures cannot be detected after consecutive experiments. There are no differences between EUV accumulated residues and VUV accumulated residues in  $\text{CH}_4 + \text{NH}_3 = 3:2$  ice mixtures. The main differences between plasma experiments of  $\text{N}_2 + \text{CH}_4$  (9:1) done at 2300 Pa. by Imanaka et al. (2004) and our experiments is the peaks located around  $2090 \text{ cm}^{-1}$ .

Why we use different initial reactants, replacing  $\text{N}_2$  by  $\text{NH}_3$  but we may get similar residues? The similarities during formation of atomic nitrogens when breaking  $\text{N}_2$  bonds in nitrogen and  $\text{NH}$  bonds in ammonia give rise to this result. When photon energy is enough to break both  $\text{NH}$  bond and  $\text{N}_2$  bond, similar experimental residues forms. Our results implies that the residues formed on Charon is similar to what we found on Titan, although their formation environments differs from gaseous phase with  $\text{N}_2$  dominating to solid phase with  $\text{NH}_3$ .

After  $\text{CH}_4 + \text{NH}_3 = 1:5, 1:10$  and  $1:20$  experiments, we notice that two new bonds are formed. One at  $1721 \text{ cm}^{-1}$  and another at  $1286 \text{ cm}^{-1}$ . These two peaks are due to MCT detector self-contamination. When we stopped adding liquid nitrogen, molecules stick onto MCT detector will be free out. They stuck onto our detector and hence produced these two peaks. Hence, we may conclude that the residues produced by  $\text{CH}_4 + \text{NH}_3$  with different ratios are the same.

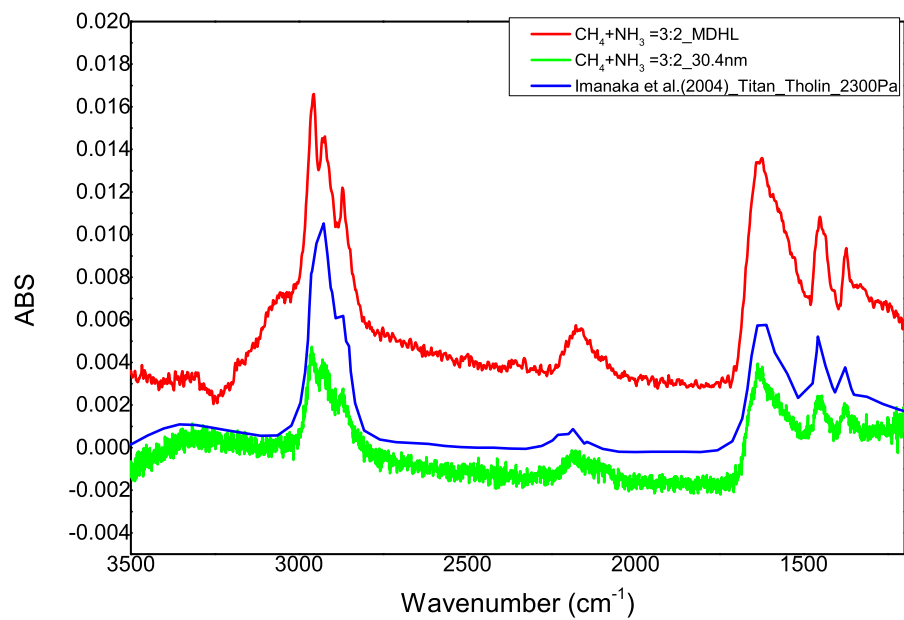


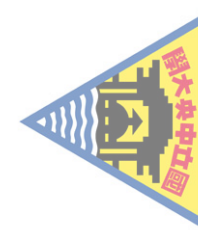
Figure 3.15: The IR spectrum of residues in after  $\text{CH}_4 + \text{NH}_3 = 3:2$  experiments and the accumulate residues after MDHL experiments and NSRRC experiments.



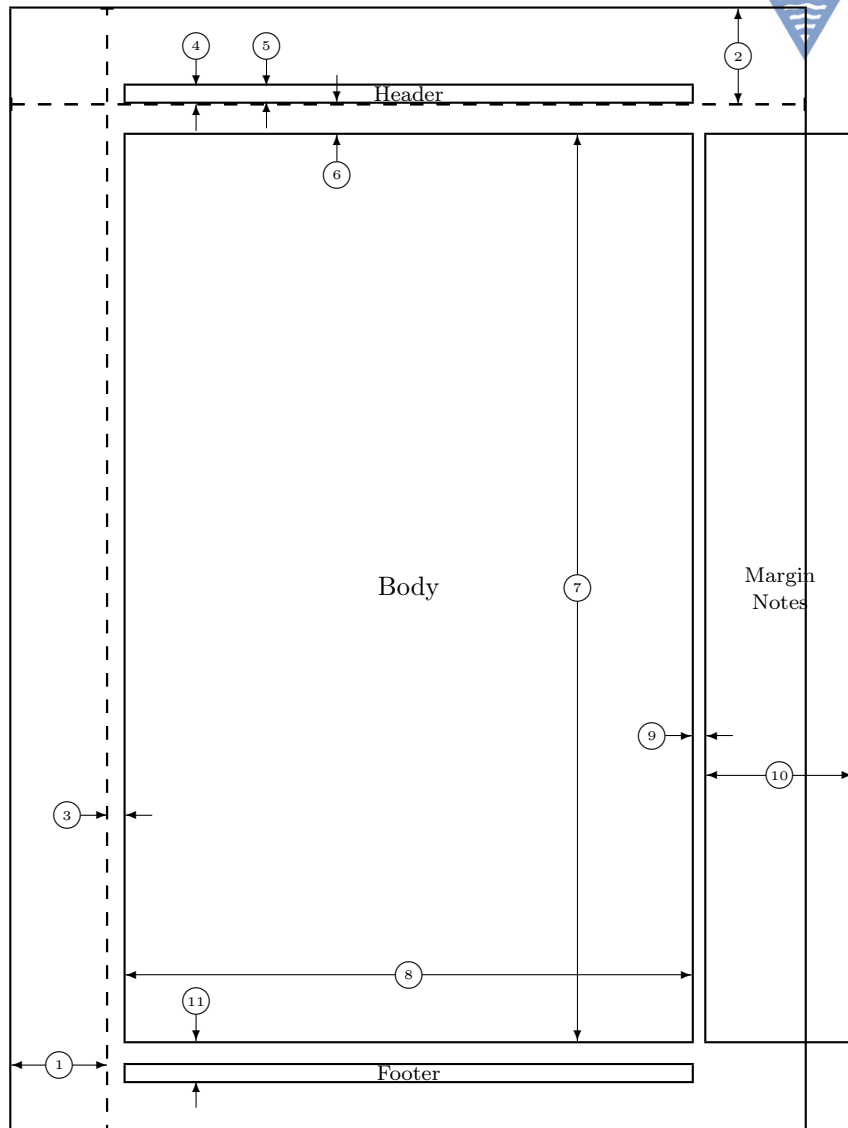
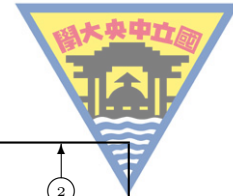


# References

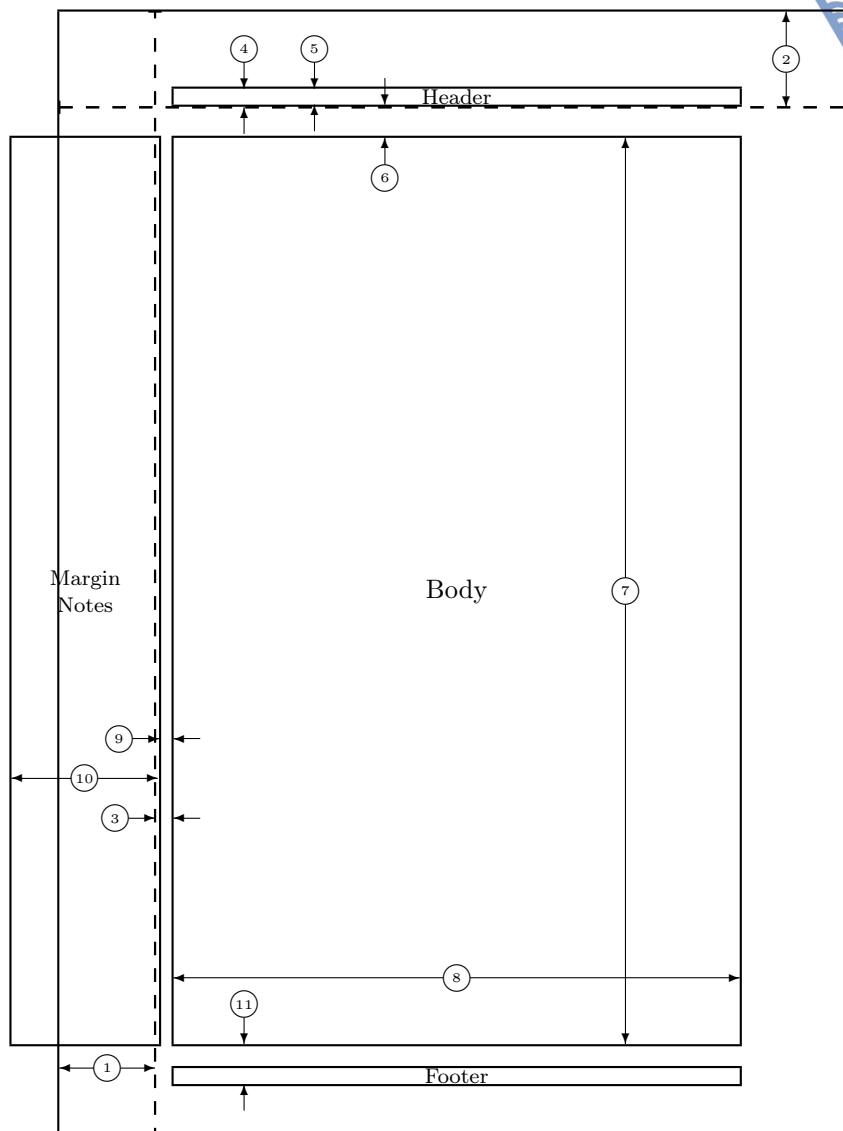
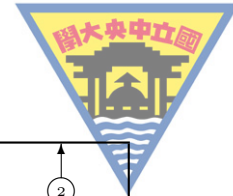
WM Grundy, DP Cruikshank, GR Gladstone, CJA Howett, TR Lauer, JR Spencer, ME Summers, MW Buie, AM Earle, K Ennico, et al. The formation of charon's red poles from seasonally cold-trapped volatiles. *Nature*, 539(7627):65–68, 2016.







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