Infrared and Vacuum Ultraviolet Spectroscopy of Interstellar Icy Mantles

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By

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> > 2020

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Dedicated to Baba, Papa, Maa & Didi

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Abstract

The dust in the interstellar medium plays a crucial role in the formation and evolution of complex molecules from simple molecular ice in the presence of energetic sources: - cosmic rays, UV photons from nearby stars. The molecular ice also exist on the surface of icy bodies in the Solar System in pure/mixture form and layered/mixed ices on the cometary nuclei. These ices are under irradiation by energetic charged particles/electron trapped in the magnetosphere of their respective planet, cosmic rays, and UV photons from the Sun. Thus, the chemical evolution of the ices in astrochemical environments is quite significant to understand the formation of molecules of life and beyond. Complex molecules and their evolution in molecular ices are being explored using observation, modelling and laboratory experiments.

The laboratory experiments are essential to interpret the observational data and provide inputs for modelling. We have performed laboratory experiments under simulated ISM/planetary body condition by growing the astrochemical ice and probing in-situ using VUV and IR spectroscopy. The IR spectroscopy is very useful to probe the morphology of the ices and also the identification of new molecules. We have discussed the VUV and IR spectroscopy experiments of pristine, layers and mixture of ices relevant to Solar System and ISM cold dust in this thesis. We have carried out VUV spectroscopy of Pluto mix (N₂: CO: CH₄: H₂O) ice analogs and Charon mix (NH₃: H₂O) ice analogs to explore the observational data of the Pluto system taken by the New Horizons mission. The VUV irradiation of SO₂ ices synthesized ozone, identified using the Hartley band, whilst comparing the broad absorption band from the Hubble Space Telescope observation of Callisto revealed the presence of ozone on the surface of Callisto.

In another experiment IR spectra of propargyl ether $(C_3H_3OC_3H_3)$, aromatic synthesizer, ice analogs attenuated the IR photons when it changes its phase from amorphous to crystalline form and there were no such attenuation was observed for the

VUV photons. Next set of experiments carried out were the VUV irradiation of aromatic (C_6H_6 and C_6H_5CN) astrochemical ices and probed using IR and VUV spectroscopy to understand the formation of complex molecules in the ice. While, VUV irradiation of organic molecular ices synthesized residue, which was left out on the substrate when the temperature of the substrate brought at ~300 K. The physical properties of the obtained residues have been analyzed using FE-SEM and HR-TEM; the results show the formation of variety of structures in residues obtained from different ice analogues. The physical nature of the residues from irradiation of benzene ice was found to have geometrical shapes, as opposed to the fluffy and random nature of ISM residues. While the residue obtained from irradiation of benzonitrile ice was observed to contain graphene sheets. This is the first synthesis of graphene in astrochemical ices irradiation. Such result will revolutionize our understanding of the ISM dust.

Keywords: Interstellar medium; Icy satellites; Astrochemistry-methods, Laboratory, Solid state techniques, Infrared spectroscopy, Vacuum Ultraviolet spectroscopy, Astrochemical dust

Abbreviations

GMRT : Giant Meterwave Radio Telescope ALMA : Atacama Large Millimeter Array JWST : James Webb Space Telescope Κ : Kelvin UV : Ultraviolet GCR : Galactic Cosmic Rays COMs : Complex Organic Molecules PAHs : Polycyclic Aromatic Hydrocarbons AGB : Asymptotic Giant Branch TMC :Taurus Molecular Clouds **KBOs** : Kuiper Belt Objects HST : Hubble Space Telescope NIMS : Near Infrared Mapping Spectrometer HR- TEM : High Resolution Transmission Electron Microscope FE-SEM : Field Emission Scanning Electron Microscope UHV : Ultra High Vacuum ISM : Interstellar Medium IR : Infrared VUV : Vacuum Ultraviolet NSRRC : National Synchrotron Radiation Research Center PRL : Physical Research Laboratory

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Chapter 1

Introduction

To-date, more than 200 molecules have been detected in the interstellar medium (ISM). These molecules are under energetic processing from cosmic particles, ultraviolet photons etc. Such energetic processing of molecules leads to the formation of complex molecules, and precursors of biomolecules. Such processing and changes taking place in the ISM are studied using observations, laboratory studies and modeling. For the last two to three decades, the observation of molecules in the interstellar medium were carried out using ground based and space based telescopes mainly at infrared wavelengths. These studies gave us an indication of the presence of a large number of molecules in the ISM. The addition of ground based observation at millimeter and submillimeter wavelengths range using telescopes such as the Nobeyama Radio Telescope, the Giant Meterwave Radio Telescope (GMRT), and the Atacama Large Millimeter Array (ALMA) etc. has enabled us to discover new molecules in the ISM, which have been predicted using a combination of experiments and models. The upcoming James Webb Space Telescope (JWST) is expected to provide exceptional information about the molecular ice in the ISM. Apart from the ISM, a plethora of molecules have also been detected on the surface of icy satellites, comets and smaller bodies in our Solar System.

1.1 Interstellar medium (ISM)

The interstellar medium is the space between the stars, and consists of ~99% gas and 1% grains with inhomogeneous composition and local particle density variations. The gas contains atomic and molecular hydrogen mainly with heavier trace elements (Table 1. 1). In the ISM, clusters composed of a mixture of gases, atomic and molecular hydrogen and small, submicron sized dust are called/known as *clouds*. Depending on the density and temperature, the interstellar clouds are classified into three different parts, diffuse clouds, translucent clouds and dense molecular clouds (Table 1. 2). The diffuse medium have very low density ~10 – 100 particles cm⁻³ and temperature of 100 – 120 K, which is characterized by atoms and ions with molecular fraction of < 0.1 as molecules can barely survive in such regions due to presence of extreme radiation. It has been a hot topic of discussion of the presence of diatomic and polyatomic molecules in diffuse clouds, which are exposed to interstellar radiation fields. Hydrogen is mainly present in the form of atoms and other atoms with lower ionization potential are fully ionized in these regions.

Element	Abundance (Absolute and relative)	
Hydrogen	93.38%	1
Helium	6.49%	0.09
Oxygen	0.064%	0.007
Carbon	0.027%	0.003
Nitrogen	0.009%	0.0009

Table 1.1: Abundance of element in ISM (Kaiser 2002, Wilson 1992).

Translucent clouds have densities of $10^2 - 10^3$ particles cm⁻³, which are surrounded by the diffuse molecular clouds, and protected from interstellar radiation. Thus the ionized carbon atoms transform to neutral atomic carbon or oxidize to form CO molecules.

Translucent clouds are least understood due to lack of observational data; the theoretical models do not agree on the chemical behaviour in this transition region.

Dense molecular clouds have densities of $10^3 - 10^6$ particles cm⁻³, temperatures of 10 – 30 K, and higher extinction than diffuse and translucent clouds due to the molecular density. The chemistry in dense molecular clouds is very different from those of diffuse clouds as the electron abundances/intense radiation is very low compared to that experienced in diffuse clouds. The reactive C ions in diffuse clouds are replaced by CO in the dense molecular clouds. Dense molecular clouds are self-gravitating, and are observed in infrared absorption and microwave emission. Most of the molecules detected in the ISM are from dense molecular clouds as OH to CO, NH₃, H₂O, and H₂CO etc. The chemistry in the ISM is driven by the radiation available there.

Table 1. 2: Molecular clouds in the ISM

Molecular Clouds	Density (cm ⁻³)	Temperature (K)
Diffuse Clouds	$10 - 10^2$	100 - 120
Translucent clouds	$10^2 - 10^3$	50 - 100
Dense Molecular Clouds	$10^2 - 10^6$	10 – 30

The molecules deep inside dense molecular clouds are protected from external UV radiation, but not from cosmic rays. Cosmic rays have sufficient energy to penetrate the clouds to interact with hydrogen and helium which are most dominant atoms present in the interior of such clouds. The cosmic ray ionizes H_2 molecules to H_2^+ and H^+ ions with branching ratios (Solmon & Werner 1971).

$$H_2$$
 + cosmic ray proton → H_2^+ + e + p (95%)
→ H^+ + H + e + p (5%)

 H_2^+ is destroyed very fast by reaction with molecular hydrogen (Bowers & Elleman 1969)

$H_2^+ + H_2 \rightarrow H_3^+ + H$

These H_2^+ , H^+ ions along with He^+ ions react with neutral species and produce secondary UV radiation, ions and electrons, which are responsible for the partial ionization and chemical reaction in the molecular clouds. The complex molecules detected in ISM, form and evolve under such irradiation from energetic sources.

1.1.1 Molecules in Space

As discussed above, the formation and evolution of molecules in the ISM are very different to that on Earth due to different extreme conditions present in the ISM. The physical condition of space dictates a very different chemistry and it is important to understand the evolution of complex molecules in space, which could lead to formation of bio-molecules responsible for the *Origin of life*. The formation routes of molecules in the ISM are studied in two different phases: gas and solid phase routes.

1.1.1.1 Gas phase chemistry

The ions-molecules reaction in the gas phase drives the chemistry of complex organics and smaller molecules. Most gas phase molecules observed in clouds can be explained by this ion -molecules chemistry. The gas phase reactions and rate constant in dense molecular clouds has been studied in detail by Herbst and Klemperer 1973.

The density of the molecular clouds vary from $10 - 10^6$ particles cm⁻³, is nearly 10^{-13} less than atmosphere of the Earth. The reactions started due to collision of the reactants; atoms/molecules with each other, which is very less probable in a low dense environment such as molecular clouds, so the reaction process/rate is very slow. The lifetime of molecular clouds are of the order of million years, (Jeffreson and Kruijssen 2018). With such large time-scales, the atom/molecules collide with each other and initiate the chemical reactions at a very slow rate. Under the very low temperature of the ISM, exothermic reactions or reactions with very low or no activation barrier are favourable. With these many restricted reaction mechanisms, the types of reactions in the ISM are limited. Three body reactions in the ISM are very rare due to the low density, in a three body reaction, the third body plays a vital role to carry away the

excess energy to prevent the product to dissociate back into its individual reactants or most probable fragments. Since, three body reactions are not very prominent in the ISM, the production of complex molecules will be very slow in the gas phase. Many models on gas phase reactions have been proposed to-date, which suggest that only gas phase reactions cannot produce the observed abundances of simple/complex molecules in the ISM (Millar et al. 1991, Garrod et al. 2008), and would require the solid phase reaction in the formation mechanism. Our focus is to understand the solid phase chemistry and desorption to gas phase to understand the complex molecule formation and evolution in ISM.

1.1.1.2 Ice phase chemistry

As discussed above, the abundance of complex molecules in the ISM cannot be explained by gas phase reactions at low temperatures (Geppert et al. 2006, Garrod et al. 2008), while considering the sublimation of ices with gas-phase chemistry models explained the abundance of molecules in the ISM (Charnley et al. 1992) which makes the solid phase chemistry very important.

The temperature of dense molecular clouds in the ISM are ~10 K, at such low temperature most of atoms, other than hydrogen and helium have sticking coefficient nearly 1, so these will stick on the cold interstellar dust grain in a single collision and form an icy mantle of sub-micron size thickness. The dust particles are carbonaceous and silicate in composition depending on the star from which the materials come, with size varying from nanometer to microns. The formation of molecules takes place on the dust grains due to diffusion and collision of the mobile atoms over the surface (Figure 1. 1). The abundant atoms in the ISM are H, He, O, C and N (Table 1. 1), so most of the primary molecules formed on the grains would constitute these atoms. Since, hydrogen is the most dominant atoms so the molecules formed from hydrogenation on the grains are also expected to be abundant such as H₂O, NH₃ and CH₄ etc. CO forms in the gas phase and condenses on the dust and CO₂ synthesize from the reaction between OH + CO (Ioppolo et al. 2011). These CO and CO₂ lead to formation of CH₃OH, H₂CO etc. on the surface. The Complex Organic Molecules

(COMs) formed in the icy mantles on dust grains in ISM and desorb thermally or nonthermally to the gas phase, which can be detected through sub-millimetre, millimetre and infrared ground based telescopic observations.



Figure 1. 1: The schematic of accretion (a), diffusion (b) and reaction (c) of atoms on the dust surface.

The interstellar ices on the dust grains in the dense molecular clouds are subjected to irradiation from UV photons from surrounding young protostars and energetic Galactic Cosmic Rays (GCRs). The flux of UV photons are 10^3 photons cm⁻² s⁻¹ with typical energy less than 13.6 eV (Prasad & Tarafdar, 1983). While the flux of cosmic rays are 10 particles cm⁻² s⁻¹ with maximum energy around 10 MeV (Strazzulla & Johnson 1991). The sub-micron dust/grain particles in the molecular clouds shield newly synthesized molecules from the energetic UV radiation field.

Water ice is the most abundant constituent of the icy mantles, with Carbon Dioxide, Carbon Monoxide, and Methanol possessing abundances of approximately 5–50% of the water ice abundance, Methane, Ammonia, and Formaldehyde are also abundant in reduced amount to that of methanol. The IR spectrum of W33A observed using Infrared Space Observatory (ISO) shows the abundance of these molecular ice (Gibb et al., 2000), and is shown in Figure 1. 2 . The number density of molecular ice with respect to water in different molecular clouds are provided in Table 1. 3.

1.1.2 Complex molecules in ISM

Organic molecules could lead to the formation of prebiotic compounds in the ISM and the chemical reactions involved in the origin of life. COMs have been observed in the
gas and solid phase in different molecular clouds. The formation of the complex molecules from simple molecules takes place at higher density and low temperature regions of the collapsing molecular clouds, and during such process, CO freeze out from the gas phase, to form a CO coating on top of water rich layers. Subsequent hydrogenation processes transform CO to H₂CO and H₂CO to CH₃OH resulting in CO ice being intimately mixed with methanol. Radical recombination processes in various starting mixtures, triggered by energetic or non-energetic sources provide pathways towards the formation of more complex molecules (Tielens and Hagen, 1982).

The rotational signature of complex organic molecules such as HCOOH (Zuckerman et al., 1971), CH₃CHO (Gottlieb, 1973), and CH₃CH₂OH (Zuckerman et al., 1975) have been observed in the ISM. The emission lines of Polycyclic Aromatic Hydrocarbons (PAHs) have been observed in interstellar regions (Tielens, 2008). The unidentified infrared emission lines at shorter wavelengths with sharp, distinct emission features in UV irradiated regions of dozens of galaxies including our own galaxy are thought to be features of PAHs. The mid-infrared emission lines in the 3 µm band, which are widely distributed in the interstellar medium are known features of the aromatic compounds. These aromatic emission bands have been observed in HII regions, reflection nebulae, planetary nebulae, AGB, active star forming regions, young stellar objects, diffuse interstellar medium, external galaxies etc. Along with emission at short wavelength, the emission in the mid IR region was reported, which are characteristics of small carbon grains with functional groups (Duley & Williams, 1981). The gas phase PAH molecules give rise to these features in mid IR as a result of vibrational relaxation on absorption of background UV photons. The Fullerene detected in the ISM from its emission in infrared region (Cami et al., 2010). Recently, Benzonitrile was detected in the Taurus Molecular Cloud (TMC) using rotational lines (McGuire et al., 2018). The schematic of chemical evolution of complex molecules from simple molecules has been shown in Figure 1. 3 and the list of molecules detected in ISM to date is given in (Table 1. 4 & Table 1. 5).



Figure 1. 2: The ISO observation of W33A containing the characteristics absorption of different molecular ices (Adopted from Gibb et al., 2000).

Sgr A* 2030 10014 14 4 \heartsuit ī $\overline{\vee}$ ī ī 2 ξ ī GL 2136 1000.3 16 13 2 ξ ī. 9 ξ ı. ī ī ī **W33A** 3.5 1001.5 0.2 15 13 1811 **~** 9 2 2 9 **GL 7009S** 1000.2 1.5 ī ï 21 ī 30 ī ī. ī. 4 $\boldsymbol{\omega}$ NGC 7538 IRS 9 10014 22 14 13 2 ∞ 2 Ś 4 \mathfrak{c} ---ı Elias 16 < 0.2 < 0.5 100 $\overset{\vee}{\omega}$ 6 > $\overline{\vee}$ 22 1818ī. ξ ī ī. CO₂ (nonpolar) CO (nonpolar) CO₂ (polar) CO₂ (total) CO (polar) Species CH₃OH HCOOH H_2CO OCS H_2O NH_3 XCN CH_4

Table 1. 3: Ice abundances (number density) toward various observed using IR spectrometer (Adopted from Gibb et al., 2000)

7 atoms	CH ₃ CHO	CH ₃ CCH	CH ₃ NH2	CH ₂ CHCN	HC ₅ N	C ₆ H	c-C ₂ H ₄ O	CH ₂ CHOH	C_6H^-	CH ₃ NCO	HC ₅ O	HOCH ₂ CN		Ľ	
6 atoms	CH ₃ OH	CH ₃ CN	NH ₂ CHO	CH ₃ SH	C_2H_4	C ₅ H	CH ₃ NC	HC ₂ CHO	H_2C_4	C_5S	$\mathrm{HC_{3}NH^{+}}$	C ₅ N	HC₄H	HC4N	c-H ₂ C ₃ O
5 atoms	HC ₃ N	НСООН	CH ₂ NH	NH ₂ CN	H_2CCO	C4H	SiH_4	$c-C_3H_2$	CH_2CN	Cs	SiC_4	H_2CCC	CH_4	HCCNC	HNCCC
4 atoms	NH ₃	H_2CO	HNCO	H_2CS	C_2H_2	C_3N	HNCS	$HOCO^{+}$	C_3O	c-C ₃ H	HCNH ⁺	H_3O+	C_3S	c-C ₃ H	HC_2N
oms	N_2O	MgCN	$\mathrm{H_{3}^{+}}$	SiCN	AINC	SiNC	HCP	CCP	AlOH	$\mathrm{H_2O^+}$	H_2Cl^+	KCN	FeCN	HO_2	TiO_2
3 at	H_2O	HCO^+	HCN	OCS	HNC	H_2S	N_2H^+	C_2H	SO_2	HCO	ONH	HCS^{+}	HOC^+	SiC_2	C_2S
toms	CP	HN	SiN	SO^+	$\rm CO^+$	HF	N_2	CF^+	PO	O_2	AlO	CN ⁻	OH^{+}	SH^+	HCl^+
2 at	CH	CN	CH^{+}	НО	CO	H_2	SiO	CS	SO	SiS	NS	C_2	NO	HCI	NaCl

Table 1. 4: Molecules in ISM (Blue is for the molecular ions) containing 2 to 7 atoms (Adopted from McGuire, 2018).

									•			P				
CH ₂ CNH	C_5N^-	HNCHCN	SiH ₃ CN	MgC_4H												
$\rm H_2COH^+$	C_4H^-	CNCHO	HNCNH	CH_3O	$\rm NH_3D^+$	H_2NCO^+	NCCNH ⁺	CH ₃ Cl	MgC ₃ N	(0		2)		
H_2CN	SiC ₃	CH ₃	C_3N^-	PH_3	HCNO	HOCN	HSCN	НООН	$1-C_3H^+$	HMgNC	HCCO	CNCN	t- HONO			
CCN	SiCSi	S_2H	HCS	HSC	NCO	CaNC	C_2N)		
C3	CO_2	CH_2	C20	MgNC	NH_2	NaCN	Si_2C		•							
HS	TiO	ArH^+	\mathbf{NS}^+	HeH ⁺	SiN	SiH	ΝΟ)	(•			5	
AICI	KCI	AIF	PN	SiC	FeO	HD	NO^+		8	8	()			

8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	≥13 atoms
CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	c-C ₆ H ₆	C ₆₀
HC(0)OCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C6H	$n-C_3H_7$	C_{70}
CH ₃ COOH	(CH ₃) ₂ O	$(CH_2OH)_2$	C ₂ H ₅ OCHO	$1-C_3H_7CN$	C_{60}^{++}
C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ OC(0)CH ₃	C ₂ H ₅ OCH ₃	c-C ₆ H ₅ CN
CH ₂ OHCHO	HC_7N	CH ₃ CHCH ₂ O		•	
1-HC ₆ H	C_8H	CH ₃ OCH ₂ OH			
CH ₂ CHCHO	$CH_3C(O)NH_2$				
CH ₂ CCHCN	C ₈ H ⁻				
H ₂ NCH ₂ CN	C_3H_6				
CH ₃ CHNH	CH ₃ CH ₂ SH)))
CH ₃ SiH ₃	CH ₃ NHCHO				
$H_2NC(O)NH_2$	HC ₇ O)		0
(NH ₂) ₂ CO				5	
		0			
	0				

Table 1. 5. Molecules containing 8 to more than 13 atoms in ISM (Adopted from McGuire, 2018).



Figure 1. 3: Schematic of simple to complex molecules and its incorporation to the planetary bodies. (Background picture of Pipe Nebula, credit – ESA, Credit for Comet, Enceladus, Titan and Earth images - https://photojournal.jpl.nasa.gov/)

1.2 Molecular Ices in the Solar System bodies

Molecular ices have been observed in abundant amounts on the Earth and other planets and their satellites, and minor bodies in the Solar System; such as icy satellites of Jupiter and Saturn, Comets and Kuiper Belt Objects (KBOs). The surface of icy satellites of Jupiter and Saturn, and the Pluto system are very low 70 – 120 K depending on the day - night cycle. Water ice is the most abundant and common ice on the surfaces of these bodies. Oxygen and oxygen bearing molecular ice; CO₂, SO₂, CO, CH₃OH ice and other CH₄, NH₃ ice etc. have been observed on these surfaces through ground based and space based telescopic observations (Carlson et al., 1999; Carlson et al., 1997; Dalton et al., 2013, Cruikshank et al., 1996). The satellites of Jupiter and Saturn orbit under the magnetosphere of their parent planet, so the surface of the satellites are under bombardments of energetic ions/electrons, charged particles trapped in the magnetosphere, cosmic rays and Solar wind, which are responsible for the chemical evolution of the satellites. The details of the ions trapped in the magnetosphere of Jupiter and Saturn along with solar winds and cosmic rays can be found in Johnson 1990. To understand the deep morphology and evolution of these planetary bodies many dedicated space missions have been launched to-date from various space organization across the world. In the very early days of space exploration via dedicated mission, the Voyager and Pioneer missions were launched. After successful completion of these mission, other missions like Galileo, Cassini and New Horizons were launched to understand the particular planetary systems. One of the important missions to explore the Solar system as well as the ISM was the space based telescope - Hubble Space Telescope, which helped the scientific community to explain the icy satellites of Jupiter and Saturn, and provided the first high resolution images of molecular clouds and star forming regions. The details of molecular ice present on the satellites, its processing and mission dedicated to it are discussed below.

1.2.1 Galilean satellites

The four largest satellites of Jupiter; Io, Europa, Ganymede and Callisto are called Galilean Moons (Figure 1. 4 (a)). The temperature of the surface of these moons are 70 K - 150 K based on their day and night cycle. In the early days, the surface characteristics of these bodies were observed using ground based telescope, later the Hubble Space Telescope (HST) and the Galileo space mission and other similar missions observed the spectra of these icy satellites at different wavelengths. Water characteristics were observed on Europa, Callisto and Ganymede (Fanale et al., 1979). Io is the volcanically active body in the Solar System. SO₂ ice was observed on Io, Europa and Callisto (Noll et al. 1997, Lane et al. 1981), and H₂O₂ was detected on the Europa (Carlson et al., 1999). The reflectance spectrum of Ganymede in the visible range identified Oxygen (O_2) and Ozone (O_3) on its surface (Spencer et al., 1995; Noll et al. 1996), while, the signature of C-H, S-H and C≡N (tholins) groups and CO₂ and SO₂ have been observed in the infrared range (McCord et al., 1997). The spectral characteristics of hydrated material (MgSO₄ and Na₂SO₄) along with other molecular characteristics such as water ice on the Galilean satellites have been observed and reported using the Near Infrared Mapping Spectrometer (NIMS) onboard the Galileo Mission (McCord et al., 2001). Water ice present on three outermost satellites of Jupiter are crystalline and amorphous in different ratio due to thermal energy and energetic particle bombardments (Hansen & McCord, 2004).

1.2.2 Saturn's satellites

Titan, the Saturnian satellite with an atmosphere, is also known to harbour molecular ices along with hydrocarbons, CO₂ ice deposits and their distribution has been reported on the surface of Titan (Hartung et al., 2006). Along with the molecular ice, fluvial activities based on liquid methane observations using the RADAR instrument onboard Cassini (Elachi et al., 2005) have been seen on the Titan's surface. Methane and Ethane lakes are present on the surface of Titan (Stofan et al., 2007) due to a liquid hydrological cycle between the surface and the atmosphere (Tokano et al., 2006). The signatures of different hydrocarbons along with Ethane and Methane in the form of

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solution have been reported on the surface of Titan (Brown et al., 2008). Hundreds of lakes of liquid hydrocarbons have been observed on this moon's surface by the Cassini spacecraft. Phoebe is the outermost large satellite of Saturn, thought to be gravitationally captured by Saturn. The water ice, CO₂ ice organics, nitriles, and cyanide compounds were mapped on Phoebe with the Cassini (Clark et al. 2005), which makes phoebe most compositionally diverse body in the Solar System. The absorption band of CO₂ was observed on Saturn's external satellites Hyperion, Iapetus and Phoebe (Filacchione et al., 2007). The signature of C-H stretching (3.53 µm) has been reported in the infrared spectra of Enceladus (Brown et al., 2006), which is described as short chain organics, while Newman et al., 2007 reported this signature as the hydrogen peroxide. Another group Hodyss et al., 2009 reported the 3.53 µm as methanol signature based on the laboratory experiments performed on methanol ice under astronomical conditions. The Cassini observed South pole of Enceladus as geologically active; jets of fine icy particles mostly water vapors vent from the subsurface of the satellite (Porco et al., 2006). The mass of the plums ejected are high mass organic cations suggesting the organics beneath the subsurface (Postberg et al., 2018).

The tenuous oxygen and CO_2 atmosphere on Rhea (Teolis et al., 2010), while Noll et al., 1997 reported the ozone on the surface of Dione and Rhea, which are mostly dominated by water ice. The image of Saturn's satellites Titan, Rhea, Dione and Enceladus is shown in Figure 1. 4 (b)).



Figure 1. 4: (a) From left to right: Galilean satellites - Ganymede, Callsito, Io, Europa (b) Saturn's satellites - Titan, Dione, Rhea and Enceladus (Credit -https://photojournal.jpl.nasa.gov/)

1.2.3 The Pluto System and Kuiper Belt Objects (KBOs)

The mission launched dedicated to explore the icy worlds; the Pluto system and KBOs (Figure 1. 5) is "New Horizons", launched in 2006, is still returning data from its scientific payloads onboard. Before the New Horizons encounter, the chemical composition of Pluto and Charon were known to be dominated by the N₂, CH₄, CO and NH₄OH ices, respectively. The flyby of New Horizons confirmed water to be present on Pluto and crystalline water and pure ammonia to exist on Charon (Brown & Calvin, 2000; Grundy et al., 2016). The geological features and activities of the molecular ices on the surface of Charon has been reported by Moore et al., 2016. The characteristic spectra of these ices have been measured by the Ultraviolet Imaging Spectrograph, P-Alice, in the 50 - 180 nm region (Stern et al., 2008). There were no experimental data available, early in the current decade to explore the observational spectra taken with P-Alice in 50 – 180 nm band. Based on which we have carried out VUV spectroscopy of Pluto and Charon mix ice analogs to understand composition and morphology of the Pluto system and KBOs. The list of molecular ice detected, so far, on these icy bodies are given in Table 1. 6.



Figure 1. 5: Pluto and Charon, image taken by New Horizons. (Credithttps://photojournal.jpl.nasa.gov/)

Apart from these icy bodies water ice has been observed in the permanently shadow region of the North pole of Mercury (Lawrence et al., 2013) and water and CO₂ ice have been observed on the poles of Mars (Kieffer et al., 1976, Phillips et al., 2011).

1.2.4 Comets

Comets are icy bodies, some of which may originate in the Kuiper Belt and are known as KBOs, while other may originate in the Oort cloud in the outer Solar System. They are typically few kilometers in diameter. The compositions of comets are believed to be most primitive molecular ices, least modifies after the formation of the Solar system, and are comparable to the composition of interstellar ice. The composition of comets can be explored using observations of the vapour trails it leaves behind when surface ice sublimate as comets approaches the Sun.

The compositions of cometary nuclei are mainly water ice mixed with simple molecules NH₃, CH₄, CO₂, and CO etc to a variety of complex organic molecules CH₃OH, HCOOH, HCOOCH₃ etc (Ehrenfreund and Charnley 2000, Bird et al. 1997 (a), 1997 (b)). The image of comet 67 P/CG is shown in Figure 1. 6.



Figure 1. 6 : Comet 67 P/CG, image taken by Rosetta mission. (Credit - ESA)

Table 1. 6: Molecular ice on the surface of icy bodies in Solar System. (Dalton, 2010, Hudson and Moore, 2001)

Planet Satel	lite Ices
Jupiter	Molecular ices
Io	SO ₂ , H ₂ O, H ₂ S
Europa	H_2O , SO_2 , CO_2 , H_2O_2 , H_2SO_2 , $MgSO_2$, and Na_2SO_2
Ganymede	H ₂ O, SO ₂ , CO ₂ , O ₂ , O ₂
Callisto	H ₂ O, SO ₂ , CO ₂ , O ₂ , Silicates
Saturn	
Enceladus	H ₂ O, CO, NH ₃ , NH ₃ .H ₂ O, H ₂ O ₂ , CH ₃ OH
Tethys	H ₂ O, CO, NH ₃ .H ₂ O
Dione	H ₂ O, CO ₂ , O ₃
Rhea	H ₂ O,CO ₂ , O ₃ , CH ₄
Hyperion	H ₂ O, CO ₂
Iapetus	H ₂ O, CO ₂ , NH ₃ .H ₂ O
Phoebe	H ₂ O, CO ₂ , HC ₃ N
Titan	H ₂ O, CO, CO ₂ , CH ₄ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₈ , HCN, HC ₃ N, C ₄ H ₂ , C ₂ N ₂ , C ₃ H ₄ , C ₆ H ₆
Uranus	
Miranda	H ₂ O, NH ₃ , hydrate
Ariel Umbriel Titania Oberon	H ₂ O, CO ₂

 Neptune

 Triton
 N2, CH4, CO, CO2, H2O

 Pluto
 N2, CH4, CO, H2O

 Charon
 H2O, N2, NH3.H2O

1.3 Chemistry in ice and laboratory experiments

As discussed above, the chemical evolution in molecular ice takes place in the presence of energetic sources; UV photons from the Sun, cosmic rays etc. Energetic irradiation on ice can lead to the dissociation of the molecules and it turn lead to chemical reactions. The chemical reactions in the ice phase are different to that of the gas phase due to less number of collision lead to an increase in life time of atoms or radicals produced via the reaction. The produced radicals/atoms with sufficient kinetic energies are called suprathermal atoms, which are responsible for the production of new molecules via collisions with surrounding atoms/molecules. The warm up of the ice also increases the reaction rate due to the increased mobility of atoms. These type of chemistry occurs on the surface of icy satellites as well as in the ISM.

The chemical evolution of molecular ice in the presence of an energetic source can be explored in the laboratory by simulating the physical conditions of the ISM/planetary bodies. Though, the vacuum attainable in the laboratory is not similar to that of the ISM, but the bulk amount of the ice and reduce the effect of contamination. The details of the set-up along with the source for irradiation has been discussed in the experimental chapter (3). We have used infrared and vacuum ultraviolet spectroscopy to probe the chemical characteristic of pure and mixture of ices as well the chemical changes induced by irradiation. The basic of the spectroscopy can be found in chapter (2). These experimental data can be used to explore the observational data and provide various inputs for modelling.

1.4 Thesis motivation and objective

1.4.1 Ozone on the planetary bodies and in ISM

Oxygen is the third most abundant element in the ISM after Hydrogen and Helium. Molecular oxygen is substantial and abundant in molecular clouds and its chemistry is essential to the ISM being a source of prebiotic chemistry that underpins the development of life. Being homo-diatomic, it is difficult to observe the infrared characteristic of pure oxygen directly. However, the presence and abundance of the homo-diatomic molecules can be observed indirectly. Ozone, an allotrope of oxygen, is a biomarker, which could be an important tracer molecule for biological activities on the planetary bodies or in the ISM, thus, ozone formation in molecular clouds and the planetary bodies are a hot topic of discussion currently. The search of ozone in the ISM is very difficult in the infrared range, as the characteristic band of the ozone overlaps with the characteristic bands of silicates. In the ultraviolet range it has a unique absorption band centered at 260 nm known as the Hartley band. Ozone has been observed in the atmosphere of Earth, and Venus (Montemessin et al., 2011) and Mars (Montemessin and Lefevre, 2013). Solid ozone has been detected on the surface of three icy satellites of Jupiter and Saturn; Ganymede, Dione and Rhea (Noll et al., 1996; Noll et al., 1997). The ozone on these surfaces are thought to be present due to irradiation of the charged particles on the water ice present on these surfaces. The ozone ice could be present on the other bodies and the ISM also but the characteristic bands of ozone in infrared overlap with the silica band, which are abundant in the ISM or planetary bodies. The precursor of ozone on the earth is oxygen, while other molecules bearing oxygen could be a source of ozone on the planetary bodies or in the ISM. The presence of the molecular oxygen in interstellar clouds was first confirmed by observation in the millimeter wavelength range (Larsson et al., 2007). Later it was detected in many of the molecular clouds, though the molecules in the clouds are subjected to different types of the energetic irradiation and presence of ozone in these regions is predicted and most probable but it has not been confirmed to-date.

Many laboratory experiments have been carried out on irradiation of Oxygen and Oxygen bearing molecular ice to synthesize Ozone. The experiments have been designed to probe at different wavelength ranges to find the unique characteristics of ozone (Sivaraman et al., 2014; Sivaraman et al., 2007; Teolis et al. 2006, Bennett & Kaiser, 2005, Teolis et al., 2005; Bahr et al., 2001).

Water, CO_2 , O_2 and SO_2 , are the most dominant molecular ice on the surface of Galilean satellites. These molecules could be responsible for ozone formation on the surface of Ganymede, though ozone could be present on other satellites too. SO_2 may be the potential candidates for ozone synthesization and UV characteristic of SO_2 overlap with the Hartley band, which can be noticed in the observational spectra of Callisto. This objective motivated us to performed photo irradiation on the SO_2 ice. The details of the experiments and result has been given in Chapter (4).

1.4.2 VUV spectroscopy of Pluto and Charon ice analogs

In the early days of the New Horizons Mission, there were no vacuum ultraviolet photoabsorption spectra of ice analogues of Pluto and Charon ice mixtures were available to compare with the returned data of the P-Alice payload of New Horizons. So, we have carried out VUV spectroscopy on Pluto mixed anologs (N₂, CO, CH₄) and mixed with water. For Charon, spectra of NH₃ and H₂O both mixed and layered along with NH₄OH have been carried out. These spectra may help to interpret the P-Alice data obtained from New Horizons. The details have been discussed in chapter (5).

1.4.3 Phases of molecular ice in the ISM

The temperature is very low (T \sim 10 K) in dense molecular clouds and ice formed at such low temperature are amorphous in structure. This has been supported by laboratory experiments (Sivaraman et al., 2007, Rahul et al., 2020). The porosity in amorphous ice traps for atoms/radicals, increases the chemical reactivity of the ice, thus the morphology of ice plays important role in chemical evolution. The energy from the external source allows molecules to reorient themselves to form crystalline

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structures, as thermal heating is the main reason for amorphous to crystalline phase changes in ices. Irradiation of energetic particles also changes the structure of ices both from amorphous to crystalline and crystalline to amorphous depending on the temperature of the molecular ice during the irradiation.

The infrared spectroscopy is a best tool to understand the morphology of ices, which is very sensitive to conformational changes in the ice during its warmup. The change in the structure of ice has been monitored using electron diffraction pattern (Kouchi et al., 1990). To-date, many experiments have been carried out to explore the change in structure of ice as a function of temperature (Dawes et al., 2007; Sivaraman et al., 2007; Sivaraman et al., 2007; Sivaraman et al., 2013; Hama et al., 2017; Hudson et al., 2018) and irradiation of UV photons (Kouchi et al., 1990) charged particles (Strazzulla et al., 1992; Moore and Hudson 1992; Barrata et al., 1994; Hansen & McCord, 2004; Leto et al., 2005; Mastrapa & Brown, 2006). The amorphous and crystalline structure of ice present on the surface of Europa, Callisto and Ganymede has been explored using experiments along with the observational data.

As discussed above, the molecules in the ISM and on the surface of satellites in the Solar System could have different lattice structures depending on the surrounding physical conditions. In another way, the structure/phase of molecular ice tells one about the thermal history of the surrounding. Since, the ice deposited at low temperatures (<10 K) have an amorphous lattice structure, the increase in temperature turns the ice crystalline, and further increase of thermal energy of the ices lead to sublimation of molecules from ice. But recently, for the first time, a molecule; Ethanethiol/Ethyl Mercaptan, detected in the ISM (Kolesnikova et al., 2014) does not follow this phase transition route as most of the molecules do; amorphous \rightarrow Crystalline \rightarrow sublimation. Pavithraa et al., 2017 have reported the reversible phase changes of Ethanethiol; amorphous \rightarrow crystalline \rightarrow amorphous. Later, (Hudson, 2017) reported the same changes in ethanol ice. So, there could be more molecules which have such characteristics.

While performing experiments to understand such properties of molecular ice we have performed experiments on propargyl ether ice, an isomer of phenol, tentatively detected in the ISM (Kolesnikova et al., 2013). The IR spectra of molecules with respect to temperature showed unexpected behavior when it changed its phase to crystalline from amorphous. The crystalline propargyl ether ice is found to blocks/attenuates the infrared beam. The details about this have been discussed in Chapter 6.

1.4.4 Dust/Refractory materials in ISM/Planetary bodies

Dust in the ISM is known to be chemical factories responsible for the evolution of complex molecules from simpler molecules. Observations of dust in the ISM was confirmed from extinction and infrared features. The dust particles are formed mostly in the circumstellar regions of stars and ejected into the ISM. Signatures of carbonaceous materials have been observed in different regions of the ISM and on the primitive surfaces of Solar System bodies; comets, asteroids and meteorites (Henning and Salama, 1998; Ehrenfreund & Charnley, 2000). The composition of dust are silicate and carbonaceous/complex organic of different materials with similar chemical functional groups. The signature of C-H stretching has been observed in the protoplanetary nebula and several extragalactic sources (Lequeux & Jourdain, 1990, Bridger et al., 1993) along with the infrared emissions in mid- IR known as aromatic infrared bands (AIBs), corresponding to Polycyclic Aromatic Hydrocarbons (PAHs) (Leger & Puget 1984, Tielens, 2008). Based on these signature the composition of dust are thought to be mixture of aromatic and aliphatic hydrocarbons (Pino et al., 2008; Carpentier et al., 2012). Cami et al., 2010 confirm the presence of C₆₀ in the ISM, C₆₀ or small PAHs could be the product of dust grains via top- down chemistry (Berne & Tielens, 2012). Or the complex organics/large PAHs or C_{60} could be a product of small PAHs reactions via bottom-up chemistry (Kroto et al., 1985; Merino et al., 2014).

Many experiments have been carried out to understand the formation of residue/dust analogs (1) irradiation on simple organic (Foti et al., 1984; Calcagno et al., 1985) (2) irradiation on inorganic (Moore et al., 2007; Sicilia et al., 2012) molecular ices (pure and mixture of ices).

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The residue from proton irradiated methane ice were micrometer sized polymer of carbon like materials (Calcagno et al., 1985). The transmission electron microscope (TEM) image of the residue showed its amorphous characteristics, viz a fluffy layers and large voids. While, the irradiation on solid Benzene produces the residue, whose composition is polycyclic compounds (Callahan et al., 2013). There is not much work done to date to understand the physical properties of the residue obtained from the irradiation of ices.

Thus, we have carried out photo-irradiation on the basic unit of PAHs; viz pure Benzene and Benzonitrile astrochemical ice analogues to understand the evolution of complex organic residues and their physical properties. The details of the experiments and the results obtained have been discussed in chapter 7 and 8.

The Conclusion and future plan has been discussed in Chapter 9.

Chapter 2

Molecular Spectroscopy and Energetic Processing

2.1 Molecular Spectroscopy

Spectroscopy provide an excellent way to understand the various energy levels of atoms and molecules. Electromagnetic radiation passing through a sample gives rise to spectral lines/bands, that are the characteristic of the sample. Electromagnetic radiation passing through the sample increases rotational, vibrational and electronic energy of a molecule, which are analysed from the spectrum (characteristics of radiation) recorded. The electronic transition/excitation are caused by UV/Visible electromagnetic radiation, while the vibrational and rotational excitation in the sample are caused by infrared and microwave radiation. The spectroscopic technique used are discussed below.

2.1.1 The electromagnetic radiation

When atoms and molecules emit/absorb electromagnetic radiation, they change from one energy state to another. The emission or absorption of electromagnetic radiation takes place in form of quantized packet of photons. For the two energy level of a molecules/atoms, E_1 and E_2 , the difference between the two energy level is equal to the energy of absorbed or emitted photons.



If the emitted photon has frequency υ then,

$$h\upsilon = E_2 - E_1$$

where, h is the Planck constant ($6.624 \times 10^{-34} \text{J s}$).

The linear difference between two maxima or minima of the wave is wavelength, λ . The product of frequency and wavelength is the velocity, c of the electromagnetic radiation.

$$c = \lambda \upsilon$$

The velocity of electromagnetic radiation in vacuum is 2.998×10^{10} cm s⁻¹.

The energy level of electromagnetic spectrum has wide range from X-rays ultraviolet - visible - infrared - microwave to radio waves as picturised below (Figure 2. 1).

The interaction of electromagnetic radiation with atoms/molecules changes its energy level. The interacted photons can characterize the internal properties of the atoms/molecules; such a study of atoms/molecules is called spectroscopy. The interaction of ultraviolet and infrared photons with atoms/molecules causes change



Figure 2. 1: The electromagnetic spectrum. IR – infrared; UV- ultraviolet, Hz-Hertz (Adopted from Struve 1989; John Wiley & Sons)

in the electron distribution and this change of configuration for a molecule is known as ultraviolet/electronic excitation and infrared/vibrational spectroscopy respectively. The configuration of molecules changes due to the change in dipole moment of molecules induced by absorption of infrared radiation. The basic about the vibrational and electronic excitation spectroscopy is discussed in next section.

2.1.2 Molecular vibrations

A atoms in stable molecules vibrates about their equilibrium position. At the minimum energy of molecule, the internuclear separation between the nuclei is r_{eq} , or simply known as bond length. The compression and extension of the bonds about the equilibrium is similar to a spring, which will follow the Hook's law. So, the restoring force will be,

 $f = -k (r - r_{eq})$

Where, k is force constant, r is internuclear distance. So, the potential energy curve of the molecule is parabolic and has the form

$$V = \frac{1}{2} k (r - r_{eq})^2$$

So, the vibration of the molecule is Harmonic oscillator. If the frequency of the oscillator ω_0 and the reduced mass of the molecule is μ . Where for two different mass m_1 and m_2

The reduced mass $\mu = \frac{m1m2}{m1+m2}$

So, the frequency of the oscillator $\omega_0 = \sqrt{\frac{k}{\mu}} \text{ rad s}^{-1}$, or $\upsilon_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz}$

where, $\omega_0 = 2\pi \upsilon_0$, to change the units of frequency from hertz to cm⁻¹, the frequency υ_0 divided by velocity of light;

$$\dot{\upsilon}_0 = = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \ \mathrm{cm}^{-1}$$

Vibrational energies are quantized similar to other energy of the molecules and can be calculated from the Schrodinger equation.

For the simple harmonic oscillator, it is very well known.

$$\mathbf{E} = (\mathbf{v} + \frac{1}{2}) \hbar \omega_0$$

v, is vibrational quantum number (0, 1, 2, 3....).

For lowest quantum number v = 0, the energy $E = \frac{1}{2} \hbar \omega_0$.

Which shows that molecules never have zero vibrational energy. Thus, the atomic nuclei in the molecules are always under motions. The further use of Schrodinger equation gives us the simple selection rules for simple harmonic oscillator that undergo vibrational change

$$\Delta v = \pm 1$$



Internuclear distance

Figure 2. 2: The schematic of the harmonic oscillator (CO molecule is in the background).

This selection rule imposes that for a vibrational transition to take place for a molecule, the change in electric dipole moment must occur during vibration when it absorbs the infrared photons. The change in dipole moment happens if the bond expands and contracts. Hence, homo-nuclear diatomic molecule will not show the vibrational spectra, such molecules are called IR inactive. Rotation of the molecule is possible, but our primary focus for the thesis is the molecular ices and rotations are not likely possible in the ice phase as all molecular rotations are hindered.

Though, the harmonic oscillation is not a true representation of real molecular vibration. The bonds are not homogeneous to obey the Hooke's law. The dissociation of molecules happens when the stretching of atoms is larger than a certain amount, where the consideration of harmonic vibration fails. Thus at higher vibrational excitation/stretching, the potential curve deviates from harmonic oscillation curve (Figure 2. 2), where the restoring force is not proportional to the displacement of atoms from equilibrium positions.

The empirical formula to fit the potential curve with good approximation was derived from Morse function (Figure 2. 3).

$$V = D_{eq} [1 - exp\{a(r_{eq} - r)\}]^2$$

'a' is constant for a particular molecule and D_{eq} is the dissociation energy.

$$a = \sqrt{\frac{k}{2Deq}}$$

The energy level of anharmonic oscillator estimated from Schrodinger equation are

$$E = \hbar\omega \left[(\nu + \frac{1}{2}) - \chi_e (\nu + \frac{1}{2})^2 \right]$$
 Joules

Where χ_e is anharmonicity constant for particular molecules ($\chi_e \ll 1$).

$$\chi_{\rm e} = \frac{\hbar\omega}{4Deq}$$

The zero point energy at v = 0 is

$$\mathbf{E} = \hbar \omega_0 \left\{ 1 - \frac{1}{2} \chi_e \right\}$$
 Joules

Which suggest the anharmonic oscillator is slightly different from harmonic oscillator and the selection rules of anharmonic oscillator are $\Delta v = \pm 1, \pm 2, \pm 3, ...$

 $\Delta v = \pm 1$ transition is known as fundamental vibration with highest intensity in the infrared spectra. The transition $\Delta v > 1$ are overtones and have reduce intensity with increase separation (Figure 2. 4). While the combination bands occurs when two fundamental bands absorb the infrared photons simultaneously.



Figure 2. 3: Anharmonic oscillator (black) and harmonic oscillator (orange) with vibrational quantum numbers (v).

Since a diatomic molecule has one degree of freedom to vibrate, but in a polyatomic molecule with N possess 3N degrees of freedom in a three co-ordinate coordinates per atoms. These degree of freedom are related to translational, rotational and vibrational motion of molecules in three dimension space. In case of linear molecules, there is no rotation along the bond axis, so two degree of rotational



Figure 2. 4: Fundamental ($\Delta v = 1$) (a) and overtone ($\Delta v > 1$) (b) of infrared bands.

motion combined with three degrees of translational motion are taken away from degrees of freedoms, thus 3N - 5 degrees of freedom for vibrational motion of a linear molecule. In case of non-linear molecules, three degrees of freedom for rotational motion and three degrees of freedom for translational motion are taken away so, 3N - 6 degrees of motion for the vibrational motion of a non-linear molecule (Figure 2. 5). These vibrational motion are known as fundamental modes or normal mode,



Figure 2. 5: Structure of nonlinear (water molecule) and linear molecule (CO₂).

where all the atoms are in phase with same frequency. The overtone mode occurs due to anharmonicity. The fundamental vibrational modes water and CO_2 molecules are shown in Figure (2. 6 & 2. 7).



Figure 2. 6: The fundamental vibrations of CO₂ molecules.



Figure 2. 7: The fundamental vibrations of water molecules.

2.1.3 Infrared spectroscopy

The vibrational characteristics of the molecules can be probed using infrared spectroscopy. Molecular vibrations are excited by infrared radiation depending on the change in the dipole moments of the molecules; $d\mu/dR$. Most molecules have a permanent dipole moment due to charge imbalance in the molecule, since different atoms in molecules attract electrons differently. The homo-nuclear diatomic molecules do not have dipole moments, such as molecular oxygen (O₂), and larger molecules that are symmetric, e.g. carbon dioxide or O-C-O. CO₂ has dipoleallowed infrared absorption features, since $d\mu/dR \neq 0$ during some vibrations. Each molecule has molecular vibrations at specific frequencies depending on the strength of the vibrating bond. In solids, interactions of molecules with surrounding molecules modify these bond strengths, which results in a range of overlapping frequencies for one type of molecular vibration. For example, H₂O symmetric stretch vibrates at a frequency of 3657 cm⁻¹ (2.7 μ m) in a vapour, and at 3000-3600 cm⁻¹ (2.8–3.3 μ m) in an amorphous ice, which changes when H₂O ice is in a mixture of the molecular ices. Organic molecules with fundamental vibration of the functional group differentiate the types of organic molecules. The stretching, twisting, banding and wagging etc. of the bonds in the molecules describe the molecular characteristics. The infrared spectroscopy is performed using Fourier Transform Infrared (FTIR) spectrometer.

Fourier transform infrared (FTIR) spectrometer has an incandescent source of light to emit a bright beam in the IR wavelength range. A half-silvered mirror reflects 50% of the incident beam toward a fixed mirror and remaining 50% towards the movable mirror (Figure 2. 8). The beams reflected from two mirrors recombine and then goes to the detector. The two beams arrive at the detector simultaneously with different optical paths: depending on the differences of optical paths of two beams, a pattern of constructive or destructive interference will therefore be created, which later converted into a signal (containing all the infrared frequency encoded in it) at the detector. The signal detected is proportional to the difference in the optical path of the two beams and to the position of movable mirror during analysis. The detected signal is then decoded using mathematical technique Fourier transformation, which provides the spectral information of the sample.

The source in the FTIR spectrometer (model - is10) is ETC EverGlo; a ceramic material, which is thermally insulated and fast operational, This source emit electromagnetic radiation in the range 4000 - 500 cm⁻¹ better than other water cooled and air cooled infrared sources. The stability of the source in 3200 - 2600 cm⁻¹ in the absorbance term is ± 0.001 for 8 hrs average. Though the spectral range of the source is 7400 - 50 cm⁻¹ we use 4000 - 500 cm⁻¹ as per requirement and spectrometer limitations (beam-splitter, windows and detector). The detector we use is deuterated triglycine sulfate (DTGS), which has spectral resolution better than 0.4 cm⁻¹.

The FTIR spectrometer has advantages over the dispersive spectroscopy as FTIR is based on non-destructive technique. The data collection speed is much better as it measure all the infrared frequencies simultaneously, and has better sensitivities as it adds many scans thereby cancelling out the random noises.



Figure 2. 8: Schematic of interferometer of FTIR spectrometer.

2.1.4 Electronic excitation and VUV/UV spectroscopy

The interaction of UV photons with atoms/molecules excite an electron from its ground state to higher electronic states, known as electronic excitation of atoms/molecules. For an electron to be excited to higher state in the molecules, there is a principle called Franck – Condon principle, which states that electronic transitions occur only in vertical lines along a fixed intenuclear separation, faster ($\sim 10^{-15}$ s) than time taken for nuclei (10^{-13} s) to respond, which means nuclei of vibrating molecules does not change its internuclear distance during the transition. This implies that the most probable transition takes place is that from the centre of the lowest vibrational level to the excited state. The electronic transition from vibrational ground state to excited state is shown in Figure 2. 9.



Figure 2. 9: The electronic transition from vibrational ground state to excited state according to Franck- Condon principle (Adopted from Banwell, 1983).

2.1.4.1 Selection Rules

The selection rules for the electronic transitions in the molecules (the state of molecules ${}^{2S+1}\Lambda_{g/u}{}^{+/-}$) are;

- (1) The change in orbital angular momentum $\Delta \Lambda = 0, \pm 1$.
- (2) The total spin momentum of the molecule remains unchanged $\Delta S = 0$
- (3) The change in total momentum $\Delta \Omega = 0, \pm 1$
- (4) The symmetry in diatomic molecules are allowed $\Sigma^+ \leftrightarrow \Sigma^+$, $\Sigma^- \leftrightarrow \Sigma^-$, $\Sigma^+ \nleftrightarrow \Sigma^-$
- (5) For homonuclear diatomic, the change is parity of molecular orbital is needed $g \leftrightarrow u$, $g \not\leftrightarrow u$, $u \not\leftrightarrow u$.

The electronic transition in a molecule can lead to its dissociation when the transition of an electron takes place from the vibrational ground state to an upper state with greater equilibrium internuclear separation (Figure 2. 10(a)). Or transition to upper state, which is unstable i.e. no minimum in the potential curve. This transition would also lead to dissociation into products with excitation energy E_{ext} (Figure 2. 10(b)).



Figure 2. 10: The dissociation of molecules in (a) stable excited state, where D''₀ is dissociation energy of ground state and D'₀ is dissociation energy of excited state, E _{ex} is excitation energy of products (b) unstable state, where E _{kinetic} is kinetic energy of products (Adopted from Banwell, 1983).

The change in electronic transition is followed by the vibrational and rotational transition, which does not appear in the electronic spectra of the molecular ice. The molecules possess two types of electronic excitations; valence transition and Rydberg transition, which takes place when an electron moves to higher energy orbital. In a valence transition, an electron excited to the valence orbital while in a

Rydberg transition, the electron moves up to a higher quantum number orbital. Both these transitions do not have significant difference in case of molecular gas but for the molecular ice (which is our target), the internuclear separation are small, so the Rydberg states are effected, which results in the broadening of vibrational fine structure with a small blue shift, or extinction of the Rydberg excitation from the electronic spectrum of the ice.

We are interested in VUV spectroscopy of molecular ice at very low temperature (4 K - 200 K). At such low temperature molecules in the ice are amorphous and show broad absorption spectra. The molecules in amorphous ice have random orientation with no rotational properties, while the vibrational excitations with slightly different energies help to overall broadening effect in the vibrational fine structure. While in crystalline ice, molecules have fixed orientation does not contribute in the broadening of the vibrational fine structure.

2.1.5 VUV/UV spectroscopy

The vacuum ultraviolet (VUV) absorption spectroscopy of the molecules are performed using dispersive methods. The VUV spectrometer consists of a VUV light source, a monochromator, entrance and exit slits, a sample compartment and a detector. The VUV beam from the source (we use synchrotron as source) passes through the entrance slit, which narrow the beam and fall on the grating in the monochromator. The grating disperse the polychromatic light and the desired wavelength are selected by changing the slit position. Then the beam of chosen wavelength passes though the sample and is recorded at the detector. The schematic of VUV spectrometer is shown in Figure 2. 11. In our experiments we have used two different reflection gratings sitting in the monochromator to cover 109 - 320 nm wavelength range; one, 600 l/mm covers the range 109 - 250 nm and the second, 450 l/mm covers the range 240 - 320 nm. LiF and CaF₂ windows are used as transmitting windows to pass the light to the detector. The detector used are photomultiplier tube (Hamamatsu R943-02) in photon counting mode. The spectral resolution is limited by the scan steps chosen during the scan.


Figure 2. 11: Schematic of dispersive VUV spectrometer set-up.

Our aim for the thesis is to investigate the formation and evolution of the molecular ice under astrochemical conditions. The details of formation of molecular ice and the processing have been discussed in upcoming section and chapters.

2.1.6 Beer Lambert's Law

To determine the absorbance of ices, the intensity of the beam recorded without depositing the ices (I_0) and after the ice deposition (I). Then, the Beer-Lambert law is used to calculate the absorbance of the ice in the recorded wavelength range.

 $I = I_0 e^{-\alpha}$

Where, α is the absorbance of the deposited ice. The cross-section of the molecular ice is a function of wavelength/photon-energy and can be calculated from the absorbance value, if the thickness and density of the sample is known and vice versa. Absorbance (α) is dependent on cross-section (σ), density of the molecular ice (n) and the thickness of the molecular ice (l).

 $\alpha = nl\sigma$

Determining the cross-section of any processed sample is very difficult due to changes in physical and chemical characteristics of the pure sample. The irradiation of the molecular ice break bonds and form new bonds; new molecules, changes structures and the optical properties of the irradiated ices.

2.2 Structure of molecular ice

In the interstellar medium, the molecules/atoms colliding with dust at very low temperature ~10 K stick to it, and form molecular ice on its surface. Molecular ices are present on the surface of satellites in the outer Solar System and on dust particles in cometary nuclei in layered/mixed form. The molecular ice could be present having different structure; amorphous (as pure, mixed and layered) or crystalline structure depending on the physical condition of the surrounding (Figure 2. 12). The morphology of the ice present in ISM or planetary bodies can be understood from the observational spectra compared with laboratory spectra of the molecules performed under recreated astrochemical conditions.



Figure 2. 12: Different kind of ices present in ISM/surface of icy bodies in ISM.

The morphology of the ice plays an important role in chemical evolution in the ISM and explain the history of energetic processing. Many experiments have been reported to-date to understand the morphology of molecular ice in ISM/surface of icy bodies in the Solar System (Mason et al., 2006; Dawes et al., 2007; Pavithraa et al., 2017). The experiments have explained that the structure of the molecular ice depends on the temperature and the rate of deposition of molecules on the dust. The molecules deposited at 10 K mostly have random orientation and structure are called amorphous. The thermal energy given to the amorphous ice will allow molecules to re-orient themselves to an ordered structure, known as crystalline structure (Figure 2. 13). Infrared spectroscopy is best tool to understand the change in morphology of ices, Sivaraman et al., 2013 reported the phase change in formamide ice deposited at 10 K (amorphous) to crystalline ice at 210 K (Figure 2. 14) via formation of various dimers during warm up of the ice. The change in the structure of the molecular ice also take place due to the irradiation of charged particle (Hansen & McCord, 2004)



Figure 2. 13: Structure change in the amorphous ice to crystalline ice due to thermal processing.

The molecular ice can exhibit both amorphous and crystalline phases simultaneously in the mixture of two different molecular ices with different sticking probabilities and mobilities. Depending on the temperature of the ice, the molecules in the mixture can have amorphous and crystalline structure in local areas of the substrate.



Figure 2. 14: Change of amorphous formamide ice (10 K) to crystalline formamide ice (210 K) with the IR spectra (Sivaraman et al., 2013)

The change in structure affects the density of the molecular ice and the trapping of atoms or molecules depends on the ice structure. As a result the structure of ice plays important role on chemical evolution of molecular ice. The large surface areas in the porous ice can adsorb the atoms/molecules, open up chemical reactions. The molecules trapped inside pores can be released thermally (Collings et al., 2003, Raut et al., 2007). These structural changes in interstellar ices can have huge impact on the chemistry in ISM and planetary bodies.

2.2.1 Processing of molecular ice

The chemical evolution in the molecular ice present on the interstellar medium and on the surface of planetary /satellite are driven by irradiation of energetic ions, fast electrons and ultraviolet (UV) photons (Figure 2. 15). The source of UV photons are stars/protostar surrounding the molecular clouds, while the source of energetic ions/electrons are cosmic rays. In case of the satellites orbiting under the parent planetary magnetosphere, ions trapped in the magnetosphere are a major source for chemical changes to take place in the icy satellites such as surface ice of Jupiter's satellites Io, Europa etc. The chemistry takes place due to the produced secondary electrons which is independent on the type of ionising radiation known as radiation chemistry. The UV photon irradiation also induce photochemical reactions and the effects of photochemistry and radiation chemistry have nearly same outcomes.

The chemical evolution of interstellar ices subjected to irradiation from both UV radiation and charged particles have been studied in the laboratory by recreating the astrochemical conditions and sources by many groups (Johnson, 1990; Kaiser, 2002). The absorption of an ultraviolet photon by a single molecule is



Figure 2. 15 The processing of ices through different energetic particles, UV photons and shock wave.

governed by optical selection rules, may lead to photo dissociation, leads to rotational, vibrational and even electronic excitation. The radical species produced may have excess K.E. of few eV, these radicals/atoms are called suprathermal. If the energy of the suprathermal atoms/radical is sufficient, it will pass barriers on the potential energy surface and allow new reaction to become feasible, which are inaccessible to the surrounding species at thermal equilibrium. The UV photons entirely absorbed within a few nm of the ice sample, while the charged particles

protons (energy MeV) may penetrate deep inside the ice target. The details of the ion irradiation and UV irradiation process has been discussed in the upcoming section.

2.2.1.1 UV Irradiation

The chemical evolution/alteration of ices in the interstellar medium is caused by the photolysis. The prime source of UV radiation in the interstellar medium is from O and B types of stars. The photons from the surrounding stars/protostars will process the



Figure 2. 16: Schematic of UV irradiation of ice analogs.

molecular ices (Figure 2. 16) in the outer molecular clouds and do not penetrate deep into the dense molecular cloud due to shielding from dust grains.

The secondary UV photons are produced from the interaction of cosmic rays with abundant H_2 , which excites the Lyman absorption bands of H_2 and as it relaxes back to the ground state after releasing a UV photon in the energy range of 11.2–13.6 eV (Prasad and Tarafdar, 1983). The grain mantles in the heart of the molecular cloud

are shielded from ionising radiation. These UV photons establish the photochemistry inside the molecular clouds. The UV irradiation in the photon energy range between 4 eV and 13 eV (~300 - 100 nm) results in the photolysis of ices and a large number of radicals may be formed. The UV irradiation on the molecular ice starts the reaction with the absorption of a photon by a molecule, say, AB, and ends with the production of one, many molecule X and Y, with X and Y different from AB. The UV processing can be divided into primary and secondary processing. The primary process, absorption of a photon by the molecule, AB, the following electronically excited state, AB*, and subsequent reaction path depending on the consumption of the excess energy of the molecule A which could be the radiative de-excitation via fluorescence, fragmentation through photo-dissociation, intramolecular rearrangement through photo-isomerization, and photoionization by losing an electron. In the secondary process, the reactions of the molecules, radicals or ions produced in the primary process with each other and/or with other molecules in their environment. Photo-addition, formation of the molecule ABA through the radical-radical reactions occurs in exothermic reactions (Salama, 1998). Which lead to formation of complex organic molecules within ice mantles. The maximum UV energy available in the molecular clouds are ~13.6 eV and the energy needed for most of photochemical reactions are approximately ≤ 10 eV dependent on the molecule and the flux. So, to understand the photochemical process in the ISM we use tuneable photons from a synchrotron source.

 $AB + hv \rightarrow AB^*$ $AB^* \rightarrow AB + hv$ $AB^* \rightarrow AB^+ + e^ AB^* \rightarrow A + B$ $AB^* + A \rightarrow ABA$

Many experiments have been carried out by a number of laboratories on photoprocessing of pure ices, binary ices and mixed multi-component ices to study the formation of new products, such as complex organics (e.g. Allamandolla et al, 1980; Bernstein et al., 1997; Gerakines et al., 1995; Gerakins et al., 1996; Hagen et.al 1979; Schutte et al., 1999).

UV radiation causes electronic excitation which can be studied using VUV photoabsorption spectroscopy. Understanding these excitation processes and the electronic structure of condensed phase compounds is important in probing the photo-chemical and photo-physical properties of ices. VUV photo-absorption of CH₄, NH₃ and H₂O ices studies of pure astrophysical-type ices have been carried out to explore the chemical evolution of interstellar molecular ices (Lu et al., 2005; Lu et al. 2008; Wu et al., 2012; Wu et al., 2013).

The experimental set-up has been described in the Chapter - 3. We have performed the VUV photoabsorption spectroscopy of SO₂, H_2O , O_2 , C_6H_6 and C_6H_5CN ices as pure and as mixtures. The results of the irradiation of these ices have been discussed in details in the Chapter 4, 5,6 and 7.

2.2.1.2 Ion Irradiation

The irradiation of charged particle/ions in molecular clouds in the ISM plays an important role in chemical evolution of ISM. Since the UV photons does not penetrate deep into the molecular clouds, the charged particles penetrate inside the molecular clouds depending on the energy and size of the ions and the density of the target molecules. Another difference with UV photon irradiation is that it interacts in the ratio of one molecule per photon while the charged particles interact with more than one molecule and produce secondary electrons during interactions. The series of events started by incident ions in solid has been shown in Figure 2. 17 and Table 2. 1.

Ions interaction could be elastic and inelastic collisions with the constituent target molecules, and consequent loss in ion energy. Which could lead to different process such as:



Figure 2. 17 Schematic of events along ion path in the ice sample (inspired from Johnson, 1990).

The ejection of atoms/molecules from the ice into the gas phase from irradiation is known as sputtering, the process has been studied in details by (Brown et al., 1978; Johnson, 1998). The ejection of molecules/atoms in gas phase from ice enhance the gas phase molecular composition, which could take place in grain mantles in the interstellar clouds, or cometary nuclei or the surfaces of icy satellites or planets. The composition of the sputtered materials could be the initial ice molecules, fragmentation products, or new species formed by chemical reactions. Another important consequence of sputtering is the physical surface turnover as material is eroded away, thus exposing the underlying layers.

Irradiation leads to change of phase from ordered crystalline structure to amorphous ice. There are many laboratory experiments reported to-date for the amorphization of crystalline ice due to ion irradiation (Baratta et al., 1991; Hudson & Moore, 1992;

Hansen & McCord, 2004). The chemical reactions due to irradiation will result in the formation of volatile species which may be trapped within the ice or leave the ice by migration through micropores which in turn changes the density of the ice, thereby directly affect the optical properties of the ice. The recrystallisation has also been reported after irradiation of the ice which takes place due excess energy is available for molecular redistribution (Hudson & Moore, 1992).

Table 2. 1: Events initiated by irradiation of ion on solid (Adopted from Johnson,1990)

Physical stage $< 10^{-13}$ s	Incident radiation	
	Ļ	
	Energy absorption	
	Radiation cascade	
	Electronic energy transfer	
	Ļ	
	Excited and ionized molecules	
	Ţ	
Physiochemical stage < 10 ⁻¹¹ s	Electronic recombination	
	Molecular dissociation	
	Rearrangements and sputtering	
	Ļ	
(Luminescence $> 10^{-9}$ s)	Residual excited species and radicals	
	Ļ	
Chemical stage $\sim 10^{-6}$ s to years	Diffusion of radicals	
(temperature and flux dependent)	Production of new molecules	
	↓	
	Molecular alteration	
	Ļ	
Long term effects	Repair and equilibrium	

One of the important process of the irradiation on ice is the formation of new species from the produced ionised/excited species. The ion get implanted/trapped in the ice depending on the thickness of the ice and energy of the ions. If the ion is reactive (i.e. S, O or H ions), it may react with the target atoms or molecules to form new species that are not native in the ice. These chemical evolution takes place on the surface of Jovian and Saturn's satellites from the irradiation of charged particles trapped in the magnetospheres. The newly formed species in the ices introduce changes in the physical properties of the ice which results in the variations in the reflection and transmission properties of ices. The change in the albedo has been observed in the inner Jovian satellites as a result of magnetospheric particle bombardment (Nelson et al., 1987). The irradiation on the ice could lead to the formation of carbon-containing species/darkening of the surfaces. Many experiments have been reported to-date to understand the carbon like material formation from the irradiation of simple organic molecular ice present in the Solar system as well in ISM (Calcagno et al., 1985; Foti et al., 1984). The alteration of the top layers of the ice.

The ice irradiation could lead to the all process mentioned above simultaneously, which can be determined both by the properties of the ices and the ions. Such studies has been done in several laboratories under astrochemical conditions (Moore and Hudson, 2000; Baragiola et al., 1999; Strazzulla, 1999). These studies have been carried out on different astrophysical ice analogs, pure ice, ice mixtures at different physical condition; temperatures with different ion energies. The interaction of ions with the target molecular ices have been studied in detail and the basics of the process are discussed below:

The charged particles scatter while interacting with molecules, lose energy in collisions and come to rest in the ice/target at the end. The collisions of the energetic charged particle with the ice/target could be of two types; (i) elastic (nuclear) collision, (ii) inelastic (electronic) collision, which occur at the same time but are studied separately. These collisions depend on the target number density (n), the absolute energy loss can be written as follows

$$dE/dx = n (S_e + S_n)$$

where dE /dx is the stopping power of the ice/target and, S_n , S_e are nuclear and electronic stopping cross sections. Nuclear stopping dominate for incident ions with

low energy and high atomic number, while the electronic stopping occurs (dominate) for incident ions with high energy and low atomic number (Johnson, 1990).

As discussed above, the charged particles travel inside the target during the interaction. This traveling range of ions into the target and stopping power of the target are calculated using computer modelling program; Stopping and Range of Ions in Matter (SRIM). This program has been developed by Zeigler & Biersack, 1985; 2010, which are based on the quantum mechanical treatment of ion-atoms collisions.

The effects of irradiation in the chemical evolution are nearly the same with different magnitude for all the three forms of irradiation (UV, ions and electrons). In the case of ion irradiation, the magnitude of the effect in chemistry depends on the size and energy of the incident charged particles, which determine the penetration inside the target and the number of ion - molecules interaction.

In case of UV photons irradiation, the photons interact in the ratio of one molecule per photon while in charged particles/electrons irradiation, the charged particle interacts with a number of molecules and produces secondary electrons during the interactions. If the energy of the charged particles are high, the penetration depth of the charged particle inside the target will be high so the number of ion- molecules interactions before the particles captured (Johnson, 1990).

The chemical reaction in the ISM and planetary bodies takes place in gas and solid phase. The reactions in gas phase or solid phase due to irradiation of charged particles or UV photons are different to each other due to different collisional frequency of produced atoms or radicals. As discussed the process of chemical evolution in earlier section *Processing of molecular ice*, the chemical reaction due to energetic irradiation could be of different types as listed in Table 2. 2.

Table 2. 2: Types of reactions the interstellar medium (Adopted from Hodgkinson, 1979, Carbo & Ginebreda, 1985)

Ion-molecule reactions		
Charge transfer		
$A^+ + B \rightarrow B^+ + A$		
Radiative association		
$A + B \rightarrow AB + hv$		
Atom transfer		
$A^+ + BC \rightarrow AB^+ + C$		
$AB^+ + C \rightarrow A^+ + BC$		
Electron recombination reactions		
Radiative		
$A^+ + e \rightarrow A + hv$		
Dissociative		
$AB^+ + e \rightarrow [AB]^* \rightarrow A + B$		
Neutral-neutral reactions		
Atom transfer		
$A + BC \rightarrow AB + C$		
Radiative association		
$A + B \rightarrow AB + hv$		
Chemionization		
$A + B \rightarrow AB^+ + e^-$		
Other reactions		
Ion-ion neutralization		
$A^+ + B^- \rightarrow AB$		
Negative ion-neutral		
$A^- + B \rightarrow AB + e^-$		
$A^- + BC \rightarrow AB^- + C$		
Photochemical reactions has been discussed in UV irradiation section		

2.3 Conclusion

The molecular vibration and electronic excitation has been discussed in this chapter. A glimpse of infrared and vacuum ultraviolet wavelengths of electromagnetic spectrum has been provided and spectroscopy in these wavelength range has been discussed to explain the vibration and electron excitation of molecules, respectively. The processing of the ices in the ISM and on the planetary bodies has been emphasized and its importance in chemical evolution along with reaction details has been provided.

Chapter 3

Experimental setup and methodology

3.1 Introduction

In order to understand icy mantles present in the Interstellar Medium (ISM) and their role in the chemical evolution we need to recreate the conditions commensurate to the cold dust in the ISM and the surface ices on the Solar System bodies. Astrochemical conditions in the laboratory need to be created that mimic ISM conditions by using a combination of Ultra High Vacuum (UHV) conditions (10⁻⁹ - 10⁻¹⁰ mbar for contamination free experiments); stainless steel chambers; a helium compressor cooled Oxygen Free High Conductivity (OFHC) copper cold tip, containing a chemically inert dust analogue and an irradiation source which can either be a synchrotron beamline or a commercially available electron gun. The dust analogue used in the experiments is dependent on the probing wavelengths, such as IR and VUV. In the case of VUV wavelengths, the source is used for both, to irradiate as well as to probe the ice analogue.

The experiments reported in this thesis were carried out at the

- (1) Physical Research Laboratory, Ahmedabad, India
- (2) National Synchrotron Radiation Research Center, Hsinchu City, Taiwan

3.1.1 Vacuum Chamber and Cryostat

The low temperature astrochemistry experimental system described in this chapter is designed and developed at the Physical Research Laboratory, Ahmedabad. A closed cycle He cryostat (ARS) (Figure 3. 1) is used reach very low temperatures, up to 4 K. Combination of resistive heater and silicon diode temperature sensor (controlled using Lakeshore Temperature Controller) is used to measure and maintain the temperature during the entire experiment. The He -V (99.999% pure) filled in the compressor attached with cryostat is used for the closed cycle (Gifford McMahon) in order to achieve the lowest temperature. The cryostat is attached to a custom made stainless steel chamber via a cross- piece that has three CF-100 and one CF-40 sized ports for mounting with other parts of the experimental chamber (Figure 3. 2). The other part of the UHV chamber contains two CF-100 ports and four CF-40 ports (Figure 3. 2). CF-100 ports are used to couple with the cross piece and the CF-40 ports were used to attach view ports / window flanges. In addition two ports were extended from the chamber, one with a CF-40 port and the other with a CF-16 port (used to connect the gasline). Assembled system is similar to that shown in Figure 3. 3. The chamber UHV base pressure of 10⁻⁹ without cryocooling and with cryo-cooling it reaches 10⁻¹⁰ mbar range, which is ultrahigh vacuum for carrying out contamination free astrochemical ices experiment. At such vacuum conditions it would roughly take \sim 3 hours to form one monolayer of residual gas on the cold surface. The tip of the cold finger contains the substrate Figure 3. 4, which acts as the ISM dust analogue will be kept at the desired temperature to sudy the molecular ices. The combination of UHV and low temperature provides a good control in making the astrochemical ice analogues and at the same time the vacuum condition is used to evacuate the sublimed molecules leaving back the substrate for the next experiment. In fact, this has limitations if any material is left over on the substrate at the end of an experiment.

The CF-16 port Figure 3. 2 is used to let the molecules into the chamber via an allmetal leak valve which is pumped to 10^{-2} to 10^{-3} mbar. The gas line pressure is measured using the MKS capacitance baratron. The opening of the capillary tube via the CF-16 port in the UHV chamber, points toward the cold substrate situated at a distance of about ~ 2 cm. IR beam from Nicolet iS-50 and iS-10 FTIR pass through the CF-40 ports. A similar setup is used at the NSRRC for irradiation at VUV wavelengths and probed using IR beam from a Bomem FTIR spectrometer. The windows/substrate used in IR and VUV experiments are KBr/ ZnSe and LiF/CaF₂, respectively. Thermal evolution of the astrochemical ices were carried out at PRL, Ahmedabad, prior to the photon irradiation experiments at the two beamlines in the National Synchrotron Radiation Research Center (NSRRC), Taiwan.



Figure 3. 1: The two stage closed cycle He cryostat with cold finger with different view angle.



Figure 3. 2: Custom made stainless steel cross piece and chamber to accommodate the cold tip containing the dust analogue.



Figure 3. 3: Assembled system used for experiments.



Figure 3. 4: The cold finger along with substrate and ice sample (b) The cross-sectional view of the sample on top of the substrate.

3.1.2 Gas line

The desired astrochemical ice can be formed on the cold substrate by using a clean gasline coupled to the UHV chamber. An all-metal leak valve (Figure 3.5) connects the UHV chamber and the gasline, where it restricts the rate of flow of molecules inside the main chamber. The schematic of the gas manifold is given in Figure 3.6 and shows several ports for connecting the samples as well as the pressure measurement devices such as baratrons. The sample used to form ice are either availale as gaseous, liquid and solids (having high vapour pressure) samples. So quartz sample holder is used to contain liquid and high vapour pressure solid chemicals, shown in Figure 3. 6. Liquid samples are subjected to freeze-pump-thaw cycle (three times) using liquid nitrogen to remove any dissolved gases. The required gas cylinders are directly connected with the gas line. To maintain purity the entire gasline is evacuated and purged everytime, with the specific chemical before any sample deposition. The gas manifold enables us to prepare gas mixtures to a desired ratio before allowing it inside the main chamber. Swagelok-VCR and CF connections are used to maintain the sample purity and at the same time to carry the sample to the UHV chamber containing the cold finger.



Figure 3. 5: The schematic of the metal cut leak valve for very precise deposition of molecules on the cooled substrate.

We have carried out experiment on pure and mixed ices. For single ice sample experiment, the molecules are directly deposited on the cold substrate using the UHV metal leak valve, while for the mixture of two or more different molecules, they are mixed in the gas manifold before deposition and gas line pressure is measured using baratrons.

Direct gas deposition at normal angle to the substrate is carried out in all the experiments reported in this thesis. So one side of the transparent substrate is coated with molecular ice. The experimental system used at NSRRC has rotatetable mount to bring the substrate at normal angle while depositing the molecules. Whereas in the experimental system in PRL the angle between substrate and the feed through are fixed at 90°. UHV chamber pressure (deposition pressure) while allowing the molecules into the chamber and deposition time are recorded in all the experiments. These two measured quantities enables us to vary the rate of deposition, either fast or slow deposition. **To pump**



Figure 3. 6: The schematic of the gas-line to prepare pure or mixture of molecules for deposition.



Figure 3. 7 : Gas deposition (CO; used for representation) at normal angle (above), substrate with icy layers rotated back to original position to record the spectra at right angle to the beam (below), at NSRRC, Taiwan.



Figure 3. 8 : Gas deposition (CO; used for representation) at right angle to the substrate (above), and substrate at 45^{0} with respect to the IR beam (below), at PRL, Ahmedabad.

In Figure 3. 7 sample deposition of CO molecules on to the substrate kept at 10 K is shown. The substrate is rotated and kept perpendicular for direct deposition of molecules from the gas line. Post-deposition, the substrate is then brought back to normal angle to the VUV beam. Whereas in the case of experiments carried out at PRL, the substrate is fixed at 45⁰ to the IR beam where the gas line is directed at right angles to the substrate Figure 3. 8. This enables simultaneous recording of the IR spectrum whilst depositing the molecules.

3.2 VUV spectroscopy

The VUV photoabsorption spectroscopy of the astrochemical ices were carried out at the BL03 high flux beamline at NSRRC, Taiwan. The VUV light is dispersed using a 6 m cylindrical grating monochromator (CGM) at the BL03 beamline of the 1.5 GeV storage ring. Data reported are carried out in the 109 - 320 nm wavelength range using two different gratings in the monochromator; one, 600 l/mm grating covers the range 109 - 250 nm and the second, 450 l/mm covers the range 240 - 320 nm. The desired wavelength are achieved using the calibrated slit position for corresponding wavelength. The calibration of monochromator is discussed in (Lu et al., 2005; Lu et al., 2008) and is operated using LabVIEW. The beam is collimated after passing through the exit slit using different optical components and then reaches the end station.

Table 3. 1: The transmission range of different substrate used during experiments.

Substrate	Transmission range	Suitable for VUV/IR
KBr	0.25 – 25 μm	IR
ZnSe	0.6 – 20 μm	IR
LiF	106 nm - 6500 nm	VUV/ near IR
CaF ₂	125 nm – 10000 nm	VUV/ near IR

The LiF and CaF₂ window are used as transmitting windows and also as substrate. The collimated VUV beam in the chamber passes through the LiF/CaF₂ window before reaching the substrate (LiF/CaF₂) containing the molecular ice Figure 3. 9. VUV photons passing through the molecular ice impinges onto a window coated with sodium salicylate. The fluorescent screen of sodium salicylate emits blue light, which is detected by a photomultiplier tube (Hamamatsu R943-02). The schematic of the VUV set up is shown in Figure 3. 10.



Figure 3. 9: Top view of the low-temperature astrochemistry system with VUV setup at NSRRC, Taiwan.





3.3 Fourier Transform Infrared Spectroscopy

The IR photons beamed towards the sample, coming off the Michelson interferometer, falls on the entry/exit windows (ZnSe/KBr) of the UHV chamber. IR photons pass through the substrate between the entry and exit windows, eventually reaching the (DTGS) detector. The schematic of infrared set-up is shown in Figure 3. 11. The FTIR spectrometer has advantages as FTIR is based on non-destructive technique, the high data collection speed (measuring all the infrared frequencies simultaneously), and best sensitivity (adding many scans and cancelling out the random noises). The infrared spectroscopy experiments have been carried out at PRL, Ahmedabad and NSRRC, Taiwan (BL 21A2).

The list of the windows used in the experiments reported are given in Table 3. 1.



Figure 3. 11: Side view of the low-temperature astrochemistry infrared spectroscopy system at PRL.

3.4 Ice irradiation

Molecular ices formed *in-situ* at low temperatures were irradiated to break the bonds and make new chemical bonds leading to the synthesis of newer molecules in the ice. For the irradiation experiments reported in this thesis, VUV photons of energy 9 eV and 10 eV were used energetic source to irradiate the icy mantles. Photon irradiation was carried out at beamlines BL 03A and BL 21 A2 of NSRRC,

Taiwan. At BL03, the radiation from the storage ring (1.5 GeV) is dispersed with a cylindrical grating monochromator and the exit slit is positioned corresponding selected wavelengths corresponding to 9 eV (137.7 nm) which is already precalibrated using absorbance lines of different molecules (Lu et al. 2005, Lu et al. 2008). The flux of the irradiating photons is controlled using the width of the exit slit. Photon irradiation produces superathermal atoms/radicals to synthesize new products in the irradiated ice. We have used synchrotron as VUV/UV photons source, using which we can tune any energy from 4 eV to >15 eV for irradiation and the changes in the ices can be probed over a wide VUV wavelength range at BL03 of NSRRC, Taiwan as well as in infrared wavelength range (in a different beamline BL 21A2). During the irradiation process the beam to detector is blocked to prevent any damage to the photon multiplier tube (PMT). While at the beamline 21A, the energy of the photons is selected using the gap between the undulators at the storage ring and there is no monochromator used (i.e. non-destructive technique). Schematic of photo-irradiation of ice is shown in Figure 3. 12.



Figure 3. 12: VUV irradiation of astrochemical ices using 9 eV photons.

3.4.1 Electron Gun

Recently we have installed an electron gun (30 keV) and coupled it with our low temperature astrochem system at PRL. The EGM-4210 Kimball electron gun (LaB₆ Cathode source), which operates under high vacuum conditions, is attached directly with the chamber (ultrahigh vacuum 10^{-9} mbar). The energy range of the gun can be tuned between 1 keV and 30 keV with beam current between 10 μ A and 5 mA. The spot size of the electron beam, which has Gaussian distribution, is 100 μ m to 10 mm and such a collimated and small spot is formed using magnetostatic focusing lens. The energy supply by the gun has a stability of <0.01 % per hour with 0.05% rms ripple at full output. The beam has a stability of 0.1% per hour with emission current control. The schematic of electron irradiation of ice is shown in Figure 3. 13.



Figure 3. 13: Schematic of electron irradiation of astrochemical ices.

3.5 Conclusion

The experimental system and methodology discussed in this chapter is widely used in the experiments carried out in this thesis. The low temperature astrochemistry experimental system, designed and developed at the astrochemistry laboratory, PRL, Ahmedabad, will be used extensively for understanding the morphology and chemical synthesis in molecular ices probed using IR spectroscopy. Whilst the VUV beamlines at NSRRC, Taiwan will be used for photon irradiation and VUV probing of molecular ices. These two spectroscopic techniques used will complement each other in order to better understand the physico-chemical nature of the astrochemical ice analogues.

Chapter 4

Ozone on Callisto

In this chapter, we present, UV (240 - 320 nm) photo-absorption spectra of Sulphur dioxide (SO₂) ice under astrochemical conditions relevant to conditions existing in both planetary/satellite environments and the Interstellar Medium (ISM). SO₂ ice was irradiated with 9 eV photons which synthesizes ozone in the irradiated ice, confirmed from the presence of the Hartley band (220 – 300 nm) in the recorded spectra. These laboratory spectra are used to fit the observed Callisto data using the Hubble Space Telescope and discuss the presence of ozone on Callisto.

4.1 Introduction

Molecular ices have been observed on the surfaces of the icy satellites of the giant planets or the planets in the outer Solar System such as the satellites of planets like Jupiter, Saturn and beyond, the dwarf planet Pluto, comets, etc. The morphology of these ices has been characterized by infrared and vacuum ultraviolet spectroscopy. Water ice is the most dominant on the surface of the icy satellites; other ices such as H₂O₂, CO₂, SO₂, CO, NH₃ have also been observed on these surfaces through spectroscopy in a different range of electromagnetic spectrum (Carlson et al. 1997; Carlson et al., 1999, Noll et al., 1997b; Dalton et al., 2013). Ozone has been observed on the surface of Ganymede, Dione and Rhea (Noll et al. 1996, Noll et al., 1997a) along with the atmosphere of Earth and Mars.

Ozone is regarded as a potential biomarker molecule, so it is important to study its formation and its chemical evolution on planetary bodies. The Hartley absorption band of ozone at 254 nm is used for its identification in both astronomical observations and laboratory experiments. The infrared spectra of ozone provides detailed information about its presence and abundance: more narrow v_3 and v_1+v_3 bands at 1043 and 2108 cm⁻¹ corresponding to the O–O asymmetric stretch vibrational mode and the symmetric-asymmetric stretch combination mode. Though the infrared characteristics of ozone overlap with the silicate bands (one of most abundant materials in ISM/planetary bodies), the Hartley band (known as a unique 'fingerprint' of the O₃ molecule) are used for ozone identification on planetary bodies. The formation process of solid ozone on the planetary bodies could be abiotic or biotic in nature. Though the formation path of ozone in the earth's atmosphere has been studied widely (Thiemens & Jackson, 1988, 1990; Thiemens, 2001), the formation is explained by the Chapman reaction mechanism (equations (1) and (2)), where M is the third body to stabilize the ozone molecule.

$$O_2(X^{3}\Sigma_g) + hv \rightarrow O(^{3}P) + O(^{3}P)$$
 (1)

$$O(^{3}P) + O_{2}(X^{3}\Sigma_{g}) + M \rightarrow O_{3}(X^{1}A_{1}) + M$$
(2)

4.1.1 Literature survey of observation of ozone on planetary

bodies

The surface composition of icy satellites is currently deduced mainly from how they appear under sunlight. Many factors affect reflectance; porosity, surface roughness, and light absorption by impurities and by products of the interactions of energetic particles and radiation with the surface, which are not well understood. The tentative detection of ozone in the polar region of the Martian atmosphere was reported by Barth & Hord, 1971. They observed the Hartley band in the reflectance spectra of Mars in the UV range using the ultraviolet spectrometer onboard the
Mariner 7 spacecraft. Later Barth et al., 1973 reported the seasonal variations of ozone in the Martian atmosphere using the Mariner 9 spacecraft's data. The presence of ozone on Mars was explained by photolysis of carbon dioxide (CO₂) producing oxygen and eventually ozone via the Chapman mechanism. The presence of solid ozone on a planetary satellite was first suggested by Nelson et al., 1987. They discussed the presence of ozone on Ganymede using the reflectance spectra observed by ultraviolet spectrometer of International Ultraviolet Explorer. The presence of solid ozone on Ganymede was confirmed by Noll et al., 1996. Noll et al., 1996 reported the reflectance spectra of Ganymede using Faint Object Spectrometer of the Hubble Space Telescope. The observed spectra have characteristics band at 260 nm, a feature they attributed to the Hartley band/continuum of ozone. The Hartley band was observed by the Galileo Ultraviolet Spectrometer (UVS) confirmed the findings and provided the first map of ozone on the surface of Ganymede (Hendrix et al., 1999). The finding of ozone on Ganymede was controversial initially, since the surface of Ganymede is covered by water ice (the infrared spectra of Ganymede's surface consists mainly of water ice, with the visible optical depth of a few hundred microns (Clark, 1980; Calvin et al., 1995)) and it was not thought possible that ozone could be formed and present in any ice/atmosphere that was not oxygen-rich. Later, Noll et al. (1997a) reported similar spectroscopic characteristics in the reflectance spectra of the Saturnian satellite's Rhea and Dione. The detection of ozone on the satellites of two different planets in regions of the Solar System with entirely different solar fluxes and quite different planetary compositions removed the possibility that there were special circumstances unique to Ganymede. The surface of these satellites has dominant water ice so, it was proposed that ozone is a by-product of irradiation of ice by charged particles trapped in the magnetosphere of Jupiter and Saturn. The list of planetary bodies on which ozone has been detected is shown in Table 4. 1. The irradiation of charged particles on water molecules dissociate them, forming and trapping O₂, which could synthesize O₃ from O₂. This process of ozone formation in the water ice-covered satellites is thus, not biological in origin. To-date there are many experiments reported of the formation of solid ozone in the laboratory from

Ozone on Callisto

oxygen bearing molecules and water under planetary conditions at a temperature range of 70- 150 K. Few of them are listed and discussed below.

References	Ozone on	Mission/Instuments	Ozone band
	Planetray body		
Barth & Hord,	Martian	Mariner 7	Hartley band
1971	atmosphere		
	(Polar region)		
Barth et al., 1973	Martian	Mariner 9	Hartley band
	atmosphere (Polar		
	region)		
Bertaux et al.,	Martian	Mars express	Hartley band
2000	atmosphere (Polar		
	region)		
Nelson et al.,	Ganymede	International	Hartley Band
1987		Ultraviolet Explorer	
Noll et al., 1996	Ganymede	Hubble Space	Hartley band
		Telescope	
Hendrix et al.,	Ganymede	Galileo	Hartley band
1999			
Noll et al., 1997a	Dione and Rhea	Hubble Space	Hartley band
		Telescope	

Table 4. 1: Literature survey of ozone detection on planetary bodies.

4.1.2 Ozone synthesis in laboratory ice analogues

To-date many laboratory experiments have been reported the formation of solid ozone by energetic electron and ion irradiation of oxygen ice and other oxygen bearing ices under astrophysical conditions. The initial laboratory experiment on solid ozone formation in low energy electron (10 eV) irradiated oxygen ices was reported by Lacombe et al., 1997. Later Baragiola et al., 1999 and Fama et al., 2002 reported the investigation of ozone synthesization in 100 keV proton irradiated oxygen ices to explain the ozone formation on icy satellites. Bennett & Kaiser, 2005 reported 5 keV electrons irradiation on molecular oxygen ice at 11 K and unravelled the mechanisms of ozone formation. Using infrared spectra of ice as a diagnostic, they reported changes in the molecular oxygen ice caused due to irradiation. They reported temperature dependent infrared and mass spectra of irradiated ice used to explore the physical and chemical characteristics of the ozone and oxygen ice. Sivaraman et al., 2007 also reported the temperature dependent ozone formation in electron irradiated oxygen ices between 11 and 30 K. They reported that the ozone monomer concentration decreases with increase in temperature due to loss of oxygen atoms due to recycling of oxygen molecules from recombination of two oxygen atoms in the ice. They have also discussed the temperature dependent ozone dimer and clusters formation using infrared spectroscopy.

Apart from the ozone synthesization from oxygen ice, many experiments have been reported on irradiation of water ice to examine the mechanism of ozone formation in irradiated water ice. Teolis et al. 2006 reported the first experimental evidence for ozone synthesization, directly from water ice, by radiolysis experiment. The trapping of molecular oxygen in water ice enhances at 130 K (Teolis et al., 2005). Later Teolis et al., 2006 reported O₂ trapping in irradiated water ice, the condensation of a fresh over-layer of water on irradiated ice suppresses sputtering of the radiolytic O₂ produced by 100 keV Ar⁺ (10¹⁶ cm⁻²), increasing the amount of O₂ trapped in the ice. The trapping of large amount of oxygen in the surface depends on the temperature and rates of irradiation. The enhancement of trapped O₂ due to condensation of water over-layers would also occur at an icy satellite. The O₂

concentration is high enough to produce the detectable amount of ozone by the irradiation of ions.

The first VUV (110 - 220) spectra of solid ozone synthesization from photo irradiated (9 eV photons) oxygen ice along with the Hartley band (230 – 300 nm) was reported by our group in 2014 (Sivaraman et al., 2014). The very same year, Jones et al., 2014, reported the UV-Vis absorption spectroscopy of ozone formation in a variety of oxygen-bearing molecular ices (oxygen, carbon dioxide, water) at 5.5 K by energetic electron (5 keV) irradiation. The ozone synthesization was confirmed in pure ices of molecular O₂, CO₂ and a mixture of H₂O and O₂. The Hartley band of synthesized ozone in the ice matrix observed in UV-Vis spectra, which they compared with the spectrum of Ganymede observed using HST. While, ozone production in the irradiated carbon dioxide-water mixtures ices was not seen by Jones et al., 2014, it was later reported by Pavithraa et al., 2019, who showed ozone formation in photo-irradiated CO₂: H₂O ice mixture while investigating the UV spectra of carbonic acid. Many such experiments were carried out on oxygen bearing molecular ices to understand the ozone formation and its implication to icy satellites. The list of experiments reported for ozone formation from oxygen bearing molecules is shown in Table 4. 2.

As discussed above, SO_2 is one of the oxygen bearing molecules detected on the surface of Galilean satellites. Noll et al. 1997b, reported the UV reflectance spectra of Callisto having the broad absorption continuum at 230 - 310 nm corresponding to SO_2 molecular ice characteristics. The absorption continuum was broad containing other molecules characteristics along with the SO_2 absorption feature. The Hartley band of ozone also lies in the same continuum range, so the observed feature in the UV range could be characteristics of SO_2 and Ozone ice.

 SO_2 is an oxygen bearing molecule and is a potential candidate for ozone synthesization in the presence of energetic irradiation. It is known that the surface of Callisto, which orbits within Jupiters' magnetosphere, is under irradiation of charged particles trapped in the magnetosphere of Jupiter. To affirm the formation of ozone from SO_2 ice, we have carried out an experiments on irradiation of SO_2 ice with energetic photons. In the next section below, we have given the

experimental details and the outcome of the experiments, discussed the results and compared the experimental result with the observational data.

Author	Ozone probing	Primary source	Irradiation
	type/range		source
Lacombe et al.,	Electron energy	O ₂	10 eV electrons
1997	loss spectroscopy		
Baragiola et al.,	Infrared	O ₂ , O ₂ : H ₂ O	100 keV protons
1999			
Fama et al., 2002	UV	O ₂	100 keV protons
Bennett & Kaiser,	Infrared	O ₂	5 keV electrons
2005			
Teolis et al., 2006	UV	H ₂ O	100 keV Ar ⁺
Teolis et al., 2007	IR and UV	O ₂	100 keV protons
Sivaraman et al.,	Infrared	O ₂	5 keV electrons
2007			
Ennis et al., 2011	Infrared	O ₂ and CO ₂	$5 \text{ keV H}^+, \text{He}^+$
Jones et al., 2014	Ultraviolet	O ₂ , CO ₂ , H ₂ O: O ₂	5 keV electrons
Sivaraman et al.,	Vacuum	O ₂	9 eV photons
2014	ultraviolet		
Pavithraa et al.,	UV	CO ₂ : H ₂ O ice	9 eV photons
2019			

Table 4. 2: Literature Survey on Ozone formation in Laboratory underastronomical conditions.

4.2 Experiment

The ultraviolet spectra of SO₂ ice were measured under simulated astrochemical conditions at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. A detail description of the experimental set-up has been discussed in Lu et al. 2005, 2008. The radiation from the high flux beamline of the storage ring was dispersed with a cylindrical-grating monochromator of 6 m focal length. Two gratings were used to cover a wide wavelength range; the first grating (600 l/mm) covered the range 109 – 250 nm, and the second (450 l/mm) covered a wide range with an overlap from 240 – 320 nm. The SO₂ molecule was deposited on a lithium fluoride (LiF) substrate pre-cooled to 9 K. The spectra were recorded before and after deposition. To obtain the absorbance spectra the incident (I₀) and transmitted (I_t) intensities were recorded, from which the absorbance of SO₂ are calculated using the Beer-Lambert law. The minimum wavelength cut off (109 nm) is determined by the material used for the entrance and exit windows; in this case, LiF was used. A spectral resolution of 1 nm was used in the absorption measurements.



Figure 4. 1: SO₂ gas deposition at LiF substrate cooled to 9 K.

SO₂ was deposited on the LiF substrate at a base pressure of 10^{-8} mbar at a temperature of 9 K, which was irradiated and processed with 9 eV photons for a couple of hours (Figure 4.1 & Figure 4. 2). The absorption spectra in the range of (220 - 320 nm) were recorded for both pure and irradiated SO₂ ice. The band of the irradiated SO₂ ice has a larger bandwidth than the pure SO₂ ice, showing that new molecule/molecules have been synthesized having a characteristic band in that range. The irradiated ice was then warmed up to 50 K while spectra were recorded at intermediate temperatures. When the irradiated ice was warmed over 50 K, the band of the irradiated ice started decreasing. The spectra were recorded at 70 K, 90 K, 100 K, 110 K, and 120 K. At 120 K, the band recorded absorbance is very low due to the ice sublimation.



Figure 4. 2: 9 eV photon irradiation on SO₂ ice, deposited at 9 K.

4.3 Result and Discussion

The UV photo-absorption spectra (220 - 320 nm) of SO₂ ice was recorded after depositing SO₂ on to a LiF substrate cooled down to 9 K temperature (Figure 4. 3). The spectra at a temperature 9 K has a peak position at 280 nm, which is in good agreement with earlier experimental results (Holtom et al., 2006). The spectra recorded after a few hours of irradiation of SO₂ ice with 9 eV photons is shown in Figure 4. 4. The spectra of irradiated SO₂ ice matrix has a larger bandwidth than pure SO₂, possibly due to the product formed from irradiation having characteristic features in the same wavelength range of 230 - 320 nm. The synthesized products in irradiated SO₂ ice would contain S and O, one of the synthesized product is ozone molecule, which has characteristics band known as 'Hartley band' at 220 - 310 nm which overlaps with SO₂ ice (Sivaraman et al., 2014).



Figure 4. 3: Photo-absorption spectra of pure SO₂ ice deposited at 9 K.



Figure 4. 4: SO₂ ice photo-absorption spectra before and after irradiation with 9 eV photons.

The temperature-dependent spectra of irradiated SO₂ ice mix have been recorded (9 - 120 K) to confirm that ozone is a by-product of the irradiation of SO₂ (Figure 4. 5). The bandwidth of the spectra at the higher temperature (>50 K) decreases with increase in temperature. The decrease in bandwidth is due to sublimation of synthesized ozone in the irradiated ice matrix (Sivaraman et al., 2014). Though, at 100 K, the recorded spectra suggest the trapping of ozone molecules in the ice matrix (Figure 4. 5). This temperature dependent spectra of irradiated ice confirms the ozone synthesization in the ice matrix as the temperature dependent spectral changes are in agreement with ozone spectra (Sivaraman et al., 2014).

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The photo-dissociation of SO₂ to SO and O (^{3}P), or SO and O (^{1}D) are the most probable. For SO₂ gas, the dissociation into SO and O (^{3}P) or SO and O (^{1}D) are < 6 eV and < 8eV respectively (Warneck et al., 1964). While dissociation of SO₂ into S and O₂ requires the



Figure 4. 5: Photo-absorption spectra of SO₂ ice before and after irradiation with energetic photons at different temperatures.

breakage of two bonds, for which the probability is very less compare to the first one (Warneck et al., 1964). The dissociation of SO_2 in SO and O provides a large number of oxygen atoms in the irradiated ice mixture. The lifetime of the first excited state atomic oxygen $O(^1D)$ in the ice matrix varies from 32 s to 780 ms at such low temperatures (Mohammed, 1990). As a result the available $O(^1D)$ in the ice mixture reacts with another oxygen atom/other radicals present in the irradiated ice to form oxygen/other molecules or after the isothermal phase, all the excited atomic oxygen $O(^1D)$ will be relaxed back to the ground state $O(^3P)$. The quenching of the excited state (1D) and ground state (3P) is expected to be a rapid process due to frequent collisions in the irradiated ice matrix; so the life-time of electronically excited oxygen atoms are expected to be less than a few micro sec to 100 ns (Mohammed, 1990; Turnipseed et al., 1991; Benderskii et al., 1994). The lifetime of ground state $O(^{3}P)$ atoms at these low temperatures are of the order of hours to days, as atomic oxygen $O(^{3}P)$ does not diffuse at very low temperatures (~10 K) (Krueger & Weitz, 1992), and available oxygen molecules in the irradiated ice mixture react with available oxygen atoms $O(^{3}P)$ to synthesize ozone molecule.

The possible reactions due to irradiation of SO_2 ice with 9 eV photons are as follows:

$$SO_2 + hv \rightarrow SO + O$$
 (3)

$$O + O \rightarrow O_2$$
 (4)

$$O_2 + O \rightarrow O_3$$
 (5)

$$SO_2 + hv \rightarrow S + O_2$$
 (6)

$$SO + O_2 \rightarrow SO_3$$
 (7)

Apart from ozone, other products also formed due to irradiation, and that will be discussed separately. The irradiated ice was warmed, and at a temperature, >30 K, the molecular oxygen present in the ice matrix, will be sublimated out. At temperatures > 60 K, ozone ice starts sublimating, which can be well observed from the spectra (Figure 4. 5), while the ozone can be present in the ice matrix at >100 K (Sivaraman et al., 2014), which was confirmed in this experiment. The ozone was still trapped in the irradiated ice matrix at 100 K. The mass spectra can add more information about the ozone sublimation with respect to temperature.

The observed absorbance value of the irradiated SO_2 ice was much higher than that of pure SO_2 ice due to the higher photoabsorption cross-section of ozone in the irradiated ice matrix. The sublimation of ozone at higher temperatures (>100 K) lowers the absorbance value along with a decrease in the bandwidth of the observed spectra. Loeffler & Hudson, 2016 reported the ozone destruction in the presence of SO_2 and water ice due to thermal reactivity while this experiment confirms the synthetization of ozone in SO_2 ice after irradiation, which does not support the ozone destruction due to thermal reaction with surrounding SO_2 .

This experimental result helps to explain the formation of ozone on the surface of icy bodies in the Solar System. SO₂ is one of the most dominant ice on the Galilean satellites, and these bodies are under irradiation of charged particles present in the magnetosphere of Jupiter, and UV photons from Sun. The irradiation on the ice alters the chemical composition of the icy satellites; alteration time depends on the flux and energy. Callisto is the fourth Galilean moon and orbits in the magnetosphere of the Jupiter; the magnetospheric plasma bombardments are more significant at the icy surface of the satellites. SO₂ is one of the major molecules (with column density of 6 x 10^{18} /cm²) detected on the surface of the Callisto using Hubble Space Telescope's Faint Object Spectrograph in UV range (Noll et al., 1997b). The observed Callisto spectra (Figure 4. 6) has a band in the 220 – 300 nm range overlapping with the SO₂ band.



Figure 4. 6: Callisto's UV spectra observed using the Hubble space telescope, the ratio of leading to trailing hemisphere spectra (Noll et al. 1997b).

The experimental spectra of SO_2 ice are very well studied with a confirmed SO_2 band centered about 280 nm. While the observed band has larger bandwidth than the SO_2 band and needs other bands to fit it. The observational data is a convolution of the three different components in the band: the first one is a band centered about 260 nm, which is corresponding to Ozone known as the Hartley band, which has been shown above the synthesization of it through irradiation of SO_2 using photons. Second is corresponding to a 280 nm centred band, for the presence of SO_2 ice (Noll et al., 1997b, Holtom et al., 2006). The third band is centred around ~309 nm, is an unknown band.



Figure 4. 7: Callisto's data fitted with three different band molecules O_3 (258 nm peaked band), SO_2 (281 nm peaked band) and one unknown band (~309 nm peaked).

The experimental data for irradiated SO_2 ice at 70 K was fitted using two bands viz. the 220 – 280 nm (Hartley band) and the 240 – 300 nm (SO₂ band). The Callisto observational spectra need three different bands for the best fitting, Figure 4. 7, and our experimental data has two of them. Thus, we conclude that *ozone is present on the surface of the Callisto*, and the presence of the third band in Callisto data *peaked at ~309 nm is unknown*. The relative contributions of the three components to the observe band area do not imply that they correspond to the abundance of relative species. Any quantitative estimates are not available due to the unavailability of optical constants of components. To explore this ~309 nm peak band, more experiments need to be performed.

4.4 Conclusion

UV absorption spectroscopy of SO₂ ice was performed in range 240 - 320 nm. The SO₂ ice, deposited at 9 K was irradiated with 9 eV photon for few hours. The irradiation on SO₂ ice leads to the ozone synthesization in the SO₂ ice matrix, confirmed by the presence of the Hartley band in the recorded UV absorption spectra. The experimental result has been used to fit the Callisto absorption feature observed in the UV reflectance spectra of the satellite using Hubble Space Telescope. The experimental data fit the Callisto's observational data with the Hartley band along with the SO₂ band and an unknown band centred at ~309 nm. The Hartley band in the Callisto's data fitting suggests the presence of ozone on the surface of Callisto along with SO₂ ice. The unknown ~309 nm band can be explored, which requires more such experiments to be performed.

Chapter 5

VUV Spectroscopy of Pluto and Charon Ice Analogs

In this chapter, we have presented and discussed the first Vacuum UltraViolet (VUV) photoabsorption spectra of ice analogues of Pluto and Charon ice mixtures. For Pluto the ice analogue is an icy mixture containing nitrogen (N₂), carbon monoxide (CO), methane (CH₄) and water (H₂O) prepared in the ratio with a 100:1:1:3, respectively. For VUV photoabsorption Charon а spectra of an ice analogue containing ammonia (NH₃) and H₂O prepared in the ratio 1:1 was recorded, a spectrum of ammonium hydroxide (NH₄OH) has also been recorded and discussed in details.

5.1 Introduction

Trans Neptunian objects (TNOs) orbit the Sun around 30 AU to hundreds of AU, the temperature of these icy bodies are \sim 30 K. These bodies are thought to be the most primitive bodies in the Solar System. The Pluto system:- Pluto and three satellites (Charon, Nix and Hydra), are a part of TNOs. Pluto is one of a largest object among TNOs and the largest in the Pluto system, with a diameter of nearly 2150 km. Charon,

the biggest satellite of Pluto, has a diameter of 1250 km, while the diameter of Nix and Hydra are below 100 km. The chemical known to be present at Pluto's surface derived from ground-based spectroscopic observations are volatile ices of N_2 and CO, along with somewhat less volatile CH₄ ice, as well as H₂O and C₂H₆ ices and more complex Tholins that are inert at the temperatures of Plutos surface (Cruikshank et al., 2006; DeMeo et al., 2010). Pluto has significant surface variegation, due to the presence of complex organic molecules, which could have been produced through chemical reactions via energetic irradiation under very low temperature.

The chemical composition of Pluto's largest satellites; Charon is reported to be entirely different (Protopapa et al., 2008) with nearly the whole surface covered by water ice, mainly in the crystalline form. The observed absorption features close to 2.2 μ m has been attributed to the presence of an ammonia hydrate (Brown & Calvin, 2000; Dumas et al., 2001, Cook et al., 2007).

Though a part of chemical composition of the Pluto system was observed using ground based telescopes, it has been very difficult to get detailed information about the physical properties of these icy bodies due to their small sizes, low albedo and large distance from Earth. For the same reason; to explore TNOs a dedicated mission, New Horizons spacecraft, was launched by NASA in 2006 and its arrival at the Pluto system, in July 2015, provided the first opportunity to examine these objects in detail (Stern et al., 2008).

5.1.1 New Horizons mission to explore the outer Solar system bodies

To explore the Pluto system and outer Solar system bodies such as KBOs, NASA launched New Horizons with many of scientific instruments aboard on January 19th 2006. The first flyby of the New Horizons to the Pluto system was in July 2015, since then it has been sending the data from its onboard scientific payloads. The LEISA imaging spectrometer and MVIC visible-near-infrared scanning camera data onboard the New Horizons have mapped colors and compositions in the Pluto system.

The color images of Pluto show nonvolatile Tholins covering the heavily cratered equatorial belt of a thousand-kilometers, which must have refreshed its surface swiftly to erase all the craters (Grundy et al., 2016). The infrared observation of the Pluto shows the diverse chemical composition of the body with the spatial distribution of materials on the Pluto's surface such as N₂, CH₄ and H₂O ices along with dark mantles. CO mixed N₂-rich ices, where CO varies spatially and the signature of tholins have been reported which could have produced by solar irradiation in CH₄-rich ices with small amounts of N₂ and CO (Grundy et al., 2016; Protopapa et al., 2017; Schmitt et al., 2017).

The infrared observation of Charon supports its H₂O ice–rich surface as per earlier report, which is unlike other outer solar system icy body. The reddish tholin coloration around its northern pole along with a few highly localized patches rich in NH₃ ice has been seen on the Charon surface (Grundy et al., 2016). These observations from the New Horizons supported the ground based observation and added more information about materials spatial distribution on the Pluto system.

The resurfaceing activity of the Pluto system is allowed by the existence of volatile ices such as N_2 and CO, which mobilize easily at the very low temperatures; 40 K. While H_2O ice on Pluto's surface is are not active on its own, it becomes active in presence of volatile ices of N_2 and CO. CH₄ ice plays a distinct role of its own. The geological diversity of the Pluto's surface has been discussed by Howard et al., 2017 using LEISA and MVIC data.

Apart from the near infrared observation of these ices, the spectra of these ices were measured using the Ultraviolet Imaging Spectrograph, P-Alice, from 50 to 180 nm region. The P-ALICE instrument, an imaging spectrograph onboard the New Horizons observed the Pluto and Charon's surface and atmosphere as well as the Kuiper Belt Objects (KBOs) by UV surface reflectivity measurements of all of these bodies and provided the relative abundances of various species (Stern et al., 2008). The instrument is an off-axis telescope feeding a Rowland-circle spectrograph with a 520–1870 Å

spectral passband, a spectral point spread function of 3–6 Å FWHM, and with a spatial field-of-view of 6 degrees long. Stern et al. 2008 has described the instrument in detail, including descriptions of its ground calibration and initial in flight performance. To explore the P-Alice data we have performed experiments on the Pluto and Charon mix ice.

5.1.2 Experiments reported to-date to understand the Pluto and Charon

The surface of Pluto and Charon are under irradiation of UV radiation from Sun and Cosmic rays, which will drive the chemistry on the icy surfaces. Lya irradiation will be absorbed in the atmosphere of Pluto and will drive the gas-phase reactions in Pluto's atmosphere. Pluto's surface chemistry is mostly driven by energetic particle bombardment (e.g., cosmic rays), while UV radiation is important at the surface during times when Pluto's atmosphere is thinnest. So, both the UV radiation and energetic particles play an important role in the chemical evolution on Pluto's surface. To explore the chemical evolution of the Pluto system's surface, there are many laboratory experiments which have been reported to-date under the Pluto's and other KBOs physical condition. For example, laboratory experiments on simple ice analogs (N_2 , CO, CH₄) has provided the characteristics of ice under different wavelength range which have/can be observed. Though there were no VUV photo-absorption spectra available, when these experiments were carried out. While, the irradiation with energetic particle, electron and UV photons of these ice were reported (Bohn et al., 1994; Moore & Hudson, 2003; Hodyss et al., 2011; Kim & Kaiser, 2012; Wu et al., 2012, Wu et al., 2013).

Bohn et al., 1994 reported the first infrared characteristic of Pluto ice analogs $(N_2:CO:CH_4)$ along with other organic molecular ice diluted in N_2 ice matrix. Moore and Hudson, 2003 reported the irradiation of Pluto ice analogs using 800 keV protons to mimic the cosmic ray irradiation of the surface of Pluto and other TNOs with similar surface ice composition. The irradiation synthesizes NH_3 , HCN, HNC and CH_2N_2 in the ice different matrix due to irradiation. While Kim & Kaiser, 2012 reported the

electron irradiation on the binary ices present on the Pluto's surface, the irradiation synthesized CH_3CHO , HCO and H_2CO in $CO:CH_4$ ice sample and HCN, HNC, CH_2N_2 in $N_2:CH_4$ ice mixture. The irradiation of the Pluto ice analogs with VUV photon and high energy ions helps the understanding of the chemical evolution of these ice analogs under energetic irradiation in ISM or icy bodies conditions.

Other experiments performed on these ice analogs have discussed the refractory residues produced from irradiation of ice and suggested the dark material present on the surface of Pluto and KBO's could be due to irradiation of ices (Strazzulla et al., 2001; Palumbo et al., 2004, Materese et al., 2014; Materese et al., 2015).

Electron irradiation (energy 1.2 keV) on mixed N₂, CH₄, and CO ices leads to the formation of residue materials along with volatiles (Materese et al., 2015). The residue were explored using multiple analytical techniques; Fourier Transfor IR (FTIR) spectroscopy, X-ray absorption near-edge structure (XANES) spectroscopy, and Gas Chromatography Mass Spetroscopy (GC-MS). The infrared spectra suggested the presence of alcohols, carboxylic acids, ketones, aldehydes, amines, and nitriles, which were supported by XANES, GCMS spectra. These materials could be the compositions of the dark materials on the surface of Pluto and other KBOs.

The observational data of the Pluto's surface can be compared with laboratory measured spectra (in corresponding wavelengths) of residues/ices formed in the laboratory. The residues produced from irradiation of ice analogs could be the representative of the complex organics found on Pluto and the experimental bands may be observed by the New Horizons. The details of the experiments reported to understand the Pluto system has been summarised in Table 5. 1.

Table 5. 1: Summary of literature survey of experiments reported to explore the Pluto and Charon System.

References	Ices	Irradiation Source	Investigation range/instruments
Bohn et al., 1994	N ₂ : CH ₄ , N ₂ : CH ₄ : CO, N ₂ , other organics	Non-irradiated	Infrared
Moore & Hudson, 2003	N ₂ : CH ₄ : CO	0.8 MeV Proton	Infrared
Hodyss et al., 2011	N ₂ : CH ₄ : CO: H ₂ O	UV photons	Infrared
Kim & Kaiser, 2012	N ₂ : CH ₄ : CO	5 keV electrons	Infrared
Wu et al., 2012	N ₂ , CH ₄ , N ₂ :CH ₄	VUV photons (9.5, 10.2, and 13.5 eV)	Infrared and VUV
Wu et al., 2013	N2, CH4, N2:CH4	500 eV electrons	Infrared and UV
Strazzulla et al., 2001	CO, N ₂ :CH ₄ :H ₂ O	30 keV ions	Infrared and Raman
Palumbo et al., 2004	N ₂ : CH ₄ : CO, H ₂ O	30 keV H ⁺ , 60 keV Ar ²⁺	Infrared and Raman

Materese et al., 2014	N ₂ : CH ₄ : CO	UV photons	Infrared, X-ray absorption near edge spectroscopy, GCMS, HR-MS
Materese et al., 2015	N ₂ : CH ₄ : CO	1.2 keV electrons	Infrared, X-ray absorption near edge spectroscopy, GCMS

VUV Spectroscopy of Pluto and Charon Ice Analogs

As discussed above, there are many experimental spectra of irradiated ice analogs of Pluto available in different wavelength range but no experimental spectra are available for non-irradiated Pluto and Charon ice analogs in VUV wavelength range (100 - 200 nm). In order to determine the morphology and composition of these ices from P-Alice data it was necessary to record laboratory spectra under appropriate simulation conditions. In this chapter we have reported the first experimental VUV (110–180 nm) photoabsorption spectra of ice analogues of both Pluto and Charon. The details of the experiments and spectral details have been discussed below. This experimental spectral signatures can also be used for other distant icy bodies such as Eris and Makemake.

5.2 Experiment

The present experiments were carried out at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. A detailed description of the experimental setup was provided in an earlier publication (Lu et al., 2005; Lu et al., 2008) and chapter 3. In brief, the incident vacuum ultraviolet light from beamline BL03 was dispersed with a 6 m Cylindrical Grating Monochromator (CGM) and passed through a gold mesh with transmission about 90%; the photocurrent was detected with an electrometer (Keithley



Figure 5. 1: Pluto mix/Charon mix molecules deposition on LiF substrate cooled to 9 K.



Figure 5. 2: Pluto mix with water molecules deposition on LiF substrate cooled to 9 K.

6512) to monitor and to normalize the beam (Lu et al., 2008). To measure an absorption spectrum, a spectrum (I₀) was recorded before deposition of the ice mixtures. Subsequently, the gaseous samples were conducted into the Ultra High Vacuum (UHV) chamber and were deposited on a Lithium Fluoride (LiF) substrate attached to a cold head of a rotary cryostat (APD HC-DE204S) maintained at 10 K. Another spectrum (I) was recorded after deposition of the ice mixtures; by this means, the absorption spectrum was derived based on Beer–Lambert's law.

The spectra of pure ices were recorded at 0.2–0.5 nm and 1.0 nm step sizes whereas the spectra of ice mixtures were recorded at 1 nm to match the step size of P-Alice.

A series of experiments were carried out to explore the VUV spectra of Pluto and Charon ice analogs. The molecules forming the ice film were premixed with required ratio before being let into the UHV chamber and deposited on a LiF substrate attached to a cold head maintained at a temperature of 10 K. The Pluto mixture (N₂:CO:CH₄ in 100:1:1) was also mixed with water in the ratio N₂: CO: CH₄: $H_2O = 100:1:1:3$ and were deposited onto the LiF substrate cooled to 10 K to explore the effect of water in the VUV spectra of the surface of Pluto (Figure 5. 1 & 5. 2). Such a mixture is an analogue of certain regions of Pluto's icy surface due to molecular compositional diversity across different regions in Pluto. In order to mimic the ice layers on Charon, NH₃ (99% pure) and H₂O molecules (in the ratio 1:1) were separately deposited onto LiF cooled to 10 K to form layers (Figure 5. 3(a)) and also pre-mixed NH₃ and H₂O molecules in gas phase were deposited onto the LiF substrate at 10 K to form the mixed molecular ice (Figure 5. 3(b)). Spectra of NH₄OH ice, as a function of temperature, were also recorded to compare with observational data on the surface ices of Charon. Due to the lack of ice thickness values for those ice mixtures used in these experiments we are unable to present the cross-section values for those spectra recorded.



Figure 5. 3: Charon mix ice analogs ((a) NH₃ below H₂O and (b) NH₃ mix with H₂O) molecules deposition on LiF substrate cooled to 10 K.

5.3 Results and Discussions

5.3.1 Pluto Ice Analogue

 N_2 , CO and CH₄ were mixed in the ratio 100: 1: 1 in order to mimic Pluto's chemical composition and the gas mixture was deposited on the LiF substrate maintained at 10 K to form an ice layer of a few nanometers thickness. Spectra were recorded at 10 K after deposition and after warming the ice to 30 K (Figure 5. 4). H₂O molecules were added to the pre-existing mixture (N₂:CO:CH₄): H₂O in the ratio (100:1:1):3 and was made to condense on the LiF substrate at 10 K with subsequent recording of spectra at 10 K and at 30 K (Figure 5. 5).



Figure 5. 4: VUV Photoabsorption spectra of Pluto ice mixtures (without water) at 10 K and warmed to 30 K.

The spectrum recorded at 10 K for the N₂:CO:CH₄ mixture was found to have three distinct sections; absorption at 110–130 nm, 130–160 nm and 160–180 nm. When comparing the characteristics of pure N₂, CH₄ and CO (Table 5. 2) in all these three distinct regions we could clearly observe the contribution from CH₄ and CO absorption in the region 110–130 nm. However, the cross-section for N₂ (Wu et al. 2012) is much lower than the CH₄ and CO so the peaks corresponding to N₂ are not clearly seen in this region. The next region 130–160 nm has peaks corresponding to CO whereas CH₄ and N₂ are not evident as they do not have significant absorption in this region. However, the last part of the spectrum, 160–180 nm, showing continuous absorption is very interesting as the primary molecules used in this experiment do not have significant absorption in this region. Absorption in this region therefore could be from the interaction of N₂, CH₄ and CO molecules at 10 K.



Figure 5. 5: VUV Photoabsorption spectra of Pluto ice mixtures (with water) at 10 K and warmed to 30 K.

N ₂ (nm)	CO (nm)	CH4 (nm)	H2O (nm)	Pluto mix (nm)	Pluto mix + water (nm)
111.5	130.5	110-133	110 - 160	121	121
113.1	132.6			123	123
114.9	135			130	130
116.7	137.2			133	133
118.5	139.7			137	137
120.3	142.2			140	140
122.2	145.3			142	142
123	148.5			145	145
124.5	152.8			148	148
125.2	156.2			152	152
126.8				155	155
127.5					
129.2					
130					
131.8					
132.8					
134.2					
135.6					
137.2					
138.6					
142					
145.5					

Table 5. 2: Peak positions observed in the photoabsorption of pure ices N₂, CO, CH₄, H₂O (Mason et al., 2006) and the Pluto ice mixtures with and without H₂O. The spectral scan steps for ice mixtures were 1 nm. The spectrum recorded after warming the ice mixture to 30 K revealed two distinct regions; 110–130 nm and 130–160 nm but the third absorption region, 160–180 nm, observed at 10 K was found to be absent at 30 K (Figure 5. 4 & 5. 5). At 30 K, absorption between 110 and 130 nm was from both CH₄ and CO but absorption between 130 and 160 nm is only from CO as CH₄ does not have any significant absorption in this region. Absence of further absorption extending to 180 nm at 30 K might be due to the N₂ matrix subliming off at 30 K leaving behind CH₄ and CO. These suggest the absorption in the 160–180 nm at 10 K could be due to the interaction of CH₄, CO with the N₂ molecules.

The spectrum recorded after adding H_2O molecules to the gas mixture and then depositing the refined mixture at 10 K was found to be similar to that recorded without the H_2O molecules. No significant changes in the spectrum were seen throughout the spectrum. This could be due to the H_2O absorption falling well within the 110–130 nm/130–165 nm regions, which is already present in the absorption spectrum of the ice mixture without H_2O . The spectrum at 30 K for the mixture with H_2O was similar to the spectrum recorded without H_2O . This clearly shows even warming up the ice has no significant H_2O effect in the photoabsorption spectrum recorded at 30 K. Temperature on Pluto surface is slightly warmer than those results presented in the experimental data. By increasing the temperature further, in experiments, molecular ice mixture was found to desorb. Therefore, spectra up to 30 K were presented for Pluto ice mixture.

5.3.2 Charon Ice Analogue

In order to experimentally simulate the conditions on Charon's surface (temperature ranges from 50 to 60 K), H₂O and NH₃ ices were studied in layered and mixed deposits on a LiF substrate cooled to 10 K with a 1:1 ratio. (Figure 5. 8 & 5. 9) presents a comparison of the VUV photoabsorption spectra of these layered and mixed ices with that of the pure H₂O and NH₃ ices. Pure NH₃ ice has a broad absorption band from 110 to 200 nm with maximum absorptions at 125 and 178 nm. Pure H₂O ice has a broad band extending till 160 nm with the maximum absorption at 145 nm. Photoabsorption spectrum of layered ices NH₃ below H₂O has a band from 110 to 200 nm with three absorption peaks at 125 nm, 145 nm and 178 nm. However, in the mixed H₂O and NH₃ ices there are only two distinct maximum absorptions at 125 and 180 nm as this could be due to the difference in the absorption cross-section of these two molecules.



Figure 5. 6: VUV Photoabsorption spectra of Charon ice mixtures at 10 K mixed and layered deposits, compared with the pure astrochemical ices of NH₃ and H₂O at 10 K, and a product of ammonia and water: NH₄OH.



Figure 5. 7: Temperature-dependent VUV photoabsorption spectra of NH₄OH.

On the surface of icy satellites like Charon, rich in H₂O and NH₃, the presence of NH₄OH is inevitable (Moore et al., 2007). It is evident from Figure (5. 6, 5. 8 & 5. 9) that the characteristic absorption of NH₄OH closely resembles that of NH₃–H₂O ice mixtures except for the tail which extends up to 190 nm. NH₄OH ice has a maximum absorption band centered at 120 nm and 145 nm followed by another absorption band centered at 172 nm, where these two peaks arise from the OH and NH absorptions, respectively, in the NH₄OH molecule. Spectra recorded by warming up the NH₄OH ice up to 130 K did not show any significant change and beyond 130 K the ice was found to sublime (Figure 5. 7).



Figure 5. 8: Temperature dependent VUV photoabsorption spectra of Charon ice analogue NH₃ below H₂O.

Unlike the Pluto ice mixtures where sublimation of molecules were observed at very low temperatures, Charon ice mixtures were warmed up to 150 K due to the larger concentration of H₂O governing the ice mixture sublimation. From spectra (Figure 5. 8) acquired at various temperatures during the warm-up process the matrix effect was clearly seen for the layered ice deposit NH₃ below H₂O. Due to a phase change in NH₃ ices (Dawes et al., 2007; Zheng et al., 2009), the spectral band in the 160–180 nm region was found to significantly shift in the absorption peak for the spectra recorded at 80 K. For these ice mixtures such change in peak position was not observed though infrared spectral studies using a similar mixture report phase change to take place in the NH₃–H₂O ice mixture (Figure 5. 9). The 145 nm peak that corresponds to H₂O appears in the ice mixture at 150 K is due to the sublimation of NH_3 molecules. The rest of the peaks corresponding to NH_3 show that the molecule is still trapped in the H_2O matrix.



Figure 5. 9: Temperature dependent VUV photoabsorption spectra of Charon ice analogue NH₃-H₂O mixture.

5.4 Conclusion and Implications

VUV photoabsorption spectra of the dominant ices on Pluto and Charon were recorded over a range of temperatures. When found in mixtures, interaction between the molecules N₂, CH₄ and CO were found to contribute to an additional absorption beyond 160 nm until 180 nm which is transparent in the respective pure ices. Addition of H₂O molecules did not affect the spectra recorded for the prime ice composition of Pluto. By simulating Charon's chemical composition using NH₃, H₂O mixtures and NH₄OH molecules we could clearly observe typical absorption bands that will allow us to know whether NH₃ exist as a mixture with H₂O or as a layer below H₂O. The difference in absorption limit for NH₃-H₂O mixture/layered deposit and NH₄OH ice may be used to differentiate between the mixtures and NH₄OH. The lack of UV absorbing atmosphere over Charon makes it easier to compare the results presented. A graphical representation of this work is provided in Figure 5. 10. Future laboratory simulation experiments will focus on the changes in the photoabsorption spectra due to irradiation of such mixtures that are studied at conditions commensurate to Pluto and Charon.



Figure 5. 10: The graphical representation of VUV Photoabsorption spectra of Pluto and Charon ice analogs.
Chapter 6

Infrared attenuation in crystalline propargyl ether ices

6.1 Introduction

In this chapter, we have discussed a temperature dependent study of the IR spectrum of propargyl ether ($C_3H_3OC_3H_3$). Our experiment has shown very interesting results when we investigated the morphology of $C_3H_3OC_3H_3$ ices under astrochemical conditions. This experiment will be very useful for future missions for astronomical observations at infrared wavelengths.

6.1.1 Infrared observation of interstellar ices

InfraRed (IR) spectroscopy plays a vital role in the study of interstellar molecules both in space-based observations and in laboratory simulations. The *Infrared Space Observatory* and the *Spitzer* space telescope operating in the Mid and Far IR wavelengths have been widely used to explore the icy nature of molecular clouds and their chemical composition by comparing the spectral features observed in the InterStellar Medium (ISM) with measurements in laboratory ice analogues. It is a powerful technique to directly observe the solid-state inventory of dense molecular clouds using background stars as a light source. The spectra observed from these Space based telescopes play a vital role in understanding the evolution of ice in low-mass protostellar environments and in find correlations, if any, between interstellar and solar system ices.

Most of the simple molecules identified in the interstellar medium are due to observation at infrared wavelengths. Here we list the few simple molecules observed in a number of sources observed in ISM. Gibb et al., 2000 reported a complete midinfrared (2.4 - 25 µm) spectra of young stellar object W33A using Short Wavelength Spectrometer of the Infrared Space Observatory (ISO). The observed spectra had major absorptions bands centered at 3.0 and 9.7 µm, which was identified to be the characteristics of water ice and silicate respectively. They calculated the column density of the icy molecules towards W33A using spectral features observed in 2.4 -5.0 µm region, which has stretching and combination mode of many ices. The column density of water $N(H_2O) = (1.1 \pm 0.3) \times 10^{19}$ cm⁻². The solid NH₃ characteristics in the line of sight of W33A was observed for the first time by Gibb et al. 2000 using inversion-mode feature at 9.0 μ m, the column density $N(NH_3) = (1.7 \pm 0.4) \times 10^{18}$ cm⁻ ², which was $\sim 15\%$ relative to H₂O towards W33A. The CH₃OH abundance was reported to be ~20%- 30% in energetic processed ices of W33A and GL 7009S. The summary of literature survey on the observation of astronomical objects are given in Table 6. 2.

The survey of molecular ice in (Young Stellar Objects) YSOs such as W33A, the observation was carried out in many other sources, Gibb et al., 2004 observed dark clouds and diffuse interstellar medium, in 2.5–30 μ m using the Infrared Space Observatory. The observed spectra had characteristics of simple molecules in the ices identified as H₂O, CO, CO₂, CH₃OH, and CH₄. With very low abundances of OCS, H2CO, and HCOOH. The evidence NH₃ and OCN⁻ ice features was also observed, but

not confirmed. They observed excess absorption at 6.0 μ m which cannot be solely attributed to H₂O ice. Later Boogert et al., 2004 reported the observation of absorption characteristics of ices in low-mass protostars B5 IRS1 and HH 46 IRS in 5–38 μ m using the Spitzer Space Telescope and at 3–5 μ m using ground-based telescopes. They observed 15 μ m characteristic of CO₂ bending mode. The column density ratio CO₂: H₂O in B5 IRS1 and HH 46 IRS was reported to be very high ~35%, while the CH₃OH abundance was reported to be very low form ground-based observation.

The absorption spectra of ices toward the stars behind the Taurus molecular clouds was observed at $5 - 20 \,\mu\text{m}$ using Spitzer IRS (Knez et al., 2005). The observed spectra have characteristic bands at 6.0 μm is the bending mode of H₂O ice and mixtures of water ice with other ice. The CO and CO₂ ice abundance was reported to be 20%–40% with respect to H₂O ice from the observed spectra. They also reported very low abundance of HCOOH and possibly NH₃.

The details of the ices in different sources in ISM (with column abundances) have been provided in Table 6. 1. Infrared spectroscopy is best tool to observe the simple molecular ice and the functional group of the organic molecular ices. And also it is very useful to observe the phase of the ice and thermal processing of ices. Laboratory experiments were performed under astrochemical conditions to understand the physical properties and chemical evolution of astrochemical ices.

Table 6. 1: Interstellar ices (with column density) observed in a few protostars, dense molecular clouds using infrared spectroscopy, the superscript (a, b, c..) are references mentioned in Table 6. 2.

Molecules		Colu	ımn densi	ty (10 ¹⁷ cm ⁻	²)	
	W33A	B5 IRS 1	HH 46	Elias 13	Elias 16	CK 2
H ₂ O	110 ^a	22 ^b	80 ^b	10 °	84 °	35°
CO (polar)	6.6 ^d	1.6 ^b	1.5 ^b			
CO (nonpolar)	2.3 ^d	2.7 ^b	0.5 ^b			
CO ₂	14.5 ^e	3.7 ^b	3.2 ^b	1.5 °	2.4 °	3.3 °
¹³ CO ₂	0.27 ^f					
CH4	1.7 ^g				0.3 ^c	0.3 ^c
CH ₃ OH	19.5 ^h			0.08 ^c	0.23 °	0.21 °
H ₂ CO	7.1 ⁱ					
НСООН	7.8 ^j					0.19 °
CH ₃ HCO	10.8 ^j					
NH ₃	17 ^a			0.6 °	0.8 ^c	0.8 ^c
XCN	3.8 ^d					

Authors	Instruments/Telescope	Object	Reference
Gibb et al., 2000	ISO	W33A	a
Boogert et al., 2004	Spitzer	B5 IRS 1, HH 46	b
Knez et al., 2005	Spitzer	Elias 13, Elias 16, CK 2	C
Chiar et al., 1998	Ground based	W33A	d
Gerakines et al., 1999	ISO	W33A	e
Boogert et al., 2000	Spitzer	W33A	f
Boogert et al., 1996; 1998	Spitzer	W33A	g
Chiar et al., 1996; Dartois et al., 1999	Ground based	W33A	h
Keane et al., 2001; Brooke et al., 1999.	ISO	W33A	i
Schutte et al., 1999	ISO	W33A	j

Table 6. 2: Literature survey of infrared observation of ices in ISM.

6.1.2 Phase changes in astrochemical ices

The investigation of astrochemical ices and their corresponding IR spectra at temperatures compatible to the ISM (10 K) laboratory ices prepared in what is usually attributed to the amorphous phase; where the molecules in the ice have random orientation. After deposition, such ices are warmed gradually or at a fixed heating rate (such as 0.5 to few K min⁻¹) to mimic thermal processing of such ices in the ISM e.g. by shocks. The subtle changes appearing in the IR spectra during the warmup phase may be related to the conformational changes related to homodimers (Sivaraman et al., 2013). However, significant changes that appear in the spectra, such as band splitting along with the appearance of sharper bands, are related to the phase change from amorphous to crystalline that take place within the ice.

Sivaraman et al. 2013 reported the subtle changes in the IR spectra of the formamide ice during warm up. They observed the phase transition in formamide ice between 155 – 160 K while warming up the formamide deposited at 30 K. At temperatures below and above the phase transition temperature they have observed spectral changes attributed to be the rearrangement between formamide dimers and polymers. Recently, by observing such changes in the IR spectra an unexpected reversible phase change was reported to occur in astrochemical ethanethiol ices (Pavithraa et al., 2017). Thus, infrared is the best tool to explore the structural changes in the astrochemical ices during its thermal and energetic processing.

6.1.3 Propargyl ether

Propargyl ether (C₃H₃OC₃H₃) is an isomer of phenol (C₆H₅OH), the laboratory rotational spectroscopy of C₆H₅OH has been done by Kolesnikova et al., 2013, and identified a number of coincidences between transitions of C₆H₅OH and unassigned lines in observation of Orion between 80 and 280 GHz (Tercero et al. 2012) and reported phenol abundance (tentative detection) in Orion KL (with a predicted column density of $\sim 8 \pm 4 \times 10^{14}$ cm⁻²).

Propargyl ether is regarded as one of the interesting molecules, awaiting discovery in ISM, in understanding the chemical complexity that surrounds the evolution of aromatic molecules in icy mantles. Though there are no experimental analysis available for the propargyl ether to-date. There are however, laboratory experiments on propargyl containing compounds which are limited to the study of propargyl alcohol ices (Hudson & Moore, 2018; Saini & Viswanathan, 2017; Sivaraman et al., 2014) and to-date, no IR and Vacuum UltraViolet (VUV) spectroscopic data are available for propargyl ether ices at temperatures commensurate with the ISM. Accordingly, propargyl ether IR and VUV spectra were recorded as a function of temperature and the observations made in both the amorphous and crystalline phases of propargyl ether.

6.2 Experimental methodology

Experiments were carried out in the 10 K astrochemical ices simulation chamber housed at the Physical Research Laboratory (PRL), India. The apparatus consists of an UltraHigh Vacuum (UHV) chamber operating at a base pressure of about 10^{-10} mbar. A sample holder containing a Zinc Selenide (ZnSe) window, used as a dust analog to form icy mantles, was cooled to 10 K using a closed cycle cryostat. Propargyl ether molecules drawn from a liquid reservoir were allowed to deposit, 30 mbar in 230 s, on the cooled ZnSe window to form an ice film Figure 6. 1. For deposition at 150 K and 170 K, a similar deposition rate was maintained. A Fourier Transform InfraRed (FTIR) spectrometer operating in the mid-IR (4000–550 cm⁻¹, step size 2 cm⁻¹) is used to probe the morphology of the propargyl ether ices. Spectra of the ice were then recorded as the ice was warmed to higher temperatures, at a rate of 5 K min⁻¹, until the propargyl ether sublimated from the ZnSe window.



Figure 6. 1. Propargyl ether vapour dep ZnSe substrate cooled to 10 K.

Vacuum UltraViolet (VUV) photoabsorption spectra of propargyl ether ices were also recorded using the experimental setup at the 03A1 beamline facility at NSRRC (Lu et al., 2005; Lu et al., 2008). A Lithium Fluoride (LiF) window was used as substrate, cooled down to 10 K onto which propargyl ether was deposited to form an ice Figure 6. 2. In order to obtain the VUV spectra of such films a spectrum of the LiF window was obtained prior to deposition *Io* and after deposition, *I*. By employing the Beer-Lambert law the absorbance of the ice could then be obtained. By warming the sample to higher temperatures and recording spectra at each temperature the temperature dependent VUV spectra of propargyl ether ices were obtained. In both the experiments the propargyl ether samples (purity 98%) were obtained from Sigma Aldrich.



Figure 6. 2. Propargyl ether vapour dep LiF substrate cooled to 10 K.

6.3 Result and discussion

The IR spectrum recorded after depositing propargyl ether molecules at 10 K, was observed to contain several peaks in the 4000–550 cm⁻¹ mid-IR region (Table 6. 3, Figure 6. 3). A peak corresponding to CH stretching was observed at 3492 cm⁻¹ and the band at 3061 cm⁻¹ was assigned to the characteristic CH₂ asymmetric stretching vibration. Whereas, the band at 2964 cm⁻¹ was assigned to the CH₂ symmetric stretching. The C=C stretching vibration in the propargyl ether molecule was observed at 2120 cm⁻¹. The set of bands observed at 1445 cm⁻¹, 1404 cm⁻¹/1347.5 cm⁻¹ and 1267 cm⁻¹/1248 cm⁻¹ was attributed to the CH₂ scissoring, CH₂ wagging and CH₂ twisting vibrations, respectively.



Figure 6. 3: IR spectra of propargyl ether ice deposited at 10 K.

Table 6	. 3.	Pea	ak p	position of	IR ba	nds observe	ed in a	amorphous	prop	argyl ether ice
formed	at	10	Κ	compared	with	calculated	band	positions	and	corresponding
assignm	ents	5.								

Amorphous (10 K), cm ⁻¹	Calculated, cm ⁻¹	Assignments (mode)
3960	3972.2	$(v_{20}+v_5)$
	3969.4	$(v_{20}+v_6)$
3914.5		
3627	3626.9	$(v_{25}+v_3)$
	3645.1	$(v_{22}+v_6)$
3492	3467.2	CH stretching(v_2/v_1)
	3467.3	
3283	3287.1	$(v_{28}+v_5)$
	3284.3	$(v_{28}+v_6)$
3248.5	3266.5	(v ₂₉ + v ₅)
	3263.7	$(v_{29}+v_6)$
3061	3081.6	CH ₂ asymmetric stretching(v ₄)
	3086.8	CH ₂ asymmetric stretching(v ₃)
2964	3034.1	CH_2 symmetric stretching(v ₅)
	3031.3	CH ₂ symmetric stretching(v ₆)
2908		
2860	2837.7	$(v_{12}+v_9)$
2120	2121	C≡C stretching(v ₇)
	2119.9	$C \equiv C$ stretching(v ₈)
2021	2036.1	$(v_{21} + v_{11})$

1953.2	1973.9	$(v_{21} + v_{12})$
1624	1620.5	$(v_{21} + v_{18})$
1445	1487.4	CH ₂ scissoring(v ₉)
	1476.5	CH ₂ scissoring(v ₁₀)
1404	1412.5	CH_2 wagging(v ₁₁)
1383	1391.4	$(v_{30} + v_{14})$
1372	1365.1	$(v_{26} + v_{20})$
1361.7	1347.9	$(v_{28} + v_{15})$
1347.5	1350.3	CH ₂ wagging(v ₁₂)
1293.5	1290.3	$(v_{28} + v_{16})$
1267	1251.8	CH ₂ twisting(v ₁₃)
1248	1243.3	CH ₂ twisting(v ₁₄)
1143.5	1145	$(v_{30} + v_{18})$
1080.5	1094.9	C-O stretching(v ₁₅)
1047	1040.8	$(v_{26} + v_{22})$
1035.6	1037.3	CH ₂ rocking (v ₁₆)
1007	1010.5	C-C stretching/COC bending/CH ₂ rocking (v ₁₇)
980	994.5	CH ₂ rocking(v ₁₉)
	996.9	C-O stretching(v ₁₈)
942	938	C-C stretching(v ₂₀)
918	931.6	$(v_{27} + v_{21})$
903.5	921.8	$(v_{27} + v_{22})$
881.5	884.9	$(v_{27} + v_{23})$

Infrared attenuation in crystalline propargyl ether ices

	883	$(v_{27} + v_{24})$
744	761.8	$(v_{30} + v_{22})$
	724.9	$(v_{30} + v_{23})$
	723	$(v_{30} + v_{24})$
685.5	680	$(v_{28} + v_{26})$
646.5	657.4	$(v_{32} + v_{23})$
610	623.5	CH bending(v ₂₁)
	613.7	CH bending(v ₂₂)
range out of 4000–600 cm ⁻¹	576.8	CH torsion(v ₂₃)
	574.9	CH torsion(v ₂₄)
	575.1	$(v_{30} + v_{26})$
	540.1	CCO in plane bending(v ₂₅)
	427	CCC in plane bending (v_{26})
	308.1	CCC in plane bending(v ₂₇)
	252.9	CCC out of plane bending(v ₂₈)
	232.3	CCC out plane bending(v ₂₉)
	148	CCH bending(v ₃₀)
	95.1	COC out of plane bending (v_{31})
	80.6	CCH bending(v ₃₂)
	43.7	CH ₂ bending(v ₃₃)

Infrared attenuation in crystalline propargyl ether ices

The band at 1080.5 cm⁻¹ was then attributed to the C-O stretching, whilst the adjacent band at 1035.6 cm⁻¹ corresponds to the CH₂ rocking vibration. The ether link, in the propargyl ether molecule, COC bending vibration was observed at 1007 cm⁻¹. However, this band can also be attributed to C-C stretching vibration too. The bands at 980 cm⁻¹ and 942 cm⁻¹ can be attributed to the CH₂ rocking/C-O stretching and C-C stretching vibrations, respectively. The band closest to the spectral limit used in this experiment was observed at 610 cm⁻¹ and that corresponds to the CH bending vibration. The band at 578.5 cm⁻¹ can be attributed to the CH torsion. Combination bands are also provided in Table 6. 3.



Figure 6. 4. IR spectra of propargyl ether ice at 10 K, 20 K and 50 K.

After slowly warming the ice, the spectrum recorded at 20 K, 50 K (Figure 6. 4) to 150 K with many interval temperature was observed to have become more intense when compared to that at 10 K though the spectral features are similar. In addition to that there was significant reduction in the transmittance (Figure 6. 5). This is peculiar since the number of absorbers has not changed. At still higher temperature the spectrum recorded at 170 K changes dramatically with significant alteration in the spectra especially in the 1500–600 cm⁻¹ region (Figure 6. 5) and the transmittance was observed to have reduced significantly. It was not straightforward to assign the bands, in the 1500–600 cm⁻¹, in the IR spectrum recorded at 170 K, so the bands observed at 170 K are given in a separate Table 6. 4.



Figure 6. 5. IR spectra of propargyl ether ice at 10 K, 150 K, 160 K and 170 K (phase change) (the rate of heating was 5 K min⁻¹).

Apart from the sharp spectral changes the attenuation observed in the IR wavelength is seen to increase at the higher temperature as the phase changes from amorphous to crystalline in the propargyl ether ices. This is an extremely unexpected result. Such a dramatic change has consequences for interpreting astronomical data where such a change in absorption could be interpreted as a change in number density.



Figure 6. 6: IR spectra of crystalline propargyl ether ice deposited at 170 K compared with the crystalline ice spectra at 10 K by cooling the sample deposited at 170 K.

The spectrum recorded after cooling the crystalline propargyl ether ice to 10 K, was observed to have similar transmittance as to the crystalline ice at 170 K (Figure 6. 6). The phase change was irreversible and the transmittance observed was found to be related to the phase change from amorphous to crystalline. Similar drastic reduction in transmittance was observed in the IR spectrum recorded after depositing propargyl ether samples at 170 K (Figure 6. 7).



Figure 6. 7: IR spectra of crystalline propargyl ether ice deposited at 170 K compared with the spectra of propargyl ether ices deposited at 10 K and 170 K.

Crys	stalline (170 K),	cm ⁻¹
4338	2054.5	1269.3
3945.5	2009.6	1236.7
3913.7	1977.5	1094
3291.7	1457.6	1026.1
3283	1451.8	1000
2924	1444	987
2900.8	1403.7	937
2864.7	1395.5	913.4
2785	1350.2	701.4
2130	1336.7	686.5
2125.4	1321	673
2106	1296.3	635
2071.8		

Table 6. 4. Tentative peak positions of bands observed in crystalline propargyl ether ice obtained by warming the ice from 10 K to 170 K.

Two prominent bands were observed in the VUV spectra of propargyl ether recorded at 10 K (i) in the 170–210 nm with a peak at 192 nm and (ii) in the 110–170 nm region with a broad band 130–160 nm region (Figure 6. 8). Upon warming the ice to higher temperatures, 100 K–150 K the band at 130–160 nm was observed to grow in intensity

and the peak at 192 nm seen to red shift by ~ 2 nm (Figure 6. 8). The spectrum at 170 K was observed to have spectral features in both the 110–170 nm and 170–210 nm regions. Further VUV spectral data analysis is not detailed in this manuscript, because the motivation behind the VUV spectral recording of propargyl alcohol was to investigate whether attenuation happens at wavelengths other than IR when propargyl ether ice turns from amorphous to crystalline. The VUV spectra recorded as a function of temperature clearly indicates no significant attenuation of propargyl ether ice in the 110–210 nm wavelength.



Figure 6. 8: Temperature-dependent VUV spectra of propargyl ether ice.

6.4 Conclusion

Propargyl ether ices formed under astrochemical icy conditions were probed by IR and VUV spectroscopic techniques. IR spectroscopy revealed that after the phase change occurred, from amorphous to crystalline, IR photons are strongly attenuated in the crystalline propargyl ether ices. For the ice probed in the VUV spectral region such an attenuation linked to phase change was not observed. Therefore, here we report the first astrochemical ice, propargyl ether, that attenuates IR photons in the mid-IR region upon phase change from amorphous to crystalline. Such an effect may be due to a change in refractive index of the propargyl ether ice. The summary of the experiment is represented in Figure 6. 9.

This experimental result has implications as the next space borne and highly sensitive, James Webb Space Telescope, will be probing the ISM at IR wavelengths and the presence of such astrochemical ices attenuating IR photons, will lead to the interpretation and analysis of IR data not being straight forward. Our observations will be useful in this regard. However, Therefore, many more laboratory experiments will be required to find if such effects are observed in other pure astrochemical ices or in similar ice mixtures.





Chapter 7

Residue from irradiated benzene ices

7.1 Introduction

In this chapter, we will discuss the Scanning Electron Microscope (SEM) image of the residue obtained from the UV irradiation of the Benzene, which provides the spectacular structure of the refractory materials. This is the first ever experiment showing the presence of dust particles with a crystal like structure in the interstellar medium. The details of the experiments and results have been discussed in following sections.

7.1.1 Organics in the ISM

Infrared observation of the Interstellar Medium (ISM) show the presence of different characteristic bands corresponding to C-H stretching, C-C stretching and different other modes which confirms the rich abundances of the organic molecules in the ISM. Simple organic molecules such as CH_4 , C_2H_2 , C_2H_6 , C_6H_6 to the first aromatic complex molecule Benzonitrile (C_6H_5CN) have been observed in ISM (Lacy et al., 1989; Boogert et al., 1996; Cernicharo et al., 1999; Cernicharo et al., 2001; McGuire et al., 2018). The signature of PAHs which could be precursors of prebiotic molecules have

also been observed in ISM (Cherchneff et al., 1992; Cherchneff, 2011), these PAHs are thought to be one of the sources of carbonaceous dust in the ISM, formed under energetic irradiation. Many PAHs consisting of a large number of carbon chains have been discovered in carbonaceous meteorites such as benzene fused Naphthalene (Elsila et al., 2005). The intense 3.4 µm band observed in the ISM has been identified as a characteristic feature of amorphous hydrogenated carbon (a-C:H) dust particles, containing mixtures of aromatic and amorphous hydrogenated carbon (Chiar et al., 2013). Most recently Mixed Aromatic/Aliphatic Nanoparticles (MAONs) have been proposed to explain other spectral signatures that are observed in the ISM (Kwok & Zhang, 2011).

To-date a large number of irradiation experiments have been carried out on simple organic molecules; CH_4 , C_2H_2 , C_2H_6 with charged particles, protons and UV photons to understand the formation of complex organics and PAHs in the laboratory under astrochemical conditions (Foti et al., 1984; Calcagno et al., 1985).

The recent detection of benzonitrile (C_6H_5CN) in interstellar space (McGuire et al., 2018) has heated up the discussion of formation and evolution of complex aromatic molecules in the ISM in the field. There have been a number of experiments carried out to understand the formation and evolution of these types of aromatic organic molecules in ISM. To address these types of problems, we have chosen a simple aromatic, C_6H_6 to carry out an VUV irradiation experiment on it.

7.1.2 VUV spectra of Benzene ice

The simple aromatic molecule benzene, C_6H_6 , has an important place in the list of astrochemical molecules due to its ring structure that is the basis for all the polycyclic aromatic hydrocarbon (PAH), the caged carbon molecules (such as Fullerenes) also has the ability to create aromatic dust. The discovery of benzene in the ISM (Chernicharo et al., 2001) was a major stepping stone in associating PAH molecules with the unidentified bands in the infrared and in the ultraviolet where in the infrared the

 $3.28 \,\mu\text{m}$ band observed in the ISM was assigned to the aromatic component of the hydrocarbon content (Chiar et al., 2000).

Many laboratory experiments have been carried out to understand the fundamental characteristics of pure benzene ice formed under the astrochemical conditions and gaseous benzene. Dawes et al., 2017 reported the VUV spectra of pure benzene ice in 120 - 240 nm. They have reported a single electron $\pi^* \leftarrow \pi$ transition from ground state ${}^{1}A_{1g}$ to three excited singlet states ${}^{1}B_{2u}$, ${}^{1}B_{1u}$ and ${}^{1}E_{1u}$ which was observed at 120 and 340 nm. In solid benzene, the ${}^{1}E_{1u} \leftarrow {}^{1}A_{1g}$ transition band centered at 192 nm with 14 nm redshift to that of benzene vapor. ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ transition band centered at 210 nm with 10 nm red-shift, ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ transition band centered at 255 nm with 2.5 nm average shift in the vibronic bands to that of vapor phase benzene. The two electron transitions ${}^{1}B_{1u}$, ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ have vibronic structure and are observed due to Herzberg-Teller coupling with intensity borrowed from ${}^{1}E_{1u}$ state via vibrational mode. The deposited benzene ice at 10 K are amorphous and crystallizes at 90 K.

7.1.3 Organic Residue/Interstellar dust

The surfaces of Cold Interstellar Dust (CID) are now thought to provide the main sites for the synthesis of complex molecules in the interstellar medium. The icy mantles of such CIDs are composed of a mixture of molecules which may be processed by a variety of energetic particles (*e.g.* UV photons, cosmic rays) leading to the formation of even more complex molecules. The majority of these synthesized molecules are latterly released into the gas phase by thermal desorption allowing them to be identified most commonly by microwave and millimeter wave spectroscopy. However, if the synthesized molecule does not sublime, even at higher temperatures (say around 300 K), then a residue remains on the existing dust surface which may then be further processed.

Many laboratory experiments have been carried out to understand the formation of organic molecules and also their dissociation both in pure ((Callahan et al., 2013) and references therein) and in mixtures of ices ((James et al., 2019) and references therein).

The irradiation of the organic molecules leads to the formation of the refractory material, residue at higher temperature, at which all the derivative volatile products sublimate from the synthesized products. The residue from simple organics (CH₄) is more complex carbon like material having very less reflectance as the amorphous carbon or other organic material; charcoal (Calcagno et al., 1985). The imaging of organic residue has been reported to be the fluffy structure of the molecules (Calcagno et al., 1985).

The irradiation on pure benzene ice and mixed with other molecules such as carbon dioxide, water, ammonia synthesized refractory materials along with the volatiles as byproducts from in irradiation sample ice. (Materese et al., 2015; McMurtry et al., 2016; James et al., 2019). The list of the literatures on the residue from irradiated benzene ice is given in the Table 7. 1. James et al., 2019 has reported the formation of residue in the electron irradiated benzene: CO_2 ice mix. The obtained residue had the characteristics of the benzoic acid. Strazzulla & Baratta, 1991 carried out irradiation experiments on benzene ice with keV protons, the irradiation synthesized many volatile byproducts along with residue, the residue remain on the substrate at higher temperature was reported to be new aromatic species having characteristics band in the aromatic region of the infrared characteristics of the residue was more intense than that of pure benzene.

Callahan et al., 2013 reported the residue formation form proton irradiated ice. The chemical composition of the residue was found to be polyphenyls as per GC-MS analysis. These polyphenyls could be the reason the intense IR bands of the residue synthesized by Strazzulla & Baratta, 1991. Many other experiments were reported for the chemical analysis of residue synthesized in irradiated benzene ice. But the physical structure of the residues that are synthesized *in situ* have been only partially explored to-date. We have reported the results on the physical structure of the residue obtained from the Vacuum UltraViolet (VUV) photon irradiation of benzene ices.

Reference	Pure/Mix	Observation	$T_{dep}(\mathbf{K})$	Irradiation source
		Technique		
Dawes	C ₆ H ₆ (Pure), C ₆ H ₆ : H ₂ O	VUV	25 K	No irradiation
Strazzulla	C ₆ H ₆ (Pure)	IR	77 K	3 keV He
Callahan	C ₆ H ₆ (Pure)	GCMS	19 K	0.8 MeV H ⁺
Ruiterkamp	C ₆ H ₆ (Pure), C ₆ H ₆ : Ar,	IR	14 K	0.8 MeV H^+ , 7.4 eV photons
	C ₆ H ₆ : H ₂ O, C ₆ H ₆ : CO,			
	C6H6: CO2			
Brunetto	C ₆ H ₆ (Pure)	IR	80 K	200 keV H ⁺ , 200 keV Ar ⁺ , 400 keV Ar ⁺⁺
Materese	C ₆ H ₆ : H ₂ O, C ₆ :H ₆ : NH ₃	GC-MS	15 - 20 K	121.6 nm photons
James	C ₆ H ₆ : CO ₂	VUV	20 K	1 keV electron
Calcagno	C ₆ H ₆ : CO ₂	IR	10 K	5 keV electron

Table 7. 1: Literature study of irradiation of benzene ice.

7.2 Experiment

The experiments were performed using the high flux beamline BL 03 on the Taiwan Light Source (TLS) at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. VUV light was dispersed with a cylindrical grating monochromator (focal length of 6 m) on a bending magnet beamline of a storage ring (1.5 GeV). More details of the experimental station can be found in the earlier publications (Lu et al., 2005; Lu et al., 2008). VUV transmission spectra were recorded before and after the deposition of the molecular ice to obtain the incident (I₀) and transmitted (I_t) intensities from which absorbance are calculated using the Beer-Lambert law. The minimum cut off wavelength is determined by the material used for the entrance and exit windows, in this case, lithium fluoride (LiF). In all the spectra a step size of 1 nm was used.



Figure 7. 1: VUV photo-absorption spectroscopy of Benzene ice at 4 K.

Benzene (Sigma-Aldrich 99.8% pure) was deposited on a LiF substrate cooled to 4 K using a Sumitomo RDK helium cryostat, the base pressure of chamber was $3.7 \ 10^{-8}$ Torr (Figure 7. 1). The pressure in the gas line filled with benzene vapour was 31 Torr. Since the aim of our experiment was to synthesize enough of the residue to allow images to be recorded we prepared quite a thick sample by depositing benzene onto the LiF substrate for 15 min at a pressure of 7 x 10^{-8} Torr in the chamber.



Figure 7. 2: Photo-irradiation (with 9 eV photons) of benzene ice at 4 K.

The photo-absorption spectrum of pure benzene ice was recorded, then the ice was irradiated with 9 eV (137.8 nm) photons for a minimum of 9 h and up to a maximum of 25 h (Figure 7. 2). Spectra were recorded after irradiation and the irradiated ice was then warmed to 300 K, with spectra recorded at 10 K intervals. After reaching 300 K the sample was left prior to being removed from the chamber and coated with a 5 nm gold/palladium coating before being placed in the sample mount of a Field Emission Scanning Electron Microscope (FE-SEM).

7.3 Result and discussion

The VUV spectrum of benzene ice formed at 4 K is shown in Figure 7. 3 and the spectral signatures observed were found to be in good agreement with those previously reported in literature (James et al., 2019; Dawes et al. 2017). However, since the purpose of the experiment was to understand the physical structure of aromatic residue, which requires a large amount of residue after irradiation, a very thick ice had to be prepared before irradiation at 4 K, thus the most



Figure 7. 3: The VUV spectra of pure benzene ice deposited at 4 K on a LiF window.



Figure 7. 4: VUV spectra of irradiated benzene ice and as a function of temperature until 300 K.

intense absorption bands of benzene in the 140 nm - 220 nm were saturated but the rest of the characteristic bands of benzene ice that appear at 240 nm - 275 nm were clearly seen. Upon irradiation using 9 eV photons, the spectral signature in the 220 nm–280 nm region was observed to alter, with a broad continuum (Figure 7. 4), a strong indication of chemical processing to have occurred in the irradiated ice, being seen. The ice was then warmed up at the rate of 5 K min⁻¹ and at 140 K most of the benzene was found to be sublime. Upon further warming the ice up to room temperature, 300 K, a residue

was observed only on the irradiated spot on the surface of the LiF window. The VUV spectrum of the residue



Figure 7. 5: VUV spectra of the residue compared with our another work on styrene ice.

recorded at 300 K had a broad absorption in the 120 nm - 300 nm range with distinct peaks at 195 nm and 254 nm. The 195 nm peak is in good agreement with residues reported previously in benzene irradiated ices. However, in this work an additional band was observed at 254 nm that could be due to the unsaturated or saturated carbon chain attached to the main aromatic ring for the characteristic band observed at 195 nm. Strazzulla & Baratta, 1991 have discussed that when benzene ices were irradiated by

keV protons under astrochemical icy condition and probed using IR spectroscopy, the intensity of the 688 cm⁻¹ benzene peak intensifies upon irradiation, which is thought to be a characteristic signature of other synthesized aromatic compounds such as polyphenyls (Callahan et al., 2013). Therefore, by



Figure 7. 6: VUV spectra of the residue at 300 K in comparison with the residue spectra at 200 K reported by James et al. 2019.

comparing the residue spectrum in Figure 7. 5 with that of pure styrene ($C_6H_5CH = CH_2$) ice formed under the similar conditions, we propose that the peak observed at 254 nm could be from aromatic molecules having a hydrocarbon chain attached to the aromatic ring. Even in the irradiated mixtures of benzene and carbon dioxide ices, benzene derivatives were reported (Figure 7. 6) (James et al., 2019).

The LiF windows containing residues were then detached from the cold head and gold/palladium coated before mounting on to the FE-SEM imaging stub. SEM images were taken at the centre of the window where photon irradiation was carried out. Several small white dots were seen at the irradiation spot Figure 7. 7. By further zooming in, we observed flat, two dimensional micrometre-sized flakes (Figure 7.8). At places close to these sites, we also observed some three dimensional particles, resembling cubes (Figure 7.9), of about a micrometre in scale. The image shown in Figure 7. 10, was observed to have a distinctive geometrical shape. Looking around the irradiation site for more particles, we could see similar cubic features and in addition features surrounded by small stick or rod shaped particles (Figure 7. 11) of approximately 100 nm. A spherical particle was also found and it was also observed to be surrounded by such micron sized rod like features Figure 7. 12. For the ice irradiated for nearly 25 h, the residue was again found to contain such cubical particles along with a thin sheet of residue (Figure 7. 13 - 7. 21). The micron sized cubical particles were found as separate pieces as well as being embedded within the thin sheet, a clear image of the cube attached with sheet Figure 7. 15. In addition, we observed rods that are half a micron thick and a few micron long, especially even "T" shaped rods (Figure 7. 18 & 7. 19) were present along with a perfect micro rod (Figure 7. 20). Apart from the cubical particles and rods, we also observe particles resembling a "triangular prism" that are a few micrometre thick (Figure 7. 17) and nearly 10 µm long. At other sites in the residue, we also found many micro-rods embedded on to the sheet (Figure 7. 21).


Figure 7. 7: FE-SEM image of the particles left after irradiation for nearly 9 hrs on top of LiF substrate.



Figure 7. 8: FE-SEM image of flakes in the residue.



Figure 7. 9: FE-SEM image of the cubes in the residue.



Figure 7. 10: FE-SEM image of the perfect cube in the residue.



Figure 7. 11: FE-SEM image of the cubes surrounded by rods shaped particles in residue.



Figure 7. 12: FE-SEM image of the spherical particles surrounded by rods in residue.



Figure 7. 13: FE-SEM image of the particles left after irradiation for nearly 25 hrs on top of LiF substrate.



Figure 7. 14 FE-SEM image of the cubes imbedded on a sheet of the residue.



Figure 7. 15: FE-SEM image of the cube attached with the sheet in the residue.



Figure 7. 16: FE-SEM image of the separate cubes in the residue.



Figure 7. 17: FE-SEM image of the triangular prism in the residue.



Figure 7. 18: FE-SEM image of the joint micro rods in the residue.



Figure 7. 19: FE-SEM image of the the "T" shaped micro rod in the residue.



Figure 7. 20: FE-SEM image of a single micro rod in the residue.



Figure 7. 21: FE-SEM image of micro rods embedded on a sheet in the residue.

7.4 Conclusion

In an attempt to understand the physical nature of the residue from benzene ice irradiation, we irradiated a benzene ice deposited at 4 K using 9 eV photons for 9 h and 25 h, which after warming to room temperature left a residue that was imaged using a FE-SEM. The VUV spectrum of the residue was observed to have aromatic and side chain absorption features from which we ascertain the residue should be a benzene derivative. Images of the residue revealed many micron sized particles of different geometrical shapes, such as cubes, rods and spheres. Besides such features sheets embedded with micro-rods were also observed. To the best of our knowledge, this is the first report showing the formation of geometrical shapes like cubes, rods and spheres from the irradiated residue of aromatic molecule. The results have implications in our understanding on the physical nature of the interstellar dust, especially the MAONs. In our future experiments we will be investigating the residues from the photon irradiation of icy non-aromatic cyclic molecules.

Chapter 8

N-Graphene synthesized in benzonitrile ice

8.1 Introduction

Cold ice covered dust particles in the InterStellar Medium (ISM) are known to be the tiny chemical factories responsible for the evolution of complex molecules observed in the ISM. The molecular complexity of the icy mantles on these cold dust grains were driven by energetic particles irradiation and temperature changes. Although the molecular ices present as icy mantles on a dust grain are volatile the change in physico-chemical nature brought by the irradiation can lead to nucleation (Strazzulla et al., 2001) producing refractory residues that may be observed at higher temperatures when simpler species are sublimed from the surface. Spectral signatures of such a residue obtained from a mixture of organic and inorganic molecular ice (Moore & Donn, 1982) has been used to explain the 3.4 µm signature in ISM clouds from space based observations. The nature of the residue depends on the chemical composition of the icy mantle undergoing irradiation under conditions commensurate to those found in the ISM and in the Solar System (Lanzerotti et al., 1985). Most of the residues are complex organic compounds (Jenniskens et al., 1993; Baratta et al., 1996; Strazzulla et al. 2001; Baratta et al., 2004; Ferini et al., 2004; Brunetto et al., 2006; Nuevo et al., 2011) and inorganic (Moore et al., 2007; Gomis & Strazzulla, 2008; Strazzulla et al., 2009; Sicilia et al., 2012; Kanuchova et al., 2017) (Table 8. 1 & Table 8. 2). For cometary ices present in the Oort cloud, such residues may form an outer web of non-volatile coating (Johnson et al., 1987, Strazzulla et al. 1991) preventing further irradiation of ice. The recent discovery of an ammoniated refractory residue (Poch et al., 2020, Altwegg et al., 2020) on comets may be a result of ice irradiation. An icy mixture containing simple ices, upon energetic processing, may also leave bio-residues (Dworkin et al., 2001; Sandford & Allamandola, 2001) that might be of interest in the Origin of Life research. There is an urgent need to understand the physical nature of the residue as it may play a key role (Potapov et al., 2020) in the chemical evolution. Residue from hydrocarbon ice irradiation was reported (Calcagno et al., 1985) to be fluffy and porous due to polymerization on carbonrich ices (Strazzulla et al., 1983) leading to micrometer-sized polymer layers (Foti et al., 1984). Nevertheless, the residues obtained by irradiating an aromatic (benzene) molecular ice were found to contain geometric shapes such as micron sized cubes and spheres, surrounded by nanoparticles (Rahul et al., 2020). The chemical analysis of the aromatic residues contained aromatic derivatives, from biphenyls to polyphenyls (Callahan et al., 2013). Characteristic spectral signatures of aromatic derivatives were present in the Vacuum UltraViolet (VUV) photoabsorption spectrum of the residue (Rahul et al., 2020). Two possibilities for the residue can be discussed, (i) Mixed Aromatic/aliphatic Organic Nanoparticles (MAONs) as dust in the place of (ii) Polycyclic Aromatic Hydrocarbons (PAH), based on space based observations in the infrared (Kwok & Zhang, 2011, 2013). So there is a dire need for more laboratory experiments to understand the physicochemical nature of the residue from astrochemical ice irradiation.

The report of the possible presence of C_{24} , a small graphene sheet (Garcia-Hernandez et al., 2011, Garcia-Hernandez et al., 2012) has led to estimates of the

concentrations of graphene in different regions of the ISM (Li et al., 2019) and suggest the presence of larger graphene sheets. Furthermore, it is expected that the presence of graphene may be concomitant with the presence of Buckminster fullerene, C_{60} , and the larger fullerene, C_{70} , already identified in the ISM (Cami et al., 2010). The formation of C_{60} is proposed to follow one of two chemical pathways; bottom – up (Kroto et al., 1985; Merino et al., 2014) and top – down (Chuvilin et al., 2010) model. The top-down model starts with PAH being converted to a larger graphene sheet which eventually synthesizes C_{60} following the pathway suggested by Berne and Tielens, 2012. Therefore, the presence of C_{60} can be used as a tracer to look for graphene rich clouds in the ISM.

Perhaps, hydrogen loss from MAONs may also form graphene. However, to-date, the formation of these allotropes of carbon have only been examined at higher temperatures that do not resemble the cold dust containing an icy mantle. Efforts were taken to understand the formation of carbon clusters in icy conditions, up to

Reference	Molecular ice	Technique	Irradiation energy, source
Strazzulla et al., 2001	H ₂ O:CH ₄ :N ₂	IR and Raman spectroscopy	He ⁺ 3 keV
Moore and Donn,1982	H ₂ O:NH ₃ :CH ₄	IR spectroscopy	H ⁺ 1 MeV
Baratta et al., 2004	highly ordered pyrolytic graphite	Raman spectroscopy	H ⁺ 3 keV
Brunetto et al., 2005	CH ₃ OH, CH ₄ , C ₆ H ₆	Vis - Near IR spectroscopy	H ⁺ / Ar ⁺ 200 keV, A ⁺⁺ 400 keV
Jenniskens et al., 1993	H ₂ O:CO:NH ₃ :CH ₄	IR spectroscopy, SEM imaging	10 eV UV, 3 keV He ⁺
Nuevo et al., 2011	H ₂ O:CH ₃ OH:CO:NH ₃ , H ₂ O:CH ₃ OH:CO:NH ₃ :C ₃ H ₈ /C ₁₀ H ₈	IR & UV spectroscopy, Mass spec	121.6 nm, 160 nm
Baratta et al., 1996	Amorphous carbon	Raman spectroscopy	3 keV He ⁺
Ferini et al., 2004	CH ₄ , H ₂ O:CH ₄ :N ₂ and CH ₃ OH:N ₂	Raman spectroscopy	He ⁺ / Ar ⁺ , 30 keV, Ar ⁺⁺ 60 keV
Strazzulla & Baratta, 1991	C ₆ H ₆	IR spectroscopy	3 keV He ⁺
Dworkin et al., 2001	H ₂ O: CH ₃ OH:NH ₃ :CO, H ₂ O:CH ₃ OH:CO	HPLC Mass spec	UV photons
Calcagno et al., 1985	CH4	IR spectroscopy, TEM	1.5 MeV protons
Foti et al., 1984	CH4	Proton Scattering	1.5 MeV protons
Callahan et al., 2013	C_6H_6	GCMS	08.8 MeV H^+
Rahul et al., 2020	C_6H_6	VUV spectroscopy, FE-SEM	UV photons, 9 eV

Table 8. 1: Summary of literature survey of the organic residue synthesized in astrochemical ices.

 C_{20} were observed to form at low temperature in an irradiated methane in neon ice matrix (Lin et al., 2014). The results reported were convincing enough to support the hypothesis that carbon atoms combine to form chain of molecules, even at such lower temperatures, which if further pursued may lead to the formation of graphene. The recent identification of molecules containing an aromatic ring with a side chain in the ISM, such as benzonitrile (McGuire et al., 2018) that can readily form (Cooke et al., 2020) at ISM conditions, provides another possible route to the formation of complex carbon structures such as graphene. Irradiation of such a compound may lead to dissociation liberating the aromatic ring which may then assemble with other rings to form a more complex PAH. In this paper we report for the first time the results of photoprocessing of benzonitrile ice prepared under ISM conditions.

Table 8. 2: Summary of the literature survey of the inorganic residue synthesised in ices.

Reference	Molecular ice	Technique	Irradiation energy,
Kaňuchová et al., 2017	H ₂ O:SO ₂	IR spectroscopy	H ⁺ 30 keV
Moore et al., 2007	SO ₂ , H ₂ S, H ₂ O:SO ₂ , H ₂ O:H ₂ S	IR spectroscopy	H ⁺ 0.8 MeV
Sicillia et al., 2012	CO ₂ , N ₂ , CO ₂ :N ₂	IR spectroscopy	H ⁺ 200 keV
Gomis & Strazzulla, 2008	H ₂ O: Sulfurous material	IR spectroscopy	H ⁺ 200 keV

8.2 The laboratory analogue experiment and observed

carbonaceous residues

VUV photoprocessing of benzonitrile ices was studied at two beamlines of Taiwan Light Source (TLS), TLS BL03 and TLS BL21A2, at the National Synchrotron Radiation Center, Taiwan. The details of the experimental system used can be found elsewhere so only salient details are presented here (Lin et al., 2014; Lu et al., 2005; Lu et al., 2008). A benzonitrile ice film was formed at 4 K, by depositing benzonitrile at 5 x 10^{-7} Torr for 60 seconds onto Lithium Fluoride (LiF) and Potassium Bromide (KBr) substrates (Figure 8. 1((a) & (b)).



Figure 8. 1: Deposition of vapour of benzonitrile on (a) LiF substrate and (b) KBr substrate, cooled to 4 K.

The ice was then irradiated by 9 eV photons for nearly 9 hours (Table 8. 2) and subsequently monitored using VUV and InfraRed (IR) spectroscopy. The amount of sample deposited is quite high for the VUV spectroscopy, however, the aim of these experiments was to synthesize residue from benzonitrile irradiation, so in order to synthesize sufficient residue and to obtain a good VUV spectrum of the residue the amount of sample used before irradiation resulted in a saturated VUV photoabsorption spectrum of benzonitrile at 4 K at lower wavelengths (110 nm - 260 nm) (Figure 8. 3). However, in the higher wavelength region, 260 nm - 290 nm, due to the lower absorption cross section three bands at 264.5 nm, 271.6 nm and 279 nm were observed. After irradiation, these band positions and shape remain unchanged, however, the increase in baseline to higher absorption was an indication of absorption from newly synthesized molecule/residue synthesized by irradiation (Figure 8. 4).



Figure 8. 2: The irradiation of ice with 9 eV photons on both substrate (separate experiments).

The temperature dependent spectra showed the sublimation of benzonitrile from irradiated ice at 185 - 190 K (Figure 8. 5) and the leaving of residue at the substrate at 295 K (Figure 8. 6). In the IR spectroscopy, the characteristic bands of the benzonitrile ice was observed at 4 K (Figure 8.7), in the irradiated benzonitrile ice at 4 K, all the characteristic bands corresponding to the amorphous benzonitrile ice was present along with a new band at 2133 cm⁻¹ (Figure 8. 8), that corresponds to the NC stretching (Accolla et al. 2018), the temperature dependent IR spectra of irradiated benzonitrile ice were observed (Figure 8. 9). The IR spectra at 150 K showed the phase change to create crystalline benzonitrile ice. Further warming the ice to room temperature resulted in desorption of the benzonitrile molecules, but left a residue on the substrate. Such a residue was not observed in a benzonitrile ice that was warmed from 4 K to room temperature without irradiation. The spectrum of residue had absorption bands in the IR (Figure 8. 10), quite similar to the benzonitrile characteristic absorption band suggesting the residue could be an aromatic derivative (containing nitrogen). While, the spectrum of residue recorded in the VUV contain the characteristic aromatic ring absorption at 190 nm and an extended absorption tail until 300 nm (Figure 8. 6). Such a spectrum in VUV is characteristic of aromatic derivatives (Rahul et al. 2020). Thus, both spectroscopic techniques i.e. IR and VUV, provide compelling evidence that the residue synthesized by VUV irradiation contains aromatic molecules.



Figure 8. 3: VUV spectra of benzonitrile ice at 4 K.



Figure 8. 4: VUV spectra of photo-irradiated benzonitrile ice at 4 K.

However, experimental evidence also suggests that the availability of carbon atoms in irradiated ices (Sie et al., 2019) may lead to the formation of carbon clusters or carbon only molecules (Lin et al., 2014).



Figure 8. 5: Temperature dependent VUV spectra of irradiated benzonitrile ice.



Figure 8. 6: VUV spectra of residue from irradiated benzonitrile warmed to 295 K.

The appearance of characteristic features corresponding to non-volatile carbon / carbon-nitrogen clusters were not observed in VUV and IR spectra, but this could be due to lower concentrations in the residue. Therefore, in order to investigate the synthesis of non-volatile carbon only or carbon nitrogen clusters from the ice irradiation, the sample



Figure 8. 7: IR spectra of benzonitrile ice at 4 K.



Figure 8. 8: IR spectra of photo-irradiated benzonitrile ice at 4 K.

was imaged using High Resolution - Transmission Electron Microscopy (HR-TEM), for which the residue obtained was scratched on to a Quantifoil TEM grid. Plasma cleaning, using a gas mixture of argon-oxygen, of the TEM grid was carried out before loading the grid for imaging.



Figure 8. 9: Temperature dependent IR spectra of irradiated benzonitrile ice.



Figure 8. 10: IR spectra of residue from irradiated benzonitrile warmed to 295 K.

In the images obtained clusters of atoms arranged within the structure of a quantum dot, max length ~ 3 nm, from aligned atoms (from d spacing (Tian et al., 2018)) were observed. Such dots were seen in many places in the residue (Figure 8. 11).



Figure 8. 11: HR-TEM image of the N-graphene sheet (a) large sheet and the insets (b - c) shows the hexagonal pattern in two different parts of the large sheet.



Figure 8. 12: The diffraction pattern of the N-Graphene.

Several nanosheets were also observed. Upon closer examination, on a scale of < 1 nm, this sheet was found to contain a hexagonal arrangement of atoms (Figure 8. 11), a structure that which confirmed by the X-ray diffraction data (Figure 8. 12).



Figure 8. 13: The EDS spectra of the N-Graphene.

The energy dispersive spectrum showed carbon and nitrogen to be present in this sheet (Figure 8. 13). From these observations we can conclude that within this residue there is evidence for the presence of nitrogen-doped graphene. In this case the quantum dot and N-doped graphene sheet were part of the other components present in a residue synthesized in laboratory analogue simulating ISM cold dust condition. The other components will be discussed in a separate publication.

8.3 Discussion

A laboratory analogue experiment of the irradiation of an icy mantle made of the recently discovered benzonitrile molecule prepared under ISM conditions has revealed, for the first time, the formation of nanoscale structure analogous to a quantum dot and N-doped graphene sheet. This observation has important consequences for our understanding of the formation and abundance of PAH molecules in the ISM. A new and simple route to the formation of complex PAH structures is demonstrated by irradiation of a simple aromatic compound. The atoms of carbon and nitrogen released by photodissociation easily diffuses within the ice upon warming leading to the formation of nanostructures. The presence of graphene suggests that C_{60} / C_{70} , via top-down model, and carbon nanotube, by rolling the sheet, may also form in irradiated aromatic ices. Graphene containing dust may be the source of C_{24} reported by (Garcia-Hernandez et al., 2011, Garcia-Hernandez et al., 2012). A variety of hydrocarbons and hydrocarbyls may result by etching graphene in hydrogen rich environments commensurate to conditions in the ISM (Martinez et al., 2014).

While graphene in hydrogen rich environment can synthesize PAH molecules the presence of NGraphene may synthesize Polycyclic Aromatic Nitrogen Heterocycles (PANHs), signatures of which may be present in spectral collection from the observations of different regions of the ISM clouds, using space and ground based observatories. Titan's stratospheric polar clouds also contain benzene ices (Vinatier et al., 2018) and the chemical composition of surface ices on Titan are also known, from laboratory experiments (Abplanalp et al., 2019), to harbour aromatic molecules such as benzene. Therefore, in a nitrogen rich environment

where benzene ices are also present, benzonitrile may readily form (Loison et al., 2019). Our experimental result showing N-graphene synthesis from benzonitrile ices therefore suggest that N-graphene may also be a component of Titan's icy clouds and surface ices. This prediction may be supported by CAPS ELS data collected during the T16 encounter of the Cassini spacecraft, at approximately 1000 km altitude (Waite et al., 2007), which with the observation of material with a few 1000's of Dalton. These high masses have been attributed to the presence of tholins (Sagan & Khare, 1979) however N-graphene might co-exist with tholins in the chemically complex clouds of Titan. Therefore, adding the possible presence of N-graphene to atmospheric models of Titan may provide clues to those physicochemical processes leading to formation of Titan's haze.

8.4 Conclusion

Irradiation of a 4 K benzonitrile ice film by 9 eV photons and subsequent warning to room temperature has demonstrated the formation of nanostructures including quantum dots and (Nitrogen doped) graphene. This important observation shows that the bottom-up model to synthesize graphene is also feasible for a cold dust grain in the ISM, which can subsequently lead to the synthesis of larger PAH molecules in hydrogen rich environment. The search for graphene sheets in the ISM should therefore be made by looking at regions where benzonitrile has been identified. Astrochemical dust models should then consider the presence of graphene and how it many influences the productivity of PAH and other hydrocarbons. In the Solar System, since benzonitrile is a likely component of the rich PAHs inventory present on Titan these results suggest that we can also expect the presence of N-graphene. The Cassini mission flyby data should therefore be reviewed to look for any spectral signatures of N-graphene and Titan atmosphere models developed to explore synthetic routes of production in the Titan haze.

Chapter 9

Summary and Future Work

In this chapter, we have presented a summary of the research work and its astrophysical implication. The aim of this thesis is to solve a few unsolved problems in the area of astrochemistry, and finding of unique characteristics of molecule under astrochemical conditions and understanding the physical properties of organic materials present in diffuse molecular clouds of the ISM. To attain the aim, we have investigated the thermal processing of pure and mixture of molecular ice and radiation processing of pure molecules using infrared and VUV as probing tools. Thermal processing represents the thermal evolution of ices from surrounding medium or star forming regions. Photo-processing from Sun was mimicked by using energetic photons from high flux beamline at a synchrotron source. Pure ice to mix ice and layer of ices was used to demonstrate experimental parameters are investigated for experiments are abundant observed molecules in interstellar ices/planetary bodies. Finally, the work presented and discussed in this thesis represent a comprehensive study of both thermal and radiation processing of different astrochemical ice analogous.

A summary of the results from Chapters, 4, 5, 6, 7 and 8 and the future scope of the work.

9.1 Summary of work

9.1.1 Ozone on Callisto

In Chapter 4, we have reported the formation of Ozone in photon irradiated SO_2 ice at 9 K. The irradiated ice mixture was warmed to high temperatures of 120 K with spectra recorded at every 10 K interval. The details of the results are summarized below.

- UV photo-absorption spectra (220 320 nm) of SO₂ ice at 9 K has a peak position at 280 nm; characteristics of SO₂.
- The spectra of irradiated SO₂ ice had larger bandwidth than pure SO₂, due to Ozone synthesization having characteristics band; the Hartley band at 220 310 nm (Sivaraman et al. 2014) overlaps with SO₂ ice.
- The temperature-dependent spectra of irradiated SO₂ ice mix showed decrease in bandwidth of spectra at higher temperature (>50 K) due to sublimation of synthesized Ozone. Even at 100 K, Ozone was found to be trapped in the ice matrix.
- The experimental result at 70 K and 100 K has been compared with UV observational data of Callisto taken by the Hubble Space Telescope (Noll et al. 1997b).
- The comparison of the experimental data with observational spectra suggests the presence of Ozone on the surface of Callisto within some reasonable physical constraints.

9.1.2 VUV photo-absorption spectroscopy of Pluto and Charon ice analogues

Temperature-dependent VUV spectra of the Pluto mix (N_2 : CO: CH₄) ice analogues with and without water at 10 K and 30 K, while the Charon mix of NH₃ and H₂O in both mix and layer ice deposited at 10 K and warmed to 140 K are presented in Chapter

3. The VUV spectra observed will help to explore observational data of the Pluto system and KBOs in the VUV range taken by the New Horizons Mission.

The VUV spectra of N_2 :CO:CH₄ mixture at 10 K has three distinct sections; absorption at 110–130 nm, 130–160 nm and 160–180 nm.

- The absorption in region 110 130 nm is due to CH₄ and CO. Since, the cross-section for N₂ is much lower (Wu et al. 2012) than CH₄ and CO, so peaks corresponding to N₂ are not clearly seen in this region.
- CO has absorption in region 130–160 nm and due to a much smaller crosssection of N₂ (Wu et al. 2012), its feature was not clearly seen in this region.
- The continuous absorption in region 160–180 nm is not characteristics of any of primary molecules used in the experiment; it could be from interaction of N₂, CH₄ and CO molecules at 10 K.

While, the spectrum of the Pluto mix ice at 30 K had only two distinct regions; absorption at 110-130 nm and 130-160 nm. The absence of 160 - 180 nm at 30 K could be due to N₂ matrix subliming off at 30 K.

The spectra of Pluto mix with H_2O ice at 10 K and 30 K was found to be similar to that recorded without H_2O molecules due to H_2O absorption falling well within 110–130 nm/130–165 nm regions.

The VUV photoabsorption spectra of these layered and mixed ices with that of pure H₂O and NH₃ ices along with NH₄OH ice at 10 K to mimic the Charon ice mix.

- Pure NH₃ ice has a broad absorption band from 110 to 200 nm with maximum absorptions at 125 and 178 nm. Pure H₂O ice has a broad band extending till 160 nm with maximum absorption at 145 nm.
- Photoabsorption spectrum of layered ices NH₃ below H₂O has a band from 110 to 200 nm with three absorption peaks at 125 nm, 145 nm and 178 nm.

- The mixed H₂O and NH₃ ices have only two distinct maximum absorptions at 125 and 180 nm as this could be due to the difference in absorption cross-section of these two molecules.
- The absorption of NH₄OH is similar to that of NH₃–H₂O ice mixtures except for the tail which extends up to 190 nm. NH₄OH ice has a maximum absorption band centered at 120 nm and 145 nm followed by another absorption band centered at 172 nm, where these two peaks arise from OH and NH absorptions, respectively.

9.1.3 Infrared attenuation from crystalline propargyl ether ice

Infrared and VUV spectra of propargyl ether ice deposited at 10 K and thermally processed were presented in Chapter 6. To date, there have been no spectroscopic studies of propargyl ether ice. The recorded spectrum of propargyl ether ice in infrared range is new and unexpected; it has opened up a new way to explore observational spectra in infrared. The results of this systematic VUV and IR study of propargyl ether are summarised below:

IR spectrum of propargyl ether ice at 10 K have several peaks in mid-IR region (4000– 550 cm^{-1}).

- CH stretching, CH₂ asymmetric, symmetric stretching, C=C stretching vibration in amorphous propargyl ether ice was observed along with CH₂ scissoring, CH₂ wagging and CH₂ twisting vibrations with normal transmission of infrared beam.
- The band attributed to C-O stretching and COC bending vibration with other characteristic was observed in infrared spectra.
- The infrared transmission decreases with increase in sample temperature and at 170 K, the ice turned crystalline from amorphous and it was not straightforward to assign the characteristic bands in 1500–600 cm⁻¹.

The VUV spectra of propargyl ether ice at 10 K has two prominent bands

- The absorption in 170–210 nm with a peak at 192 nm and in 110–170 nm region with a broad band 130–160 nm region. At higher temperature, 100 K–150 K, the absorption band at 130–160 nm had an increase in absorbance and peak at 192 nm red shifted by ~2 nm.
- The spectrum at 170 K has spectral features in both 110–170 nm and 170– 210 nm regions. The VUV spectra recorded as a function of temperature clearly indicates no significant attenuation of propargyl ether ice in 110–210 nm wavelength.

Performing both the infrared and VUV spectroscopy of astrochemical propargyl ether ice suggests the infrared beam attenuation from crystalline propargyl ether ice.

9.1.4 Residue from irradiated benzene ice

To date, many experiments have been reported that explore the chemical properties of refractory residue obtained in irradiated simple molecular ice. But, a few experiments have been performed to explore the physical properties of these residue. In order to explore the physical properties of such residues we have carried out irradiation of simple aromatic (benzene) ice at 4 K. VUV spectrum of pure and irradiated benzene ice has been measured. The spectrum of pure ice has intense absorption in 140 nm - 220 nm, and are saturated due to thickness of the ice and band at 240 nm - 275 nm was normal.

The spectra of irradiated ice in 220 nm–280 nm region has been found to be altered with a broad continuum, a strong indication of chemical processing to have occurred in the irradiated ice. The summary of the experimental result is as follow:

 At 300 K, a residue was observed only on the irradiated spot on the surface of LiF window. The VUV spectrum of the residue had a broad absorption in 120 nm - 300 nm range with distinct peaks at 195 nm and 254 nm. • The 195 nm peak in the spectra is aromatic characteristic of the residue. While, band observed at 254 nm could be due to unsaturated or saturated carbon chain attached to the main aromatic ring.

The FE-SEM images of both residues were performed to understand the physical properties of the residue.

- FE-SEM image of the residue obtained after irradiation of Benzene ice for 9 hours showed two dimensional micrometre-sized flakes, three dimensional particles, resembling cubes of about a micrometre in scale. At other site of the residue, cubic features surrounded by small stick or rod shaped particles of ~100 nm.
- A spherical particle was also found and it was also observed to be surrounded by such micron sized rod like features.
- FE-SEM image of the residue obtained after 25 hours of irradiated benzene ice has such cubical particles along with a thin sheet of residue. Micron sized cubical particles in separate pieces are found to be embedded within thin sheet.
- Rods of half a micron thick and a few micron long were present along with a
 perfect micro rod, apart from the cubical particles and rods, a "triangular prism"
 of a few micrometre thick and nearly 10 µm long. Micro-rods embedded on to
 sheet were observed in the residue.

9.1.5 N-Graphene synthesis in Benzonitrile ice

To further understand the physical properties of the residue, we have irradiated the recently detected molecules in the ISM; benzonitrile, which has aromatic ring and attached a carbon-nitrogen chain. The benzonitrile vapour was deposited at 4 K for thick ice to synthesize the residue and irradiated with 9 eV photons for 9 hr and spectra of pure and irradiated ice analogues were measured in both IR and VUV wavelength range.

The spectra of irradiated ice in the 110 nm–260 nm region was found to have been altered, an indication of chemical processing to have occurred in the irradiated ice. The summary of the experimental result is as follow:

- At 295 K, a residue was observed on the irradiated spot on the surface of LiF and KBr substrate.
- The VUV spectrum of the residue had a broad absorption in the 110 nm 260 nm range with distinct peaks at 190 nm and an extended absorption tail until 300 K.
- The 190 nm peak in the spectra is due to the aromatic characteristic of the residue.
- While the IR spectra of the residue is quite similar to that of pure benzonitrile at 4 K, suggest the residue to be of aromatic derivative.

The HR-TEM images of the residues were performed to understand the physical properties of the residue.

- The HR-SEM image of residue showed the presence of a two dimensional Graphene sheet.
- The diffraction spectrum of the same shows the hexagonal structure of the graphene sheet.
- The energy dispersive spectrum of the residue shows the elemental composition of carbon and nitrogen, confirms N-Graphene.

The experimental result suggest the presence of graphene in the ISM as well in the Titan's icy clouds and surface ice.

9.2 Future work

Since the synthesization of graphene is reported for the first time in astrochemical ices, and possible presence of C_{24} , a small graphene sheet has already been reported in the ISM, which suggest the presence of larger graphene sheets. The graphene sheet could

deform and form more complex structure in the ISM. Fullerenes (C_{60}) have already been identified in the ISM and there are two proposed chemical pathways for its formation; bottom – up and top – down model. The top-down model starts with PAH being converted to a larger graphene sheet which eventually synthesizes C_{60} following the pathway suggested by Berne and Tielens, 2012.

The experimental work on the formation of N-Graphene in benzonitrile astrochemical ice analogue irradiated by UV photons emphasizes on the possibility of C_{60} formation in astrochemical ices, as graphene is known to be the intermediate in the formation of C_{60} . The detection of molecules containing an aromatic ring with a side chain in the ISM, such as benzonitrile, which synthesizes large carbon sheet; graphene under irradiation via bottom-up pathway, which can lead to the synthesis of C_{60}/C_{70} . Irradiation of aromatic ice may lead to dissociation, liberating aromatic ring which may then assemble with other rings to make graphene which eventually will deform to C_{60} . However, C_{60} synthesis in astrochemical ice analogues are yet to be demonstrated in laboratory experiments. Thus, our aim for next experiments are to synthesize C_{60} in astrochemical ices and understand the evolution of such complex molecules in the ISM.
References

- Abplanalp, M. J., Frigge, R., & Kaiser, R. I. (2019). Low-temperature synthesis of polycyclic aromatic hydrocarbons in Titan's surface ices and on airless bodies. *Science Advances*, 5(10), eaaw5841.
- Accolla, M., Pellegrino, G., Baratta, G. A., Condorelli, G. G., Fedoseev, G., Scirè, C., . . . Strazzulla, G. (2018). Combined IR and XPS characterization of organic refractory residues obtained by ion irradiation of simple icy mixtures. A&A, 620, A123.
- Allamandola, L. J., Greenberg, J. M., Norman, C. A., & Hagen, W. (1980, January 01, 1980). The chemical identification of grain mantles by infrared spectroscopy. Paper presented at the Interstellar Molecules.
- Altwegg, K., Balsiger, H., Hänni, N., Rubin, M., Schuhmann, M., Schroeder, I., . . . Fuselier, S. A. (2020). Evidence of ammonium salts in comet 67P as explanation for the nitrogen depletion in cometary comae. *Nature Astronomy*, 4(5), 533-540.
- Bahr, D. A., Famá, M., Vidal, R. A., & Baragiola, R. A. (2001). Radiolysis of water ice in the outer solar system: Sputtering and trapping of radiation products. *Journal of Geophysical Research: Planets*, 106(E12), 33285-33290.
- Banwell, C. N. (1983). *Fundamentals of molecular spectroscopy* [by] C. N. Banwell. London, New York: McGraw-Hill.
- Baragiola, R. A., Atteberry, C. L., Bahr, D. A., & Jakas, M. M. (1999a). Solid-state ozone synthesis by energetic ions. *Nuclear Instruments and Methods in Physics Research B*, 157, 233.
- Baragiola, R. A., Atteberry, C. L., Bahr, D. A., & Jakas, M. M. (1999b). Solid-state ozone synthesis by energetic ions. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 157(1), 233-238.
- Baratta, G. A., Arena, M. M., Strazzulla, G., Colangeli, L., Mennella, V., & Bussoletti, E. (1996). Raman spectroscopy of ion irradiated amorphous carbons. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 116(1), 195-199.
- Baratta, G. A., Castorina, A. C., Leto, G., Palumbo, M. E., Spinella, F., & Strazzulla, G. (1994). Ion irradiation experiments relevant to the physics of comets. *Planetary* and Space Science, 42(9), 759-766.
- Baratta, G. A., Leto, G., Spinella, F., Strazzulla, G., & Foti, G. (1991). The 3.1 mu.m feature in ion-irradiated water ice. *Astronomy and Astrophysics*, 252, 421.
- Baratta, G. A., Mennella, V., Brucato, J. R., Colangeli, L., Leto, G., Palumbo, M. E., & Strazzulla, G. (2004). Raman spectroscopy of ion-irradiated interplanetary carbon dust analogues. *Journal of Raman Spectroscopy*, 35(6), 487-496.
- Barth, C. A., & Hord, C. W. (1971). Mariner Ultraviolet Spectrometer: Topography and Polar Cap. *Science*, *173(3993)*, 197.

- Barth, C. A., Hord, C. W., Stewart, A. I., Lane, A. L., Dick, M. L., & Anderson, G. P. (1973). Mariner 9 Ultraviolet Spectrometer Experiment: Seasonal Variation of Ozone on Mars. *Science*, 179(4075), 795.
- Benderskii, A. V., & Wight, C. A. (1994). Photochemistry of ozone in solid mixtures with argon. *The Journal of Chemical Physics*, 101(1), 292-298.
- Bennett, C. J., & Kaiser, R. I. (2005). Laboratory Studies on the Formation of Ozone (O3) on Icy Satellites and on Interstellar and Cometary Ices. *The Astrophysical Journal*, 635(2), 1362-1369.
- Berné, O., & Tielens, A. G. G. M. (2012). Formation of buckminsterfullerene (C60) in interstellar space. Proceedings of the National Academy of Sciences, 109(2), 401.
- Bernstein, M. P., Allamandola, L. J., & Sandford, S. A. (1997). Complex organics in laboratory simulations of interstellar/cometary ices. Advances in Space Research, 19(7), 991-998.
- Bird, M. K., Huchtmeier, W. K., Gensheimer, P., Wilson, T. L., Janardhan, P., & Lemme, C. (1997). Radio detection of ammonia in comet Hale-Bopp. Astronomy and Astrophysics, 325, L5.
- Bird, M. K., Janardhan, P., Wilson, T. L., Huchtmeier, W. K., Gensheimer, P., & Lemme, C. (1997). K-band Radio Observations of Comet Hale-Bopp: Detections of Ammonia and (Possibly) Water. *Earth Moon and Planets*, 78, 21.
- Bohn, R. B., Sandford, S. A., Allamandola, L. J., & Cruikshank, D. P. (1994). Infrared Spectroscopy of Triton and Pluto Ice Analogs: The Case for Saturated Hydrocarbons. *Icarus*, 111(1), 151-173.
- Boogert, A. C. A., Ehrenfreund, P., Gerakines, P. A., Tielens, A. G. G. M., Whittet, D. C. B., Schutte, W. A., ... Prusti, T. (2000). ISO-SWS observations of interstellar solid 13CO2: heated ice and the Galactic 12C/ 13C abundance ratio. Astronomy and Astrophysics, 353, 349-362.
- Boogert, A. C. A., Helmich, F. P., van Dishoeck, E. F., Schutte, W. A., Tielens, A. G. G. M., & Whittet, D. C. B. (1998). The gas/solid methane abundance ratio toward deeply embedded protostars. *Astronomy and Astrophysics*, *336*, 352-358.
- Boogert, A. C. A., Pontoppidan, K. M., Lahuis, F., Jorgensen, J. K., Augereau, J. C., Blake, G. A., . . . Stapelfeldt, K. R. (2004). Spitzer Space Telescope Spectroscopy of Ices toward Low - Mass Embedded Protostars. *The Astrophysical Journal Supplement Series*, 154(1), 359-362.
- Boogert, A. C. A., Schutte, W. A., Tielens, A. G. G. M., Whittet, D. C. B., Helmich, F. P., Ehrenfreund, P., . . . Prusti, T. (1996). Solid methane toward deeply embedded protostars. *Astronomy and Astrophysics*, 315, L377-L380.
- Bowers, M. T., & Elleman, D. D. (1969). Kinetic Analysis of the Concurrent Ion–Molecule Reactions in Mixtures of Argon and Nitrogen with H2, D2, and HD Utilizing Ion -

Ejection–Ion - Cyclotron - Resonance Techniques. *The Journal of Chemical Physics*, 51(10), 4606-4617.

- Bridger, A., Wright, G. S., & Geballe, T. R. (1994). *Dust Absorption in NGC1068*. In (Vol. 190, pp. 537).
- Brooke, T. Y., Sellgren, K., & Geballe, T. R. (1999). New 3 Micron Spectra of Young Stellar Objects with H2O Ice Bands. *The Astrophysical Journal*, 517(2), 883-900.
- Brown, M. E., & Calvin, W. M. (2000). Evidence for Crystalline Water and Ammonia Ices on Pluto's Satellite Charon. *Science*, 287(5450), 107.
- Brown, R. H., Clark, R. N., Buratti, B. J., Cruikshank, D. P., Barnes, J. W., Mastrapa, R. M. E., . . . Sotin, C. (2006). Composition and Physical Properties of Enceladus' Surface. *Science*, 311(5766), 1425.
- Brown, R. H., Soderblom, L. A., Soderblom, J. M., Clark, R. N., Jaumann, R., Barnes, J. W., . . . Nicholson, P. D. (2008). The identification of liquid ethane in Titan's Ontario Lacus. *Nature*, 454(7204), 607-610.
- Brown, W. L., Lanzerotti, L. J., Poate, J. M., & Augustyniak, W. M. (1978). "Sputtering" of Ice by MeV Light Ions. *Physical Review Letters*, 40(15), 1027-1030.
- Brunetto, R., Barucci, M. A., Dotto, E., & Strazzulla, G. (2006). Ion Irradiation of Frozen Methanol, Methane, and Benzene: Linking to the Colors of Centaurs and Trans -Neptunian Objects. *The Astrophysical Journal*, 644(1), 646-650.
- Calcagno, L., Foti, G., Torrisi, L., & Strazzulla, G. (1985). Fluffy layers obtained by ion bombardment of frozen methane: Experiments and applications to Saturnian and Uranian satellites. *Icarus*, 63(1), 31-38.
- Callahan, M. P., Gerakines, P. A., Martin, M. G., Peeters, Z., & Hudson, R. L. (2013). Irradiated benzene ice provides clues to meteoritic organic chemistry. *Icarus*, 226(2), 1201-1209.
- Cami, J., Bernard-Salas, J., Peeters, E., & Malek, S. E. (2010). Detection of C60 and C70 in a Young Planetary Nebula. *Science*, 329(5996), 1180.
- Carbo, R., & Ginebreda, A. (1985). Interstellar chemistry. *Journal of Chemical Education*, 62(10), 832.
- Carlson, R. W., Anderson, M. S., Johnson, R. E., Smythe, W. D., Hendrix, A. R., Barth, C. A., . . . Matson, D. L. (1999). Hydrogen Peroxide on the Surface of Europa. *Science*, 283(5410), 2062.
- Carlson, R. W., Smythe, W. D., Lopes-Gautier, R. M. C., Davies, A. G., Kamp, L. W., Mosher, J. A., . . . Fanale, F. P. (1997). The distribution of sulfur dioxide and other infrared absorbers on the surface of Io. *Geophysical Research Letters*, 24(20), 2479-2482.
- Carpentier, Y., Féraud, G., Dartois, E., Brunetto, R., Charon, E., Cao, A.-T., . . . Pino, T. (2012). Nanostructuration of carbonaceous dust as seen through the positions of the 6.2 and 7.7 μm AIBs. *A&A*, *548*, A40.

- Cernicharo, J., Heras, A. M., Tielens, A. G. G. M., Pardo, J. R., Herpin, F., Guélin, M., & Waters, L. B. F. M. (2001).]Infrared Space Observatory's Discovery of C4H2, C6H2, and Benzene in CRL 618. *The Astrophysical Journal*, 546(2), L123-L126.
- Cernicharo, J., Yamamura, I., González-Alfonso, E., de Jong, T., Heras, A., Escribano, R., & Ortigoso, J. (1999). The ISO/SWS Spectrum of IRC +10216: The Vibrational Bands of C2H2 and HCN. *The Astrophysical Journal*, 526(1), L41-L44.
- Charnley, S. B., Tielens, A. G. G. M., & Millar, T. J. (1992). On the Molecular Complexity of the Hot Cores in Orion A: Grain Surface Chemistry as ``The Last Refuge of the Scoundrel". *The Astrophysical Journal, 399*, L71.
- Cherchneff, I. (2011/03/1). The formation of Polycyclic Aromatic Hydrocarbons in evolved circumstellar environments.
- Cherchneff, I., Barker, J. R., & Tielens, A. G. G. M. (1992). Polycyclic Aromatic Hydrocarbon Formation in Carbon-rich Stellar Envelopes. *The Astrophysical Journal*, 401, 269.
- Chiar, J. E., Adamson, A. J., & Whittet, D. C. B. (1996). Three Micron Hydrocarbon and Methanol Absorption in Taurus. *The Astrophysical Journal*, 472, 665.
- Chiar, J. E., Gerakines, P. A., Whittet, D. C. B., Pendleton, Y. J., Tielens, A. G. G. M., Adamson, A. J., & Boogert, A. C. A. (1998). Processing of Icy Mantles in Protostellar Envelopes. *The Astrophysical Journal*, 498(2), 716-727.
- Chiar, J. E., Tielens, A. G. G. M., Adamson, A. J., & Ricca, A. (2013). The structure, origin, and evolution of Interstellar hydrocarbon grains. *The Astrophysical Journal*, 770(1), 78.
- Chiar, J. E., Tielens, A. G. G. M., Whittet, D. C. B., Schutte, W. A., Boogert, A. C. A., Lutz, D., . . . Bernstein, M. P. (2000). The Composition and Distribution of Dust along the Line of Sight toward the Galactic Center. *The Astrophysical Journal*, 537(2), 749-762.
- Chuvilin, A., Kaiser, U., Bichoutskaia, E., Besley, N. A., & Khlobystov, A. N. (2010). Direct transformation of graphene to fullerene. *Nature Chemistry*, 2(6), 450-453.
- Clark, R. N., Brown, R., Baines, K., Bellucci, G., Bibring, J. P., Buratti, B., ... Hoefen, T. (2005/08/1). Cassini VIMS compositional mapping of Surfaces in the Saturn System and the role of water, cyanide compounds and carbon dioxide.
- Collings, M. P., Dever, J. W., Fraser, H. J., McCoustra, M. R. S., & Williams, D. A. (2003). Carbon Monoxide Entrapment in Interstellar Ice Analogs. *The Astrophysical Journal*, 583(2), 1058-1062.
- Cook, J. C., Desch, S. J., Roush, T. L., Trujillo, C. A., & Geballe, T. R. (2007). Near -Infrared Spectroscopy of Charon: Possible Evidence for Cryovolcanism on Kuiper Belt Objects. *The Astrophysical Journal*, 663(2), 1406-1419.
- Cooke, I. R., Gupta, D., Messinger, J. P., & Sims, I. R. (2020). Benzonitrile as a Proxy for Benzene in the Cold ISM: Low-temperature Rate Coefficients for CN + C6H6. *The Astrophysical Journal*, 891(2), L41.

- Cruikshank, D. P., Mason, R. E., Dalle Ore, C. M., Bernstein, M. P., Quirico, E., Mastrapa, R. M., . . . Owen, T. C. (2006/09/1). *Ethane on Pluto and Triton*.
- Dalton, J. B. (2010). Spectroscopy of Icy Moon Surface Materials. *Space Science Reviews*, 153(1), 219-247.
- Dalton, J. B., Cassidy, T., Paranicas, C., Shirley, J. H., Prockter, L. M., & Kamp, L. W. (2013). Exogenic controls on sulfuric acid hydrate production at the surface of Europa. *Planetary and Space Science*, 77, 45-63.
- Dartois, E., Schutte, W., Geballe, T. R., Demyk, K., Ehrenfreund, P., & D'Hendecourt, L. (1999). Methanol: The second most abundant ice species towards the high-mass protostars RAFGL7009S and W 33A. Astronomy and Astrophysics, 342, L32-L35.
- Dawes, A., Mukerji, R. J., Davis, M. P., Holtom, P. D., Webb, S. M., Sivaraman, B., . . . Mason, N. J. (2007). Morphological study into the temperature dependence of solid ammonia under astrochemical conditions using vacuum ultraviolet and Fouriertransform infrared spectroscopy. *The Journal of Chemical Physics*, 126(24), 244711.
- Dawes, A., Pascual, N., Hoffmann, S. V., Jones, N. C., & Mason, N. J. (2017). Vacuum ultraviolet photoabsorption spectroscopy of crystalline and amorphous benzene. *Physical Chemistry Chemical Physics*, 19(40), 27544-27555.
- DeMeo, F. E., Dumas, C., de Bergh, C., Protopapa, S., Cruikshank, D. P., Geballe, T. R., . . Barucci, M. A. (2010). A search for ethane on Pluto and Triton. *Icarus*, 208(1), 412-424.
- Duley, W. W., & Williams, D. A. (1981). The infrared spectrum of interstellar dust: Surface functional groups on carbon. *Monthly Notices of the Royal Astronomical Society*, 196(2), 269-274.
- Dumas, C., Terrile, R. J., Brown, R. H., Schneider, G., & Smith, B. A. (2001). Hubble Space Telescope NICMOS Spectroscopy of Charon's Leading and Trailing Hemispheres. *The Astronomical Journal*, 121(2), 1163-1170.
- Dworkin, J. P., Deamer, D. W., Sandford, S. A., & Allamandola, L. J. (2001). Selfassembling amphiphilic molecules: Synthesis in simulated interstellar/precometary ices. *Proceedings of the National Academy of Sciences*, 98(3), 815.
- Ehrenfreund, P., & Charnley, S. B. (2000). Organic Molecules in the Interstellar Medium, Comets, and Meteorites: A Voyage from Dark Clouds to the Early Earth. Annual Review of Astronomy and Astrophysics, 38(1), 427-483.
- Elachi, C., Wall, S., Allison, M., Anderson, Y., Boehmer, R., Callahan, P., . . . Zebker, H. (2005). *Cassini Radar Views the Surface of Titan. Science*, *308*(5724), 970.
- Elsila, J. E., de Leon, N. P., Buseck, P. R., & Zare, R. N. (2005). Alkylation of polycyclic aromatic hydrocarbons in carbonaceous chondrites. *Geochimica et Cosmochimica Acta, 69(5),* 1349-1357.
- Famá, M., Bahr, D. A., Teolis, B. D., & Baragiola, R. A. (2002). Ion beam induced chemistry: the case of ozone synthesis and its influence on the sputtering of solid

oxygen. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 193(1), 775-780.

- Fanale, F. P., Brown, R. H., Cruikshank, D. P., & Clake, R. N. (1979). Significance of absorption features in Io's IR reflectance spectrum. *Nature*, 280(5725), 761-763.
- Ferini, G., Baratta, G. A., & Palumbo, M. E. (2004). A Raman study of ion irradiated icy mixtures. Astronomy and Astrophysics, 414, 757-766.
- Filacchione, G., Capaccioni, F., McCord, T. B., Coradini, A., Cerroni, P., Bellucci, G., ... Newman, S. (2007). Saturn's icy satellites investigated by Cassini-VIMS: I. Fulldisk properties: 350–5100 nm reflectance spectra and phase curves. *Icarus*, 186(1), 259-290.
- Foti, G., Calcagno, L., Sheng, K. L., & Strazzulla, G. (1984). Micrometre-sized polymer layers synthesized by MeV ions impinging on frozen methane. *Nature*, 310(5973), 126-128.
- García-Hernández, D. A., Rao, N. K., & Lambert, D. L. (2011). Are C60 molecules detectable in circumstellar shells of R coronae borelis stars? *The Astrophysical Journal*, 729(2), 126.
- García-Hernández, D. A., Villaver, E., García-Lario, P., Acosta-Pulido, J. A., Manchado, A., Stanghellini, L., . . . Cataldo, F. (2012). Infrared study of fullerene planetary nebulae. *The Astrophysical Journal*, 760(2), 107.
- Garrod, R. T., Weaver, S. L. W., & Herbst, E. (2008). Complex Chemistry in Star -

forming Regions: An Expanded Gas - Grain Warm - up Chemical Model. *The Astrophysical Journal*, 682(1), 283-302.

- Geppert, W. D., Hamberg, M., Thomas, R. D., Österdahl, F., Hellberg, F., Zhaunerchyk, V., . . . Larsson, M. (2006). Dissociative recombination of protonated methanol. *Faraday Discussions*, 133(0), 177-190.
- Gerakines, P. A., Schutte, W. A., & Ehrenfreund, P. (1996). Ultraviolet processing of interstellar ice analogs. I. Pure ices. *Astronomy and Astrophysics*, *312*, 289.
- Gerakines, P. A., Schutte, W. A., Greenberg, J. M., & van Dishoeck, E. F. (1995). The infrared band strengths of H2O, CO and CO2 in laboratory simulations of astrophysical ice mixtures. *Astronomy and Astrophysics*, 296, 810.
- Gerakines, P. A., Whittet, D. C. B., Ehrenfreund, P., Boogert, A. C. A., Tielens, A. G. G.
 M., Schutte, W. A., . . . de Graauw, T. (1999). Observations of Solid Carbon Dioxide in Molecular Clouds with theInfrared Space Observatory. *The Astrophysical Journal*, 522(1), 357-377.
- Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. (2004). Interstellar Ice: The Infrared Space Observatory Legacy. *The Astrophysical Journal Supplement Series*, 151(1), 35-73.

- Gibb, E. L., Whittet, D. C. B., Schutte, W. A., Boogert, A. C. A., Chiar, J. E., Ehrenfreund, P., . . . Kerkhof, O. (2000). An Inventory of Interstellar Ices toward the Embedded Protostar W33A. *The Astrophysical Journal*, 536(1), 347-356.
- Gomis, O., & Strazzulla, G. (2008). Ion irradiation of H2O ice on top of sulfurous solid residues and its relevance to the Galilean satellites. *Icarus*, *194*, 146-152.
- Gottlieb, C. A. (1973, January 01, 1973). *Detection of Acetaldehyde in Sagittarius*. Paper presented at the Molecules in the Galactic Environment.
- Grundy, W. M., Binzel, R. P., Buratti, B. J., Cook, J. C., Cruikshank, D. P., Dalle Ore, C. M., . . . Young, L. A. (2016). Surface compositions across Pluto and Charon. *Science*, 351(6279), aad9189.
- Hagen, W., Allamandola, L. J., & Greenberg, J. M. (1979). Interstellar molecule formation in grain mantles: The laboratory analog experiments, results and implications. *Astrophysics and Space Science*, 65(1), 215-240.
- Hama, T., Ishizuka, S., Yamazaki, T., Kimura, Y., Kouchi, A., Watanabe, N., . . . Pirronello, V. (2017). Fast crystalline ice formation at extremely low temperature through water/neon matrix sublimation. *Physical Chemistry Chemical Physics*, 19(27), 17677-17684.
- Hansen, G. B., & McCord, T. B. (2004). Amorphous and crystalline ice on the Galilean satellites: A balance between thermal and radiolytic processes. *Journal of Geophysical Research: Planets*, 109(E1).
- Hartung, M., Herbst, T. M., Dumas, C., & Coustenis, A. (2006). Limits to the abundance of surface CO2 ice on Titan. *Journal of Geophysical Research: Planets, 111(E7)*.
- Hendrix, A. R., Barth, C. A., & Hord, C. W. (1999). Ganymede's ozone-like absorber: Observations by the Galileo ultraviolet spectrometer. *Journal of Geophysical Research: Planets*, 104(E6), 14169-14178.
- Henning, T., & Salama, F. (1998). Carbon in the universe. Science, 282(5397), 2204-2210.
- Herbst, E., & Klemperer, W. (1973). The Formation and Depletion of Molecules in Dense Interstellar Clouds. *The Astrophysical Journal*, 185, 505.
- Hodgkinson, G. J. (1979). Interstellar chemistry. Journal of the British Astronomical Association, 89, 331.
- Hodyss, R., Parkinson, C. D., Johnson, P. V., Stern, J. V., Goguen, J. D., Yung, Y. L., & Kanik, I. (2009). Methanol on Enceladus. *Geophysical Research Letters*, 36(17).
- Holtom, P. D., Dawes, A., Mukerji, R. J., Davis, M. P., Webb, S. M., Hoffman, S. V., & Mason, N. J. (2006). VUV photoabsorption spectroscopy of sulfur dioxide ice. *Physical Chemistry Chemical Physics*, 8(6), 714-718.
- Howard, A. D., Moore, J. M., Umurhan, O. M., White, O. L., Anderson, R. S., McKinnon, W. B., . . . Young, L. A. (2017). Present and past glaciation on Pluto. *Icarus*, 287, 287-300.

- Hudson, R. L. (2017). An IR investigation of solid amorphous ethanol Spectra, properties, and phase changes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 187, 82-86.
- Hudson, R. L., & Moore, M. H. (1992). A far-IR study of irradiated amorphous ice: an unreported oscillation between amorphous and crystalline phases. *The Journal of Physical Chemistry*, 96(15), 6500-6504.
- Hudson, R. L., & Moore, M. H. (2001). Radiation chemical alterations in solar system ices: An overview. *Journal of Geophysical Research: Planets, 106(E12), 33275-33284.*
- Hudson, R. L., & Moore, M. H. (2018). Interstellar Ices and Radiation-induced Oxidations of Alcohols. *The Astrophysical Journal*, 857(2), 89.
- Ioppolo, S., van Boheemen, Y., Cuppen, H. M., van Dishoeck, E. F., & Linnartz, H. (2011). Surface formation of CO2 ice at low temperatures. *Monthly Notices of the Royal Astronomical Society*, 413(3), 2281-2287.
- James, R. L., Jones, N. C., Hoffmann, S. V., & Dawes, A. (2019). VUV spectroscopy of an electron irradiated benzene : carbon dioxide interstellar ice analogue. RSC Advances, 9(10), 5453-5459.
- Jeffreson, S. M. R., & Kruijssen, J. M. D. (2018). A general theory for the lifetimes of giant molecular clouds under the influence of galactic dynamics. *Monthly Notices of the Royal Astronomical Society*, 476(3), 3688-3715.
- Jenniskens, P., Baratta, G. A., Kouchi, A., de Groot, M. S., Greenberg, J. M., & Strazzulla, G. (1993). Carbon dust formation on interstellar grains. Astronomy and Astrophysics, 273, 583.
- Johnson, R. E. (1990). Energetic Charged-Particle Interactions with Atmospheres and Surfaces.
- Johnson, R. E. (1998). Sputtering and Desorption from Icy Surfaces. In B. Schmitt, C. De Bergh, & M. Festou (Eds.), Solar System Ices: Based on Reviews Presented at the International Symposium "Solar System Ices" held in Toulouse, *France, on March* 27–30, 1995 (pp. 303-334). Dordrecht: Springer Netherlands.
- Johnson, R. E., Cooper, J. F., Lanzerotti, L. J., & Strazzulla, G. (1987). Radiation Formation of a Non-Volatile Comet Crust. *Astronomy and Astrophysics*, 187, 889.
- Jones, B. M., Kaiser, R. I., & Strazzulla, G. (2014a). UV-VIS, Infrared, and Mass spectroscopy of electron irradiated frozen oxygen and carbon dioxide mictures with water. *The Astrophysical Journal*, 781(2), 85.
- Kaiser, R. I. (2002). Experimental Investigation on the Formation of Carbon-Bearing Molecules in the Interstellar Medium via Neutral–Neutral Reactions. *Chemical Reviews*, 102(5), 1309-1358.
- Kaňuchová, Z., Boduch, P., Domaracka, A., Palumbo, M. E., Rothard, H., & Strazzulla, G. (2017). Thermal and energetic processing of astrophysical ice analogues rich in SO2. A&A, 604.

- Keane, J. V., Tielens, A. G. G. M., Boogert, A. C. A., Schutte, W. A., & Whittet, D. C. B. (2001). Ice absorption features in the 5-8 μm region toward embedded protostars. *A&A*, 376(1), 254-270.
- Kieffer, H. H., Chase, S. C., Martin, T. Z., Miner, E. D., & Palluconi, F. D. (1976). Martian North Pole Summer Temperatures: Dirty Water Ice. *Science*, *194*(4271), 1341.
- Kim, Y. S., & Kaiser, R. I. (2012). Electron irradiation of Kuiper belt surface ices: Ternary N2-CH4-CO mixtures as a case study. *The Astrophysical Journal*, 758(1), 37.
- Knez, C., Boogert, A. C. A., Pontoppidan, K. M., Kessler-Silacci, J., van Dishoeck, E. F., Evans Ii, N. J., . . . Lahuis, F. (2005). Spitzer Mid-Infrared Spectroscopy of Ices toward Extincted Background Stars. *The Astrophysical Journal*, 635(2), L145-L148.
- Kolesniková, L., Daly, A. M., Alonso, J. L., Tercero, B., & Cernicharo, J. (2013). The millimeter wave tunneling-rotational spectrum of phenol. *Journal of Molecular Spectroscopy*, 289, 13-20.
- Kolesniková, L., Tercero, B., Cernicharo, J., Alonso, J. L., Daly, A. M., Gordon, B. P., & Shipman, S. T. (2014). Spectroscopic Characterization and Detection of Ethyl Mercaptan in Orion. *The Astrophysical Journal*, 784, L7.
- Kouchi, A., & Kuroda, T. (1990). Amorphization of cubic ice by ultraviolet irradiation. *Nature*, *344*(6262), 134-135.
- Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., & Smalley, R. E. (1985). C60: Buckminsterfullerene. *Nature*, 318(6042), 162-163.
- Krueger, H., & Weitz, E. (1992). O(3P) atom lifetimes and mobilities in xenon matrices. *The Journal of Chemical Physics*, *96*(*4*), 2846-2855.
- Kwok, S., & Zhang, Y. (2011). Mixed aromatic-aliphatic organic nanoparticles as carriers of unidentified infrared emission features. *Nature*, 479, 80-83.
- Kwok, S., & Zhang, Y. (2013). Inidentified infrared emission bands:: PAHs or MAONs? *The Astrophysical Journal*, 771(1), 5.
- Lacombe, S., Cemic, F., Jacobi, K., Hedhili, M. N., Le Coat, Y., Azria, R., & Tronc, M. (1997). Electron-Induced Synthesis of Ozone in a Dioxygen Matrix. *Physical Review Letters*, 79(6), 1146-1149.
- Lacy, J. H., Evans, N. J., II, Achtermann, J. M., Bruce, D. E., Arens, J. F., & Carr, J. S. (1989). Discovery of Interstellar Acetylene. *The Astrophysical Journal*, 342, L43.
- Lane, A. L., Nelson, R. M., & Matson, D. L. (1981). Evidence for sulphur implantation in Europa's UV absorption band. *Nature*, 292(5818), 38-39.
- Lanzerotti, L. J., Brown, W. L., & Johnson, R. E. (1985). Laboratory Studies of Ion Irradiations of Water, Sulfur Dioxide, and Methane Ices. In J. Klinger, D. Benest, A. Dollfus, & R. Smoluchowski (Eds.), Ices in the Solar System (pp. 317-335). Dordrecht: Springer Netherlands.

- Larsson, B., Liseau, R., Pagani, L., Bergman, P., Bernath, P., Biver, N., ... Witt, G. (2007). Molecular oxygen in the ρ Ophiuchi cloud ***. *A&A*, 466(3), 999-1003.
- Lawrence, D. J., Feldman, W. C., Goldsten, J. O., Maurice, S., Peplowski, P. N., Anderson, B. J., . . . Weider, S. Z. (2013). Evidence for Water Ice Near Mercury's North Pole from MESSENGER Neutron Spectrometer Measurements. *Science*, 339(6117), 292.
- Leger, A., & Puget, J. L. (1984). Identification of the "unidentified" IR emission features of interstellar dust ? *Astronomy and Astrophysics*, 500, 279.
- Lequeux, J., & Jourdain de Muizon, M. (1990). The 3.4 and 12 micrometer absorption bands in the proto-planetary nebula CRL 618. *Astronomy and Astrophysics, 240*, L19.
- Leto, G., Gomis, O., & Strazzulla, G. (2005). The reflectance spectrum of water ice: Is the 1.65 mu msp peak a good temperature probe? Memorie della Societa Astronomica *Italiana Supplementi*, *6*, 57.
- Li, Q., Li, A., & Jiang, B. W. (2019). How much graphene in space? Monthly Notices of the Royal Astronomical Society, 490(3), 3875-3881.
- Lin, M.-Y., Lo, J.-I., Lu, H.-C., Chou, S.-L., Peng, Y.-C., Cheng, B.-M., & Ogilvie, J. F. (2014). Vacuum-Ultraviolet Photolysis of Methane at 3 K: Synthesis of Carbon Clusters up to C20. *The Journal of Physical Chemistry A*, 118(19), 3438-3449.
- Loeffler, M. J., & Hudson, R. L. (2016). What is eating ozone ? Thermal reactions between SO2 and O3: Implication for icy environments. *The Astrophysical Journal*, 833(1), L9.
- Loison, J. C., Dobrijevic, M., & Hickson, K. M. (2019). The photochemical production of aromatics in the atmosphere of Titan. *Icarus*, 329, 55-71.
- Lu, H.-C., Chen, H.-K., Cheng, B.-M., Kuo, Y.-P., & Ogilvie, J. F. (2005). Spectra in the vacuum ultraviolet region of CO in gaseous and solid phases and dispersed in solid argon at 10 K. Journal of Physics B: Atomic, Molecular and Optical Physics, 38(20), 3693-3704.
- Lu, H.-C., Chen, H.-K., Cheng, B.-M., & Ogilvie, J. F. (2008). Absorption spectra in the vacuum ultraviolet region of small molecules in condensed phases. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *71*(4), 1485-1491.
- Martínez, J. I., Martín-Gago, J. A., Cernicharo, J., & de Andres, P. L. (2014). Etching of Graphene in a Hydrogen-rich Atmosphere toward the Formation of Hydrocarbons in Circumstellar Clouds. *The Journal of Physical Chemistry C*, 118(46), 26882-26886.
- Mason, N. J., Dawes, A., Holtom, P. D., Mukerji, R. J., Davis, M. P., Sivaraman, B., . . . Shaw, D. A. (2006). VUV spectroscopy and photo-processing of astrochemical ices: an experimental study. *Faraday Discussions*, *133(0)*, 311-329.
- Mastrapa, R. M. E., & Brown, R. H. (2006). Ion irradiation of crystalline H2O–ice: Effect on the 1.65-µm band. *Icarus*, 183(1), 207-214.

- Materese, C. K., Cruikshank, D. P., Sandford, S. A., Imanaka, H., Nuevo, M., & White, D. W. (2014). Ice Chemistry on Outer Solar System Bodies: Carboxylic Acids, Nitriles, and Urea Detected in Refractory Residues Produced from the UV Photolysis of N2CH4:CO-Containing Ices. *The Astrophysical Journal*, 788, 111.
- Materese, C. K., Nuevo, M., & Sandford, S. A. (2015). N- AND O-heterocycles produced from the irradiation of benzene and naphthalene in H2O/NH3- containing ices. *The Astrophysical Journal*, 800(2), 116.
- McCord, T. B., Carlson, R. W., Smythe, W. D., Hansen, G. B., Clark, R. N., Hibbitts, C. A., . . . Martin, P. D. (1997). Organics and Other Molecules in the Surfaces of Callisto and Ganymede. *Science*, 278(5336), 271.
- McCord, T. B., Hansen, G. B., & Hibbitts, C. A. (2001). Hydrated Salt Minerals on Ganymede's Surface: Evidence of an Ocean Below. *Science*, 292(5521), 1523.
- McGuire, B. A. (2018). 2018 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules. *The Astrophysical Journal Supplement Series*, 239(2), 17.
- McGuire, B. A., Burkhardt, A. M., Kalenskii, S., Shingledecker, C. N., Remijan, A. J., Herbst, E., & McCarthy, M. C. (2018). Detection of the aromatic molecule benzonitrile (C6H5CN) in the interstellar medium. *Science*, 359(6372), 202.
- McMurtry, B. M., Saito, S. E. J., Turner, A. M., Chakravarty, H. K., & Kaiser, R. I. (2016). On the formation of benzoic acid and higher benzene carboxylic acids in interstellar model ice grains. *The Astrophysical Journal*, 831(2), 174.
- Merino, P., Švec, M., Martinez, J. I., Jelinek, P., Lacovig, P., Dalmiglio, M., . . . Martin-Gago, J. A. (2014). Graphene etching on SiC grains as a path to interstellar polycyclic aromatic hydrocarbons formation. *Nature Communications*, 5(1), 3054.
- Millar, T. J., Herbst, E., & Charnley, S. B. (1991). The Formation of Oxygen-containing Organic Molecules in the Orion Compact Ridge. *The Astrophysical Journal*, 369, 147.
- Mohammed, H. H. (1990). O(1D) lifetime shortening in SF6 matrix. *The Journal of Chemical Physics*, 93(1), 412-415.
- Montmessin, F., Bertaux, J. L., Lefèvre, F., Marcq, E., Belyaev, D., Gérard, J. C., . . . Vandaele, A. C. (2011). A layer of ozone detected in the nightside upper atmosphere of Venus. *Icarus*, 216(1), 82-85.
- Montmessin, F., & Lefèvre, F. (2013). Transport-driven formation of a polar ozone layer on Mars. *Nature Geoscience*, 6(11), 930-933.
- Moore, J. M., McKinnon, W. B., Spencer, J. R., Howard, A. D., Schenk, P. M., Beyer, R. A., . . . Wilhelms, D. E. (2016). The geology of Pluto and Charon through the eyes of New Horizons. *Science*, *351*(6279), 1284.
- Moore, M. H., & Donn, B. (1982). The Infrared Spectrum of a Laboratory-Synthesized Residue - Implications for the 3.4-MICRON Interstellar Absorption Feature. *The Astrophysical Journal*, 257, L47.

- Moore, M. H., Ferrante, R. F., Hudson, R. L., & Stone, J. N. (2007). Ammonia–water ice laboratory studies relevant to outer Solar System surfaces. *Icarus*, 190(1), 260-273.
- Moore, M. H., & Hudson, R. L. (1992). Far-Infrared Spectral Studies of Phase Changes in Water Ice Induced by Proton Irradiation. *The Astrophysical Journal*, 401, 353.
- Moore, M. H., & Hudson, R. L. (2000). IR Detection of H2O2 at 80 K in Ion-Irradiated Laboratory Ices Relevant to Europa. *Icarus*, 145(1), 282-288.
- Moore, M. H., & Hudson, R. L. (2003). Infrared study of ion-irradiated N2-dominated ices relevant to Triton and Pluto: formation of HCN and HNC. *Icarus*, *161(2)*, 486-500.
- Moore, M. H., Hudson, R. L., & Carlson, R. W. (2007). The radiolysis of SO2 and H2S in water ice: Implications for the icy jovian satellites. *Icarus*, 189(2), 409-423.
- Nelson, R. M., Lane, A. L., Matson, D. L., Veeder, G. J., Buratti, B. J., & Tedesco, E. F. (1987). Spectral geometric albedos of the Galilean satellites from 0.24 to 0.34 micrometers: Observations with the international ultraviolet explorer. *Icarus*, 72(2), 358-380.
- Newman, S. F., Buratti, B. J., Jaumann, R., Bauer, J. M., & Momary, T. W. (2007). Hydrogen Peroxide on Enceladus. *The Astrophysical Journal*, 670(2), L143-L146.
- Noll, K. S., Johnson, R. E., Lane, A. L., Domingue, D. L., & Weaver, H. A. (1996). Detection of Ozone on Ganymede. *Science*, 273(5273), 341.
- Noll, K. S., Johnson, R. E., McGrath, M. A., & Caldwell, J. J. (1997b). Detection of SO2 on Callisto with the Hubble Space Telescope. *Geophysical Research Letters*, 24(9), 1139-1142.
- Noll, K. S., Roush, T. L., Cruikshank, D. P., Johnson, R. E., & Pendleton, Y. J. (1997a). Detection of ozone on Saturn's satellites Rhea and Dione. *Nature*, 388(6637), 45-47.
- Nuevo, M., Milam, S. N., Sandford, S. A., De Gregorio, B. T., Cody, G. D., & Kilcoyne, A. L. D. (2011). XANES analysis of organic residues produced from the UV irradiation of astrophysical ice analogs. *Advances in Space Research*, 48(6), 1126-1135.
- Palumbo, M. E., Ferini, G., & Baratta, G. A. (2004). Infrared and Raman spectroscopies of refractory residues left over after ion irradiation of nitrogen-bearing icy mixtures. *Advances in Space Research*, 33(1), 49-56.
- Pavithraa, S., Methikkalam, R. R. J., Gorai, P., Lo, J. I., Das, A., Raja Sekhar, B. N., . . . Sivaraman, B. (2017). Qualitative observation of reversible phase change in astrochemical ethanethiol ices using infrared spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 178, 166-170.
- Phillips, R. J., Davis, B. J., Tanaka, K. L., Byrne, S., Mellon, M. T., Putzig, N. E., . . . Seu, R. (2011). Massive CO2 Ice Deposits Sequestered in the South Polar Layered Deposits of Mars. *Science*, 332(6031), 838.

- Pino, T., Dartois, E., Cao, A.-T., Carpentier, Y., Chamaillé, T., Vasquez, R., . . . Bréchignac, P. (2008). The 6.2 micron band position in laboratory and astrophysical spectra: a tracer of the aliphatic to aromatic evolution of interstellar carbonaceous dust. A&A, 490(2), 665-672.
- Poch, O., Istiqomah, I., Quirico, E., Beck, P., Schmitt, B., Theulé, P., . . . Tosi, F. (2020). Ammonium salts are a reservoir of nitrogen on a cometary nucleus and possibly on some asteroids. *Science*, 367(6483), eaaw7462.
- Porco, C. C., Helfenstein, P., Thomas, P. C., Ingersoll, A. P., Wisdom, J., West, R., . . . Squyres, S. (2006). Cassini Observes the Active South Pole of Enceladus. *Science*, 311(5766), 1393.
- Postberg, F., Khawaja, N., Abel, B., Choblet, G., Glein, C. R., Gudipati, M. S., . . . Waite, J. H. (2018). Macromolecular organic compounds from the depths of Enceladus. *Nature*, 558(7711), 564-568.
- Potapov, A., Jäger, C., & Henning, T. (2020). Ice Coverage of Dust Grains in Cold Astrophysical Environments. *Physical Review Letters*, 124(22), 221103.
- Prasad, S. S., & Tarafdar, S. P. (1983). UV radiation field inside dense clouds Its possible existence and chemical implications. *The Astrophysical Journal*, 267, 603.
- Protopapa, S., Boehnhardt, H., Herbst, T. M., Cruikshank, D. P., Grundy, W. M., Merlin, F., & Olkin, C. B. (2008). Surface characterization of Pluto and Charon by L and M band spectra. *Astronomy and Astrophysics*, 490, 365-375.
- Protopapa, S., Grundy, W. M., Reuter, D. C., Hamilton, D. P., Dalle Ore, C. M., Cook, J. C., . . . Young, L. A. (2017). Pluto's global surface composition through pixel-by-pixel Hapke modeling of New Horizons Ralph/LEISA data. *Icarus*, 287, 218-228.
- Rahul, K. K., Shivakarthik, E., Meka, J. K., Das, A., Chandrasekaran, V., Rajasekhar, B. N., . . . Sivaraman, B. (2020). Residue from vacuum ultraviolet irradiation of benzene ices: Insights into the physical structure of astrophysical dust. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 231, 117797.
- Raut, U., Teolis, B. D., Loeffler, M. J., Vidal, R. A., Famá, M., & Baragiola, R. A. (2007). Compaction of microporous amorphous solid water by ion irradiation. *The Journal* of Chemical Physics, 126(24), 244511.
- Sagan, C., & Khare, B. N. (1979). Tholins: organic chemistry of interstellar grains and gas. *Nature*, 277(5692), 102-107.
- Saini, J., & Viswanathan, K. S. (2017). Discerning Near-Isoergic Isomers. A Matrix Isolation Infrared and ab Initio Study of the Propargyl Alcohol Dimers. *The Journal of Physical Chemistry A*, 121(7), 1448-1459.
- Salama, F. (1998). UV Photochemistry of Ices. In B. Schmitt, C. De Bergh, & M. Festou (Eds.), Solar System Ices: Based on Reviews Presented at the International Symposium "Solar System Ices" held in Toulouse, France, on March 27–30, 1995 (pp. 259-279). Dordrecht: Springer Netherlands.

- Schmitt, B., Philippe, S., Grundy, W. M., Reuter, D. C., Côte, R., Quirico, E., ... Weaver, H. A. (2017). Physical state and distribution of materials at the surface of Pluto from New Horizons LEISA imaging spectrometer. *Icarus*, 287, 229-260.
- Schutte, W. A., Boogert, A. C. A., Tielens, A. G. G. M., Whittet, D. C. B., Gerakines, P. A., Chiar, J. E., . . . de Graauw, T. (1999). Weak ice absorption features at 7.24 and 7.41 MU M in the spectrum of the obscured young stellar object W 33A. *Astronomy and Astrophysics*, 343, 966.
- Sicilia, D., Ioppolo, S., Vindigni, T., Baratta, G. A., & Palumbo, M. E. (2012). Nitrogen oxides and carbon chain oxides formed after ion irradiation of CO:N2 ice mixtures. *A&A*, 543.
- Sie, N. E., Caro, G. M. M., Huang, Z. H., Martín-Doménech, R., Fuente, A., & Chen, Y. J. (2019). On the Photodesorption of CO2 Ice Analogs: The Formation of Atomic C in the Ice and the Effect of the VUV Emission Spectrum. *The Astrophysical Journal*, 874(1), 35.
- Sivaraman, B., Jamieson, C. S., Mason, N. J., & Kaiser, R. I. (2007). Temperature dependent Formation of Ozone in Solid Oxygen by 5 keV Electron Irradiation and Implications for Solar System Ices. *The Astrophysical Journal*, 669(2), 1414-1421.
- Sivaraman, B., Mukherjee, R., Subramanian, K. P., & Banerjee, S. B. (2014). Benzene formation on interstellar icy mantles containing propargyl alcohol. *The Astrophysical Journal*, 798(2), 72.
- Sivaraman, B., Nair, B. G., Raja Sekhar, B. N., Lo, J. I., Sridharan, R., Cheng, B. M., & Mason, N. J. (2014). Vacuum ultraviolet photoabsorption of pure solid ozone and its implication on the identification of ozone on Moon. *Chemical Physics Letters*, 603, 33-36.
- Sivaraman, B., Raja Sekhar, B. N., Nair, B. G., Hatode, V., & Mason, N. J. (2013). Infrared spectrum of formamide in the solid phase. *Spectrochimica Acta Part A: Molecular* and Biomolecular Spectroscopy, 105, 238-244.
- Solomon, P. M., & Werner, M. W. (1971). Low-Energy Cosmic Rays and the Abundance of Atomic Hydrogen in Dark Clouds. *The Astrophysical Journal, 165*, 41.
- Spencer, J. R., Calvin, W. M., & Person, M. J. (1995). CCD Spectra of the Galilean Satellites: Molecular Oxygen on Ganymede. *Journal of Geophysical Research*, 100, 19049-19056.
- Stern, S. A., Slater, D. C., Scherrer, J., Stone, J., Dirks, G., Versteeg, M., ... Siegmund, O. H. W. (2008). ALICE: The Ultraviolet Imaging Spectrograph Aboard the New Horizons Pluto–Kuiper Belt Mission. *Space Science Reviews*, 140(1), 155.
- Stofan, E. R., Elachi, C., Lunine, J. I., Lorenz, R. D., Stiles, B., Mitchell, K. L., . . . West, R. (2007). The lakes of Titan. *Nature*, 445(7123), 61-64.
- Strazzulla, G. (1999). Ion irradiation experiments and nitrogen bearing species on Jovian and Saturnian icy surfaces. *Planetary and Space Science*, 47(10), 1371-1376.

- Strazzulla, G., & Baratta, G. A. (1991). Laboratory study of the IR spectrum of ionirradiated frozen benzene. Astronomy and Astrophysics, 241, 310-316.
- Strazzulla, G., Baratta, G. A., Johnson, R. E., & Donn, B. (1991). Primordial comet mantle: Irradiation production of a stable organic crust. *Icarus*, *91(1)*, 101-104.
- Strazzulla, G., Baratta, G. A., Leto, G., & Foti, G. (1992). Ion-beam-induced amorphization of crystalline water ice. *EPL (Europhysics Letters)*, 18, 517.
- Strazzulla, G., Baratta, G. A., & Palumbo, M. E. (2001). Vibrational spectroscopy of ionirradiated ices. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 57(4), 825-842.
- Strazzulla, G., Calcagno, L., & Foti, G. (1983). Polymerization induced on interstellar grains by low-energy cosmic rays. *Monthly Notices of the Royal Astronomical Society*, 204, 59P-62P.
- Struve, V. W. S (1989). *Fundamental of Molecular Spectroscopy*. John Wiley& Sons, Chichester.
- Strazzulla, G., Garozzo, M., & Gomis, O. (2009). The origin of sulfur-bearing species on the surfaces of icy satellites. *Advances in Space Research*, *43*, 1442-1445.
- Strazzulla, G., & Johnson, R. E. (1991). *Irradiation Effects on Comets and Cometary Debris. In IAU Collog. 116*: Comets in the post-Halley era (Vol. 167, pp. 243).
- Teolis, B. D., Jones, G. H., Miles, P. F., Tokar, R. L., Magee, B. A., Waite, J. H., . . . Baragiola, R. A. (2010). Cassini Finds an Oxygen–Carbon Dioxide Atmosphere at Saturn's Icy Moon Rhea. *Science*, 330(6012), 1813.
- Teolis, B. D., Loeffler, M. J., Raut, U., Famá, M., & Baragiola, R. A. (2006). Ozone Synthesis on the Icy Satellites. *The Astrophysical Journal*, 644(2), L141-L144.
- Teolis, B. D., Vidal, R. A., Shi, J., & Baragiola, R. A. (2005). Mechanisms of O2 sputtering from water ice by keV ions. *Physical Review B*, 72(24), 245422.
- Tercero, B., Margulès, L., Carvajal, M., Motiyenko, R. A., Huet, T. R., Alekseev, E. A., . . . Cernicharo, J. (2012). Microwave and submillimeter spectroscopy and first ISM detection of 18O-methyl formate*. A&A, 538, A119.
- Thiemens, M. H. (2001). The Mass-Independent Ozone Isotope Effect. Science, 293(5528), 226.
- Thiemens, M. H., & Jackson, T. (1988). New experimental evidence for the mechanism for production of isotopically heavy O3. *Geophysical Research Letters*, 15(7), 639-642.
- Thiemens, M. H., & Jackson, T. (1990). Pressure dependency for heavy isotope enhancement in ozone formation. *Geophysical Research Letters*, 17(6), 717-719.
- Tian, P., Tang, L., Teng, K. S., & Lau, S. P. (2018). Graphene quantum dots from chemistry to applications. *Materials Today Chemistry*, *10*, 221-258.

- Tielens, A. G. G. M. (2008). Interstellar Polycyclic Aromatic Hydrocarbon Molecules. Annual Review of Astronomy and Astrophysics, 46(1), 289-337.
- Tielens, A. G. G. M., & Hagen, W. (1982). Model calculations of the molecular composition of interstellar grain mantles. *Astronomy and Astrophysics*, 114, 245.
- Tokano, T., McKay, C. P., Neubauer, F. M., Atreya, S. K., Ferri, F., Fulchignoni, M., & Niemann, H. B. (2006). Methane drizzle on Titan. *Nature*, 442(7101), 432-435.
- Turnipseed, A. A., Vaghjiani, G. L., Gierczak, T., Thompson, J. E., & Ravishankara, A. R. (1991). The photochemistry of ozone at 193 and 222 nm. *The Journal of Chemical Physics*, 95(5), 3244-3251.
- Vinatier, S., Schmitt, B., Bézard, B., Rannou, P., Dauphin, C., de Kok, R., . . . Flasar, F. M. (2018). Study of Titan's fall southern stratospheric polar cloud composition with Cassini/CIRS: Detection of benzene ice. *Icarus*, *310*, 89-104.
- Waite, J. H., Young, D. T., Cravens, T. E., Coates, A. J., Crary, F. J., Magee, B., & Westlake, J. (2007). The Process of Tholin Formation in Titan's Upper Atmosphere. Science, 316(5826), 870.
- Warneck, P., Marmo, F. F., & Sullivan, J. O. (1964). Ultraviolet Absorption of SO2: Dissociation Energies of SO2 and SO. *The Journal of Chemical Physics*, 40(4), 1132-1136.
- Wilson, T. L., & Matteucci, F. (1992). Abundances in the interstellar medium. *Astronomy and Astrophysics Review*, 4, 1-33.
- Wu, Y.-J., Chen, H.-F., Chuang, S.-J., & Huang, T.-P. (2013). Ultraviolet and infrared spectra of electron bombarded solid nitrogen and methane diluted in solid nitrogen. *The Astrophysical Journal*, 768(1), 83.
- Wu, Y.-J., Wu, C. Y. R., Chou, S.-L., Lin, M.-Y., Lu, H.-C., Lo, J.-I., & Cheng, B.-M. (2012). Spectra and Photolysis of Pure Nitrogen and Methane Dispersed in Solid Nitrogen with Vacuum-Ultraviolet Light. *The Astrophysical Journal*, 746, 175.
- Zheng, W., Jewitt, D., & Kaiser, R. I. (2009). Infrared spectra of Ammonia Water ices. *The Astrophysical Journal Supplement Series*, 181(1), 53-61.
- Ziegler, J. F., & Biersack, J. P. (1985). The Stopping and Range of Ions in Matter. In D. A. Bromley (Ed.), Treatise on Heavy-Ion Science: Volume 6: Astrophysics, Chemistry, and Condensed Matter (pp. 93-129). Boston, MA: Springer US.
- Ziegler, J. F., Ziegler, M. D., & Biersack, J. P. (2010). SRIM The stopping and range of ions in matter (2010). Nuclear Instruments and Methods in Physics Research B, 268, 1818.
- Zuckerman, B., Ball, J. A., & Gottlieb, C. A. (1971). Microwave Detection of Interstellar Formic Acid. The Astrophysical Journal, 163, L41.
- Zuckerman, B., Turner, B. E., Johnson, D. R., Clark, F. O., Lovas, F. J., Fourikis, N., . . . Penfield, H. (1975). Detection of interstellar trans-ethyl alcohol. *The Astrophysical Journal*, *196*, L99.

Publications

 Residue from vacuum ultraviolet irradiation of benzene ices: Insights into the physical structure of astrophysical dust. K. K. Rahul, E. Shivakarthik, J K Meka, A. Das, V. Chandrasekaran, B. N. Rajasekhar, J-I Lo, B-M Cheng, P. Janardhan, A. Bhardwaj, N. J. Mason, B. Sivaraman

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 231, 117797, 2020.

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 Infrared attenuation due to phase changes from amorphous to crystalline observed in astrochemical propargyl ether ices, K. K. Rahul, J K Meka, S. Pavithraa, P. Gorai, A. Das, J-I Lo, B. N. Rajasekhar, B-M Cheng, P. Janardhan, A. Bhardwaj, B. Sivaraman

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 224, 117393, 2020.

- Vacuum Ultraviolet Photoabsorption of Prime Ice Analogues of Pluto and Charon, S. Pavithraa, J-I Lo, K. Rahul, B M Cheng, N J Mason, B. Sivaraman Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 190, 172 – 176, (2018).
- 4. N-Graphene synthesized in astrochemical ices, K K Rahul, M Ambresh, D Sahu, J K Meka, S -L Chou, Y -J Wu, D Gupta, A Das, J -I Lo, B -M Cheng, B N Rajasekhar, A Bhardwaj, N J Mason, B Sivaraman. (Under review)

Publication (not related to thesis)

 Sticking of dust/ micrometeorite particles on to ices at high impact velocities -Implications for astrochemical ice enrichment. E. Shivakarthik, J. K. Meka, Harish, V. S. Surendra, K. K. Rahul, R. Thombre, H. Hill, S. Vijayan, B. Sivaraman *Planetary and Space Science*, 104972, 2020.