Study of Cometary Coma: From Simple Molecules to Complex Organics

A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

by

Sana Ahmed

(Roll No. 17330026)

Under the supervision of

Dr. Kinsuk Acharyya

Planetary Sciences Division

Physical Research Laboratory, Ahmedabad, India.



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY GANDHINAGAR

2022

the memory of my late grandfather Md. Khurshaid Anwar

to

DECLARATION

I declare that this written submission represents my ideas in my own words and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

> Name: Sana Ahmed Roll No: 17330026

Date: 05 August 2022

CERTIFICATE

It is certified that the work contained in the thesis titled "Study of Cometary Coma: From Simple Molecules to Complex Organics" by Sana Ahmed (Roll no: 17330026), has been carried out under my supervision and that this work has not been submitted elsewhere for degree.

I have read this dissertation and in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

> Dr. Kinsuk Acharyya (Thesis Supervisor)

> Associate Professor Planetary Sciences Division Physical Research Laboratory Ahmedabad, India

Date: 05 August 2022

Acknowledgements

I would like to express my gratitude to my thesis supervisor Dr. Kinsuk Acharyya, without whose presence this work would not have seen the light of day. I am thankful to him for introducing me to the exciting field of cometary sciences.

I thank the Doctoral Studies Committee members Dr. Neeraj Srivastava, Prof. Shashikiran Ganesh and Dr. Aveek Sarkar for regularly reviewing my work, and offering fruitful suggestions. I also thank Susarla Raghuram and Aravind K for their scientific insights and suggestions. I acknowledge the support of the academic and administrative sections, library and computer centre at Physical Research Laboratory, and the administrative section at IIT Gandhinagar, for their assistance in academic-related matters. I acknowledge the computation facility, 100TFLOP HPC Cluster, Vikram-100, at Physical Research Laboratory, which I have extensively used for this thesis. Thanks to Goldy Ahuja for his help in proof-reading this thesis.

I am indebted to my office mate Vikas Soni, for the scientific discussions that strengthened this thesis, and also for his constant presence in good and bad times. My years spent in Ahmedabad are definitely memorable, and I have my colleagues and hostel mates to thank for that. I would particularly like to mention Rahul Kushwaha and Sandeep Rout for the stimulating socio-political discussions. I am grateful to my parents, sister, and the rest of my family, for being my personal cheerleaders.

Finally, I would like to thank the cast and crew of Netflix's Money Heist, for making the greatest show on Earth, and giving the anthem 'Bella Ciao'.

Sana Ahmed

Abstract

Comets are numerous objects surviving from the early formation stages of the Solar System, and they are made up of frozen volatiles and dust grains. The frozen volatile material of the cometary interior can be regarded as the oldest and largely unprocessed material of the Solar System. This makes comets the ideal candidates to study the early formation history of the Solar System. Cometary volatiles have been detected both in situ and by remote observations of the cometary atmosphere or coma. One of the major sources of knowledge about the structure and composition of comets comes from studies of the coma. Numerical modeling studies of the coma give a quantitative understanding of the physics and chemistry in the coma gas.

In this thesis work, a numerically robust chemical-hydrodynamical coma model has been built, which can be used to study the coma of comets having a wide range of volatile compositions. This model is based on applying fluid conservation equations to a spherically symmetric coma in a steady state. The model involves collision-dominated flow, a multifluid treatment of the coma-gas, active gas-phase chemistry, and heating and cooling mechanisms. An extensive chemical network is used, which includes chemical reactions involving complex organic molecules and ions. Cooling mechanisms due to vibrational and electronic excitation of CO molecules have also been added.

The model is used to simulate the coma of the interstellar comet 2I/Borisov. This comet shows a high CO/H₂O ratio (~ 1), which makes it a notable exception when compared with Solar System comets, which are dominated by the outgassing of water molecules from the nucleus. The model results show that the high CO/H₂O ratio will affect the chemistry and dynamics of the coma. It is found that the high CO abundance alters the temperature profile and results in high abundances of CO⁺ and HCO⁺ ions in the coma. These two ions affect the formation/destruction rates of other ions such as H₂O⁺, H₃O⁺, and N-bearing ions. In addition, higher abundances are seen for assorted organic neutrals and ions in the interstellar comet, compared to a typical Solar System comet of the Halley-type composition.

Improvements in observational capabilities have resulted in the detection of many new organic species in a large number of comets. While organic species can originate from the nucleus, comets showing moderate to high activity can reach sufficient coma densities for organic molecules to form by active gas-phase coma chemistry. The coma model has been used to study the comets C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy) and C/2014 Q2 (Lovejoy) with respect to their organic abundances. The gas-phase organic formation pathways in the comae of these comets and the resulting coma abundances of organic neutrals and ions due to these gas-phase formation mechanisms are examined. The efficiency of coma chemistry towards forming neutral organic molecules in the coma, as opposed to these molecules outgassing from the nucleus, is discussed.

The volatile composition of 2I/Borisov will provide insights into the prevailing conditions of its host system. A comparative study of the interstellar comet with Solar System comets will aid in making a chemical inventory of 2I/Borisov's natal disk, including possible organics that could be present. Answering the questions of how organic chemistry works in cometary environments will improve our understanding of the formation and distribution of organics in the Solar System and the terrestrial delivery of organic molecules.

Keywords: Comets, Comae, Comet volatiles, Complex organic molecules

List of Publications

- Sana Ahmed & Kinsuk Acharyya, 2021, "Gas-phase Modeling of the Cometary Coma of Interstellar Comet 2I/Borisov", The Astrophysical Journal, 923, 91. https://doi.org/10.3847/1538-4357/ac2a42
- Sana Ahmed & Kinsuk Acharyya, 2021, "Multifluid modelling of cometary coma for diverse range of parent volatile compositions", EGU General Assembly Conference Abstracts, EGU21-14559. https://doi. org/10.5194/egusphere-egu21-14559
- Sana Ahmed & Kinsuk Acharyya, "Investigations on the Coma Formation of Organic Species", under review. https://doi.org/10.48550/ arXiv.2207.13288

List of Figures

1.1	Extract from the <i>Book of Silk</i> compiled by Chinese astronomers
	around 300 B.C., found in 1973 at the Mawangdui archaeologi-
	cal site in China. This is regarded as the first definitive atlas of
	comets, in which more than two dozen comets are documented,
	linking them to calamitous events that occurred at the time of
	their appearance. Image Source: https://deepimpact.astro.
	umd.edu/science/comets-cultures.html

5

- 1.2 Nucleus of comet 67P/Churyumov-Gerasimenko by Rosetta's OSIRIS narrow-angle camera on August 3, 2014, from a distance of 285 kilometers. The image resolution is 5.3 meters per pixel. Image Credit: ESA/Rosetta/MPS for OSIRIS Team MPS/UPD/LAM/IAA/SSO/INTA/UPM/DASP/IDA. 9
- 1.3 Schematic (not to scale) of the main cometary features, showing the coma, the hydrogen cloud, and the plasma and dust tails. The bow shock and the contact surface are shown in the inset figure. Image credit: ESA. https://sci.esa.int/web/giotto/ -/13767-the-comet-main-features-and-scales 12

2.1	Schematic showing the gas-phase formation of species, starting	
	from methanol.	49
2.2	Schematic showing the gas-phase formation of species, starting	
	from ethanol.	50

4.1 Volatile production rates for the interstellar comet 2I/Borisov. The uncertainties in measurements are shown by the vertical error bars, while the downward pointing arrows indicate upper limits on the measurements. Reference: Fitzsimmons et al., 2019 (CN, C_2); Opitom et al., 2019 (H₂O, CN, C₂, C₃); Bannister et al., 2020 (CN, C_2 , NH_2 ; Bodewits et al., 2020 (H_2O , CO); Cordiner et al., 2020 (CO, HCN, CH_3OH, CS) ; de León et al., 2020 (CN, C_2) ; Lin et al., 2020 (CN, C₂, C₃); Kareta et al., 2020 (CN, C₂); McKay et al., 2020 (H₂O); Xing et al., 2020 (H₂O); Aravind et al., 2021 (CN, 80 Temperature profiles for (a) comet 2I/Borisov and (b) Halley-type 4.2comet. T_n , T_e and T_i denote the temperatures of the neutral, electron and ion fluids respectively. 87 4.3Variation of the heating and cooling rates per unit volume for the neutral and electron fluids for (a) comet 2I/Borisov and (b) Halley-type comet. The labels 'Chem-n' and 'Chem-e' denote the net energy gained due to chemical reactions by the neutral and electron fluids, respectively. The other labels denote the energy lost by the electrons due to elastic scattering from H_2O and COmolecules ('e-H₂O elas' and 'e-CO elas') and inelastic scattering from H_2O and CO molecules leading to the rotational and vibrational excitation of H₂O and the vibrational excitation of CO ('e- H_2O rot', 'e- H_2O vib' and 'e-CO vib'). 88 4.4Variation of the flux of (a) parent volatiles, and (b), (c), (d) electrons and assorted ions, with cometocentric distance in 2I/Borisov. 90 Major formation (solid lines) and destruction (dashed/dotted 4.5lines) pathways of (a) CO⁺ (b) HCO⁺, in 2I/Borisov. 92 4.6Major formation (solid lines) and destruction (dashed/dotted lines) pathways of (a) H_2O^+ (b) H_3O^+ , in 2I/Borisov. 944.7Major formation (solid lines) and destruction (dashed/dotted lines) pathways of (a) NH_2^+ (b) NH_3^+ (c) NH_4^+ , in 2I/Borisov. 96

- 4.8 Flux of large organic ions and neutrals for 2I-type (solid lines) and Halley-type abundances (dashed lines). The species show (a) higher abundance for the 2I-type composition (b) nearly equal abundances, and (c) higher abundance for the Halley-type composition, while (d) shows the abundances of species when H₂CO is added to the 2I-type comet composition. 101
- 4.9 The solid lines show the variation of the number density with cometocentric distance for major cometary ions in 2I/Borisov when ionization due to solar wind is considered. The dashed lines show the number density of ions when solar wind is not considered.105

- 5.11 Coma formation rates for the species (a) NH_2CHO and (b) NH_2CHOH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dot-
- 5.12 Coma formation rates for the species (a) HC_3N and (b) HC_3NH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013
- 5.13 Variation of the flux of the N-bearing neutral organic species and their corresponding protonated forms (a) CH_3CN and CH_3CNH^+ , (b) NH_2CHO and NH_2CHOH^+ , and (c) HC_3N and HC_3NH^+ , for different cometary compositions. The solid lines indicate the neutral species abundances and the dashed lines indicate the protonated species abundances. 141
- 5.14 Coma formation rates for the species (a) $CH_3OCH_4^+$ and CH₃OCH₃ (b) CH₃COOH. In (a), the black and red lines (scale: left y-axis) show the net coma formation rate P_i of CH₃OCH₄⁺ and CH_3OCH_3 respectively, and the other colored lines (scale: right y-axis) show the relative rates of the major formation reactions for $CH_3OCH_4^+$. In (b), the black and colored lines show the net coma formation rate P_i , and the relative reaction rate respectively, for CH_3COOH . The line styles in (a) and (b) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012

- 6.1 Variation of the flux of the CHO-bearing organic species
 (a) HCOOCH₃, (b) HCOOH, (c) CH₃CHO, (d) C₂H₅OH, (e)
 (CH₂OH)₂, and (f) CH₂OHCHO, for different cometary compositions. The solid lines indicate the species abundances due to their formation in the coma by gas-phase chemistry. The dashed lines indicate the species abundances in the coma due to outgassing from the nucleus.
 155
- 6.2 Variation of the flux of the N-bearing organic species (a) CH₃CN,
 (b) NH₂CHO, and (c) HC₃N, for different cometary compositions. The solid lines indicate the species abundances due to their formation in the coma by gas-phase chemistry. The dashed lines indicate the species abundances in the coma due to outgassing from the nucleus.
 156
- 6.3 Cometocentric distance variation of the number densities of the H-abstracted radicals CH₂CH₂OH, CH₃CHOH and CH₂OH, and the species from which they form namely C₂H₅OH and CH₃OH, for the comets (a) C/1996 B2, (b) C/2012 F6, (c) C/2013 R1, and (d) C/2014 Q2.

6.4 Cometocentric distance variation of the number densities of neutral radicals bearing carbon atoms, for the comets (a) C/1996 B2,
(b) C/2012 F6, (c) C/2013 R1, and (d) C/2014 Q2. 162

List of Tables

- 2.1 Data on the proton affinity of some neutral cometary species, evaluated and compiled by Hunter & Lias (1998). The species are arranged in decreasing order of their proton affinities. 42
- 3.1 The thermal energy source terms \hat{G}_k , k = n, i, e due to the different types of chemical reactions included in the model. Θ_k is the mean kinetic energy of a particle belonging to the fluid ksuch that $\Theta_n = \frac{3}{2}k_BT_n$, $\Theta_i = \frac{3}{2}k_BT_i$ and $\Theta_e = k_BT_e$. ΔE is the mean exo/endo-thermicity of the chemical reaction. $\dagger m_{\rm T}$ is the sum of the masses of the reactants, $m_{\rm CC'} = m_{\rm C} + m_{\rm C'}$ and $m_{\rm CC'C''} = m_{\rm C} + m_{\rm C'} + m_{\rm C''}$. References: [1] Draine (1986), [2] Rodgers & Charnley (2002), [3] Weiler (2006).

67

3.2	Reactions showing the excitation and de-excitation of the elec- tronic states of CO, resulting in the cooling of the electron fluid
	(Schmidt et al., 1988)
4.1	Input volatile production rates used as model inputs for $2I/Borisov$
	at 2.01 AU. The production rates for CS_2 , C_2H_2 and NH_3 are
	calculated from the photodissociation branching ratios of their
	respective product species
4.2	Relative abundance percentage with respect to water, for the Solar
	System comet 1P/Halley (Bockelée-Morvan et al., 2004) 85
4.3	Solar wind parameters used at 2.01 AU, taken from Hansen et al.
	(2007)
5.1	Parameters used as model inputs for the different comets. Refer-
	ences for $Q_{\rm H_{2}O}$ are Mumma et al. 1996 (C/1996 B2), Combi et al.
	2014 (C/2012 F6), Combi et al. 2018 (C/2013 R1 and C/2014
	Q2). References for the radius are https://ssd.jpl.nasa.gov/
	(C/1996 B2), Paradowski 2020 (C/2013 R1, C/2014 Q2) 115
5.2	Volatile species abundance percentages with respect to H_2O , used
	as model inputs. The superscript a against some of the volatiles
	abundances indicates the reported upper limit for this species.
	The references for the abundances are C/1996 B2: McPhate et al.
	(1996); Lis et al. (1997); Bockelée-Morvan et al. (2004), C/2012
	F6: Biver et al. $(2014, 2016)$; Paganini et al. $(2014b)$; Lippi et al.
	(2020), C/2013 R1: Biver et al. (2014); Paganini et al. (2014a),
	C/2014 Q2: Biver et al. (2015); Dello Russo et al. (2022) 116

Contents

A	bstra	ct					i		
Li	List of Publications iii								
Li	st of	Figure	es				\mathbf{v}		
Li	st of	Tables	S				xiii		
1	Intr	oducti	ion				3		
	1.1	Histor	ical Overview		•		5		
	1.2	Physic	cal Structure		•		7		
		1.2.1	The Nucleus				7		
		1.2.2	The Coma		•		10		
		1.2.3	The Hydrogen Cloud				11		
		1.2.4	The Plasma and Dust Tails				12		
		1.2.5	Plasma Regions and Boundaries				14		
	1.3	Comp	osition of Comets				17		
		1.3.1	Main Constituents				18		
		1.3.2	Hydrocarbons				19		
		1.3.3	CH_3OH and H_2CO				20		
		1.3.4	Complex Organics				21		
		1.3.5	Interstellar Comet Composition				22		
	1.4	Comet	t Classifications				23		
		1.4.1	Dynamical Classification				23		
			1.4.1.1 Periodicity				23		
			1.4.1.2 Orbital Period				23		

		1.4.2 Compositional Classification				
			1.4.2.1 Carbon-Chain Species Abundances	5		
			1.4.2.2 CO_2 and CO Abundances $\ldots \ldots \ldots 2$	6		
			1.4.2.3 Organic Abundances	7		
			1.4.2.4 Comet Taxonomy	7		
	1.5	Coma	Modeling	7		
		1.5.1	Coma Collisional Region	8		
		1.5.2	Physical and Chemical Processes in the Coma 2	9		
		1.5.3	Historical Overview of Coma Modeling	9		
	1.6	Impor	tance of Studying Comets	1		
	1.7	Work	Objectives	2		
	1.8	Thesis	Overview	4		
2	Che	mical	Network and Reaction Pathways 3	7		
	2.1	Types	of Chemical Reactions	7		
		2.1.1	Photolytic Processes	7		
		2.1.2	Electron Impact and Recombination Processes	9		
		2.1.3	Radiative Processes	0		
		2.1.4	Reactions of Ions and Neutrals	1		
	2.2	Reacti	ion Rates			
		2.2.1	Photolytic Rates	5		
		2.2.2	Bimolecular Reaction Rates	6		
		2.2.3	Ion-dipole Reaction Rates	6		
	2.3	Forma	tion Pathways of Organic Species	8		
		2.3.1	Formation Pathways Starting from Alcohols 4	8		
			2.3.1.1 Formation from CH_3OH	8		
			2.3.1.2 Formation from C_2H_5OH	9		
		2.3.2	Formation of Aliphatic Diols	0		
		2.3.3	Formation of Acids and Aldehydes	1		
			2.3.3.1 Formic Acid	1		
			2.3.3.2 Acetaldehyde	1		
		2.3.4	Formation of N-bearing Organics	2		

		$2.3.4.1 \text{Acetonitrile} \dots \dots \dots \dots \dots \dots \dots \dots \dots $	52
		2.3.4.2 Formamide	52
		2.3.4.3 Cyanopolyynes	53
	2.4	Reaction Databases and Other Sources	53
3	Gas	Phase Coma Model 5	55
	3.1	Hydrodynamical Description	55
	3.2	Model Equations	58
		3.2.1 Simplifications	59
	3.3	Initial Conditions	32
	3.4	Source Terms	33
		3.4.1 Number Density Source Term	33
		3.4.2 Thermal Energy Source Terms	35
		3.4.2.1 Chemical Reactions	35
		3.4.2.2 Elastic Scattering $\ldots \ldots \ldots$	36
		3.4.2.3 Inelastic Scattering	<u> 5</u> 9
	3.5	Photochemistry	71
		3.5.1 Photo Cross Section and UV Flux Data	73
	3.6	Interaction with the Solar Wind	74
		3.6.1 Charge Exchange	75
		3.6.2 Electron Impact	75
	3.7	Numerical Approach	76
4	Stu	dy of the Interstellar Comet 2I/Borisov 7	79
	4.1	Observations of 2I/Borisov	31
	4.2	Model Inputs	33
		4.2.1 Input Volatile Production Rate of 2I/Borisov	33
		4.2.2 Inputs: Volatile Abundance of H ₂ O-Rich Comet and Nu-	
		cleus Size	34
	4.3	Results	36
		4.3.1 Temperature Profile	36
		4.3.2 Coma Chemistry	39
		4.3.2.1 Species Abundances	39

			4.3.2.2 CO^+ and HCO^+				
			4.3.2.3 H_2O^+ and H_3O^+				
			4.3.2.4 N-bearing ions				
			4.3.2.5 Complex ions				
	4.4	Discus	ssions				
		4.4.1	Effect of CO Abundance on Energy Exchange Rates 97				
		4.4.2	Effect of CO Abundance on Reaction Rates				
		4.4.3	Effect of CO Abundance on Ionic Composition 99				
		4.4.4	Effect of CO Abundance on Organic Composition 100				
		4.4.5	Effect of Solar Wind on Ionic Composition 103				
		4.4.6	Dissociative Recombination Rates				
	4.5	Summ	nary				
5	Stu	dy of t	the Formation of Organics in the Coma 111				
	5.1	Impor	tance of Cometary Organics				
	5.2	Come	ts Studied in this Work				
		5.2.1	C/1996 B2 (Hyakutake)				
		5.2.2	C/2012 F6 (Lemmon) 113				
		5.2.3	C/2013 R1 (Lovejoy)				
		5.2.4	C/2014 Q2 (Lovejoy)				
	5.3	Model	Inputs				
	5.4	4 Results					
		5.4.1	Temperature Profiles				
		5.4.2	Species Formation in the Coma				
			5.4.2.1 CHO-bearing organics				
			5.4.2.2 N-bearing organics				
			5.4.2.3 Other Organics: CH_3OCH_3 , CH_3COOH and HC_5N141				
		5.4.3	Upper Limits on Formation Rates				
		5.4.4	Formation of Glycine				
	5.5	Summ	nary				
6	Cor	netary	Organics: Efficiency of Coma Chemistry 151				
	6.1	Clues	from the Interstellar Medium				

	6.2	Coma Abundances due to Gas-Phase Chemistry					
	6.3 Role of Gas Phase Chemistry						
	6.3.1 Chemical Reactions Forming Organic Species						
			6.3.1.1	Neutral-Neutral Bimolecular Reactions	160		
			6.3.1.2	Ion-Neutral, Proton Transfer and Radiative As-			
				sociation Reactions	163		
			6.3.1.3	Dissociative Recombination Reactions	164		
		6.3.2	Effect of	Temperature on Reaction Rates	165		
	6.4	Summa	ary		166		
7	Con	clusior	ns, Impli	cations and Future Work	167		
	7.1	Conclu	sions		167		
	7.2	Implica	ations		169		
	7.3	Future	Work		171		
A	Maj	or Org	ganic For	mation Reactions	173		
Bi	bliog	raphy			185		

Chapter 1

Introduction

Comets are the most numerous objects of the Solar System, and they, along with asteroids, are thought to be the relics of Solar System formation, that were created and processed in the primordial solar nebula (Weissman et al., 2002). Asteroids are the parent bodies of most meteorites, and they formed by the accretion of solids in the inner warm and dense regions of the solar nebula (Brownlee et al., 2006). On the other hand, comets are assumed to have formed in the outer regions, where the temperatures were low enough for the formation of frozen volatiles, and the density was sufficient to allow effective condensation. The orbit of Jupiter at 5.2 AU is taken to be the boundary between the asteroid and comet formation zones (Weissman et al., 2002). There are several concurrent models that deal with the origin of cometary ices, including the inheritance of amorphous ices from the prestellar core (Meech et al., 2009). While comets may not be entirely pristine, the cometary ices can be considered to be the least-altered material surviving from the formative period of the Solar System. The cometary material originally existed in the solar nebula as microscopic interstellar grains and nebular condensates, which then coagulated into macroscopic bodies ranging in size from tens to hundreds of kilometers (Weidenschilling, 2004). These icy planetesimals may have formed the cores of the giant planets (Chambers, 2007) and they may have also contributed to the volatile inventory of the terrestrial planets, including the delivery of prebiotic organic material (Ehrenfreund & Charnley, 2000; Marty et al., 2016). Studies of the elemental and molecular

compositions, and the isotopic ratios of cometary materials, and comparison to laboratory experiments and to other objects within and outside the Solar System is essential to obtain insights into comet formation and evolution.

Present day comets reside in two distinct reservoirs, namely the Oort cloud and the Kuiper Belt (divided into the classical Kuiper Belt, the scattered disk and the extended disk populations; Morbidelli et al., 2008). However, it is assumed that the cometary populations formed closer to the Sun than where they currently reside, as densities in the solar nebula at large distances from the Sun would have been too low for planetesimals to form. Migration of the giant planets scattered the comets either inwards, causing the period of Late Heavy Bombardment (LHB) 4.0-3.8 billion years ago (Marty et al., 2016), or outwards to their current locations (Gomes et al., 2005). The number of known comets at present is ~ 5000, which is a miniscule fraction of the total comet population that is estimated to be more than a trillion. Comets have been observed for centuries, but have been studied as astronomical phenomena since only the previous few hundred years.

Comets and asteroids contain abundant quantities of both inorganic as well as organic species, and a subset of cometary organics are of prebiotic interest (Oro et al., 1991; Irvine, 1998; Altwegg et al., 2016; Dalai et al., 2016; Kwok, 2016). Many of these organic molecules have also been observed in the interstellar medium, suggesting a common formation pathway. Impact processes are likely to have transported volatiles and organics to the terrestrial planets, including the Earth. Therefore, comets may have played a decisive role in the prebiotic chemistry that began after the LHB (Chyba & Sagan, 1997). The organic composition of comets has been estimated from remote observations (Bockelée-Morvan & Biver, 2017), while in situ spacecraft missions such as *Rosetta* have greatly enhanced the organic inventory of comets (Capaccioni et al., 2015; Goesmann et al., 2015; Le Roy et al., 2015; Altwegg et al., 2016, 2019; Schuhmann et al., 2019).



Figure 1.1: Extract from the *Book of Silk* compiled by Chinese astronomers around 300 B.C., found in 1973 at the Mawangdui archaeological site in China. This is regarded as the first definitive atlas of comets, in which more than two dozen comets are documented, linking them to calamitous events that occurred at the time of their appearance. Image Source: https://deepimpact.astro.umd.edu/science/comets-cultures.html

1.1 Historical Overview

Many references to comets have been made since ancient times, including findings of their carved images on rock walls in North America and islands of the Pacific, and their mention in early Chinese histories and by ancient Greek and Roman philosophers such as Aristotle, Seneca and Pliny the Elder. Aristotle and Ptolemy did not consider comets to be celestial phenomena; while Aristotle wrote about comets in his treatise on terrestrial phenomena, *Meteorologica*, he did not mention them in his work on heavenly bodies. The first comet that was recorded reliably in multiple historical texts was the one observed by the Chinese in 613 B.C. The appearance of comets in early times was considered to be an omen for calamities and tragedies. A beneficial outcome of these superstitious beliefs is that cometary apparitions were recorded, and this information is quite valuable to modern astronomers. Some of the cometary apparitions have been visually impressive or memorable, and these are termed as great comets.

It was only in the sixteenth century that comets were established to be celestial objects that existed outside the Earth's atmosphere. This was the result of parallax measurements of the Great Comet of 1577 by Tycho Brahe and Michael Maestlin, which initiated an era of positional measurements in cometary astronomy. In 1705, Edmond Halley used Newtonian mechanics to calculate the orbits of 23 comets that appeared between 1337 and 1698. He noted that the orbital elements for three of the cometary apparitions were quite similar, and deduced that it was the same comet. He predicted its return in 1758, and this speculation proved correct, causing the comet to be named after him and become famously known as comet Halley. Orbital calculations have enabled investigators to trace the appearances of comet Halley backwards through many centuries, and identify its mention in ancient records dating as far back as 240 B.C.

The modern era in cometary science began with the formulation of three path-breaking ideas in 1950-51. These were the proposal of the icy-conglomerate model of the cometary nucleus (Whipple, 1950), the identification of a distant cometary population known as the Oort cloud (Oort, 1950) and the explanation of the motion of features in cometary plasma tails due to interactions with the solar wind (Biermann, 1951). The late 1970s witnessed an increased interest in comets, mostly due to the predicted return of comet Halley in 1986. The first in situ mission to a comet was the *International Cometary Explorer* (ICE) that made a tail passage of 21P/Giacobini-Zinner, and later also passed through Halley's sphere of influence. In situ measurements of comet Halley by five spacecrafts (*Giotto, Sakigake, Suisei, Vega 1* and 2) confirmed Whipple's icy-conglomerate model and also led to the detection of several cometary molecules and ions. Since then, spacecraft missions to other comets and improved remote observational facilities have led to significant advances in the study of comets. The direct examination of cometary material is particularly crucial in understanding

the composition of comets. In this context, the *Deep Impact* space probe designed to study the cometary interior by releasing an impactor into the comet 9P/Tempel, and the Stardust cometary sample return mission to 81P/Wild 2 have been scientifically important. The findings of the Deep Impact mission advanced our knowledge of cometary nuclei, and some of these results include the observation of surface features and morphological diversity of 9P/Tempel (Thomas et al., 2007) and the presence of micrometer sized subsurface H_2O grains (Sunshine et al., 2007). Analysis of the samples returned from 81P/Wild 2 by Stardust enabled the detection of glycine and other amino acids (Glavin et al., 2008; Elsila et al., 2009) and also established the importance of large-scale mixing in the early Solar System through the presence of high temperature phase minerals such as chondrules in the cold cometary ices (Brownlee et al., 2006). The hugely successful Rosetta mission to 67P/Churyumov-Gerasimenko was the first spacecraft to orbit a comet, and the in situ observations more than doubled the number of species known to be present in comets (Rubin et al., 2019). The *Rosetta* mass spectrometers probed the comet's isotopic composition, which has implications on comet formation and volatile delivery to the early Earth (Altwegg et al., 2015; Marty et al., 2017; Hoppe et al., 2018). The continuous two-year monitoring of the comet enabled the observation of changes in the morphology and composition of the nucleus with time and the strong seasonal effects (De Sanctis et al., 2015; Fornasier et al., 2016).

1.2 Physical Structure

1.2.1 The Nucleus

The central solid body of a comet is the nucleus, which is generally a few kilometers in size and is made up of frozen gases and dust. Small cometary nuclei may have sizes measuring several hundred meters, for example the comet 71P/Clark has an estimated radius of 680 m (Lamy et al., 2000). The largest cometary nucleus is reported to be that of the comet C/2014 UN₂₇₁ (Bernardinelli–Bernstein), which has a radius ~ 60 km (Hui et al., 2022). Using data obtained from the NE- OWISE mission, Bauer et al. (2017) constrained the sizes for a debiased sample of comets. They find that the mean nucleus diameter of Jupiter family comets (JFCs) is 1.3 km, while this is 2.1 km for long-period comets (LPCs). Additionally, the median diameter for JFCs is 3 km, which is midway between the values of 3.2 km and 2.8 km reported by Meech et al. (2004) and Fernández et al. (2013), respectively. The cumulative size-frequency distribution of the nucleus sizes yields a power law relationship $N(>D) \sim D^{-\beta}$, where N is the number of comets with diameter greater than D.

Since the nucleus has a relatively small size, its mass, density, gravity and escape velocity are low, and hence it is irregularly shaped since gravitational compaction of the fluffy nuclear material does not occur (Keller, 1990). In the outer Solar System where the solar radiation flux is negligible, comets are not active and consist only of their nuclei. The nucleus consists of a loose collection of condensed volatiles like water, carbon monoxide, methane, ammonia, carbon dioxide and other condensed molecules, in a matrix of dust and mineral particles. An approximate description of the compositional structure of the nucleus that is widely accepted in the present day was proposed by Whipple, who described cometary nuclei as "dirty snowballs" or an "icy conglomerate" of refractory dust and primary ices (Whipple, 1950).

Numerous models have been proposed to explain the internal structure and density of the nucleus (Weissman & Lowry, 2008), and comet formation models are an intensive area of research. The relative abundances of refractory materials and volatile ices or the refractory-to-ice mass ratio within the nucleus is an important tracer of comet formation and evolution. It is still unclear if the mixing of ices and refractories took place on a microscopic level by the formation of ice mantles around micrometer sized grains, or at macroscopic scales by the mixing of ice grains and refractory grains, or a combination of both. The refractory-to-ice ratio also affects the thermal properties of the nucleus and the cometary outgassing activity, since accelerated dust particles that leave the nucleus may also contain ices. *Rosetta* provided the opportunity to measure the refractory-to-ice ratio and the coma dust-to-gas ratio for an extended period of time. Although these measurements are of low precision, yet it is indicated


Figure 1.2: Nucleus of comet 67P/Churyumov-Gerasimenko by *Rosetta's* OSIRIS narrow-angle camera on August 3, 2014, from a distance of 285 kilometers. The image resolution is 5.3 meters per pixel. Image Credit: ESA/Rosetta/MPS for OSIRIS Team MPS/UPD/LAM/IAA/SSO/INTA/UPM/DASP/IDA.

that the dust-to-gas ratio may not be representative of the refractory-to-ice ratio (Choukroun et al., 2020).

The composition of cometary nuclei is not known precisely because molecules exist in the condensed phase and their spectral analysis using ground and space based telescopes is challenging. In addition, the nucleus sizes are too small to be resolved by remote observations. On the rare occasion when a comet with a large and probably resolvable nucleus enters the inner Solar System (for example in the case of comet Hale-Bopp), the coma obscures the nucleus from view. Hence, the only means of studying the cometary nucleus in detail is by in situ measurements using interplanetary space probes (Keller et al., 2004). Comet 1P/Halley was the target of several in situ measurements, and observations taken by the *Giotto* space probe revealed the nucleus to possess a dark crust with low albedo, while the volatiles are located below the crust (Sagdeev et al., 1986; Keller et al., 1987). Images of the comets 19P/Borrelly acquired by the *Deep Space I* mission, 9P/Tempel obtained by *Deep Impact* and 67P/Churyumov-Gerasimenko (<math>67P/C-G) by the OSIRIS camera aboard the *Rosetta* mission confirm the low surface albedo of cometary nuclei (Soderblom et al., 2002; Buratti et al., 2004; Li et al., 2007; Fornasier et al., 2015). Particles that have radii that are larger than the critical radius (the largest size that can be entrained by the sublimating gas) accumulate on the surface, leading to the formation of surface features that were observed on 9P/Tempel (Kobayashi et al., 2013). Reflectance spectra of 67P/C-G suggest that the low albedo is due to the presence of refractory organics in dust grains, containing polyaromatic compounds mixed with sulfides and Fe-Ni alloys (Quirico et al., 2015).

1.2.2 The Coma

As a comet enters the inner Solar System, the temperature of the outer surface of the nucleus increases due to the solar radiation field. Volatile gases sublimate from the nucleus, expand outwards and entrain the dust particles from the surface, leading to the formation of the coma (Keller, 1990). The nucleus and the coma are collectively known as the head of the comet, and this can extend upto 2-3 million kilometers. Most comets become active inside the orbit of Jupiter (~ 5 AU) when sublimation of water ice drives cometary outgassing. However, few comets have been observed to show activity at larger heliocentric distances (Meech et al., 2009; Kulyk et al., 2016; Womack et al., 2017), though they tend to be extremely faint and this introduces an observational bias. A prime example of such a comet is C/2017 K2 (PanSTARRS) that exhibited activity out to a heliocentric distance of 23.7 AU (Jewitt et al., 2017; Meech et al., 2017b; Hui et al., 2018).

The nucleus has insufficient mass and cannot gravitationally bind its atmosphere, so the coma is interpreted to be in the steady state (Huebner, 1990). Sublimation from the nucleus continuously replenishes the outflowing gas, and the coma is frequently observed as stable and unchanging. However, sudden changes in the brightness and structure of the coma is not uncommon, and features may rapidly alter within several hours. Various processes have been proposed to explain cometary outbursts, such as the formation of surface craters through internal explosions (Brownlee et al., 2004) or the crystallization of amor-

phous ice that releases heat and triggers outbursts (Prialnik & Bar-Nun, 1992). Spatial structures are also seen in the comae of many comets, in both the gas and dust components (Combi et al., 2004; Schleicher & Farnham, 2004). Cometary comae are a natural laboratory for many unique and intriguing astrophysical phenomena (Ip & Axford, 1990). The mean free path near the nucleus is small, resulting in frequent molecular collisions and interactions (Keller, 1990). Ionization and dissociation processes in the coma result in the formation of ions and radicals. Fragmented species created by the photolysis of parent molecules are also present in the bulk of the coma. Detailed analyses of high-resolution spectra show that the observed coma emissions are due to two kinds of excitation mechanisms: radiative processes and collisional excitation (Bockelée-Morvan et al., 2004; Feldman et al., 2004; Bodewits et al., 2022). A knowledge of the excitation mechanisms and molecular and atomic data can be used to derive column densities of the observed species from the spectrophotometric data. With suitable modeling, the column densities can be used to deduce the relative abundances of the parent species in the ice (Combi et al., 2004).

1.2.3 The Hydrogen Cloud

The head of the comet (namely, the nucleus and the coma) is surrounded by a hydrogen cloud, that was first predicted by Biermann (1968). Subsequently, observations of large clouds of Lyman- α emission around the comets Tago-Sato-Kosaka 1969g (C/1969 T1) and Bennett (C/1969 Y1) led to the discovery of hydrogen clouds (Brandt & Chapman, 2004). Since H₂O is the dominant cometary volatile, its photodissociation produces H, O and OH, that are present in the hydrogen cloud. The ultraviolet imager instrument of the *Suisei* space probe recorded the variation of the intensity of Lyman- α with time, in the hydrogen cloud of comet 1P/Halley. The total brightness of the hydrogen cloud was observed to change periodically, and also exhibit pulsations (Kaneda et al., 1986). The observed hydrogen cloud of 1P/Halley had a shell structure, which was the result of outbursts from the nucleus (Hirao, 1986).

The hydrogen envelope can be extremely large, with observable emissions



Figure 1.3: Schematic (not to scale) of the main cometary features, showing the coma, the hydrogen cloud, and the plasma and dust tails. The bow shock and the contact surface are shown in the inset figure. Image credit: ESA. https://sci.esa.int/web/giotto/-/13767-the-comet-main-features-and-scales

detected at distances greater than 10^7 km from the nucleus (Combi et al., 2000). The energy released due to photodissociation gives the H atoms excess velocity in the range of 4 - 24 km s⁻¹ (Keller & Meier, 1976; Combi et al., 2004). Collisions in the inner coma can thermalize the H atoms partially, which affects the bulk velocity distribution. The Solar Wind Anisotropies (SWAN) instrument on the Solar and Heliospheric Observatory (SOHO) has enabled the imaging of the full H coma, and long term monitoring by this instrument has provided measurements of hydrogen Lyman- α for many comets (Combi et al., 2018, 2019, 2021).

1.2.4 The Plasma and Dust Tails

The cometary plasma and dust tails form when the solar wind and the solar radiation pressure influence the motion of the constituents of the coma as the comet approaches the sun (Brandt & Chapman, 2004). Typically, cometary tails have a size of around 10 million kilometers, but can even extend up to hundreds

of millions of kilometers. The two tails are morphologically different; the plasma tail or the type I tail is long and thin, while the dust tail or the type II tail has a diffuse and curved appearance. The plasma tail is made up of molecular ions such as CO^+ and H_2O^+ , along with protons, other ions and electrons, and often appears blue in color due to ionic emissions (Bobrovnikoff, 1942). The plasma tail is observed for comets at distances < 1.5 - 2 AU from the sun and results from the interaction of cometary charged particles with the solar wind. Indeed, observations of plasma tails provided the necessary evidence to prove the existence of the solar wind (Biermann, 1951). Comets at larger heliocentric distances and those whose perihelion distances are too close to the sun may not show plasma tails. The ion velocities in the plasma tail vary from about 10 km s⁻¹ near the head of the comet to nearly 250 km s⁻¹ far out from the head (Brandt & Chapman, 2004).

The cometary dust tail is made up of dust particles that are entrained from the nucleus by the sublimating volatile molecules (Brandt & Chapman, 2004). Different sized dust particles obtain different velocities, with submicrometer-sized particles reaching nearly the velocity of the escaping gases (~ 1 km s⁻¹), while particles larger than a centimeter hardly reach the gravitational escape velocity (~ 1 m s⁻¹) of the cometary nucleus (Grün & Jessberger, 1990). The motion of dust particles is influenced by the solar radiation pressure which repels the particles and solar gravity which attracts them. These two forces vary as r^{-2} , and one can define an effective gravity as their difference, which decides the nature of the orbit of the particle (Finson & Probstein, 1968). The effective gravity depends on particle size, shape and composition, and the diffuse and curved nature of the dust tail is due to different particles following separate orbits.

The two tails are oriented in different directions and do not point in the exact antisolar direction. As the comet approaches the sun, the first to form is the coma, followed by the development of the plasma tail and the dust tail. These then disappear in reverse order after the perihelion passage of the comet (Huebner, 1990). The observation of cometary tails also depends on the viewing geometry. Chinese astronomical records make a distinction between *beixing* and *huixing*, that is, comets without and with a tail, respectively. Comets that have

a tail have been described as *beixing* when they are in opposition and the tail is not visible (Needham, 1959). Sometimes the viewing geometry is such that when the Earth crosses the orbital plane of the comet, dust particles appear as a spike emanating from the coma, and directed towards the sun, creating an antitail. This phenomenon occurs when dust particles remain in the cometary orbital plane due to a weaker influence by the solar radiation pressure, forming a disk, which is visible side-on as a spike when the Earth passes through the plane (Gary & Odell, 1974).

1.2.5 Plasma Regions and Boundaries

The two types of plasma at a comet are (1) the light solar wind ions, and (2) the cometary plasma consisting of heavy ions that are created due to the ionization of the neutral coma gas. The addition of slow, heavy cometary ions to the high velocity solar wind leads to mass-loading of the solar wind (Biermann et al., 1967; Szegö et al., 2000). This interaction results in the creation of large-scale structures in the form of boundaries and regions characterized by changes in the plasma parameters. The plasma structures in the cometary environment are dependent on the scale size, and therefore the gas production rate from the nucleus. Thus, the outgassing activity may be divided into three categories, following Goetz et al. (2022): weakly active (production rate $< 10^{26} \text{ mol s}^{-1}$), intermediately active ($10^{26} \text{ mol s}^{-1} < \text{production rate} < 5 \times 10^{27} \text{ mol s}^{-1}$).

The solar wind gets decelerated strongly in the vicinity of the comet as a result of mass-loading. For a comet such as 1P/Halley, that has a high production rate, mass-loading effects were seen at distances $> 10^6$ km from the nucleus (Mukai et al., 1986; Neubauer et al., 1986). The bow shock is formed at the boundary where the solar wind flow transitions from supersonic to subsonic. The existence of two permanent boundaries, namely the bow shock and the contact surface, were predicted by computer simulations (Ip & Axford, 1982; Schmidt & Wegmann, 1982), and later confirmed by spacecraft flybys. In situ measurements by *Suisei* during its encounter with 1P/Halley provided evidence of the bow

shock at a cometocentric distance of about 4.5×10^5 km (Mukai et al., 1986) and similar observations were also made by *Vega 1* and *2* and *Giotto* (Galeev et al., 1986; Gringauz et al., 1986c). A plasma structure detected at comet 67P/C-G was identified as an infant bow shock, that may manifest as a more developed cometary bow shock at higher activity (Gunell et al., 2018; Goetz et al., 2021). *Rosetta* did not travel far enough from the comet to cross the bow shock during higher outgassing rates.

The bow shock and the contact surface create three general plasma interaction regions: an upstream region outside the bow shock, the cometosheath located between the bow shock and the contact surface, and a diamagnetic cavity between the contact surface and the nucleus. The cometosheath is the region where both solar wind ions and cometary pickup ions are present. Plasma features present in the cometosheath include the cometopause, a magnetic pileup boundary and an ion pileup boundary. Additionally, Cravens (1989) also proposed the concept of a collisionopause, which is a boundary inside of which collisions dominate the plasma dynamics. Three boundaries that have been observed by spacecrafts are proposed to be collisionopauses, namely the cometopause, the cometary ion collisionopause, and the electron exobase.

The cometopause is the boundary where the plasma composition changes from predominantly solar wind ions to predominantly cometary ions (Gringauz et al., 1986b; Fuselier et al., 1988; Mendis et al., 1989; Coates, 1997). Its existence is disputed by some (Reme et al., 1994) while others have determined it to be a permanent feature (e.g., Gringauz & Verigin, 1991; Sauer et al., 1995). Cravens (1989) describes the cometopause as the collisionopause for solar wind proton charge exchange. *Rosetta's* instruments did not observe the cometopause (Mandt et al., 2016), though it may have been observed as it was forming (Behar et al., 2017), while Williamson et al. (2022) found plasma characteristics that suggest the formation of the cometosheath. Inwards of the cometopause, further collisionopause boundaries could form, namely the ion-neutral collisionopause that depends on the composition of the ion flow (Mandt et al., 2016, 2019) and the electron-neutral collisionopause or the electron exobase that depends on electron energy (Henri et al., 2017). Piling up of the magnetic field becomes more pronounced in the plasma region between the cometopause and the contact surface. *Giotto* observed a sharp magnetic pileup boundary during its inbound journey of the Halley flyby (Neubauer, 1988). However, this was not observed on the outbound leg, suggesting that the boundary is a transient feature (Gringauz & Verigin, 1991). Within the magnetic pileup region but outside the contact surface, the *Vega* probes and *Giotto* observed an ion pileup region (Balsiger et al., 1986; Gringauz et al., 1986a; Vaisberg et al., 1987), characterized by a sharp drop in the ion number density as detected by *Giotto* at a distance ~ 12000 km (Häberli et al., 1995). This is proposed to form because decreasing distance from the nucleus leads to a decrease in the electron temperature and an increase in the ion recombination rate (Ip et al., 1987).

The diamagnetic cavity is a magnetic field-free region that exists within the contact surface, where the solar wind cannot penetrate. The presence of this region was confirmed by the magnetometer data obtained from the *Giotto* flyby (Neubauer et al., 1986). Data taken by the *Rosetta* magnetometer revealed signatures of a diamagnetic cavity around 67P/C-G (Goetz et al., 2016), though its size was larger than that predicted earlier (e.g., Benna & Mahaffy, 2006; Hansen et al., 2016).

A comet may move to a higher outgassing regime on its approach to the sun. In the weakly active comet, the influence of cometary ions on the solar wind is small and no boundaries form. The intermediately active comet is the stage where the solar wind is decelerated significantly and boundaries begin to form, though they may disappear and reappear on short timescales. The strongly active comet is the classical comet picture that exhibits most of the plasma regions discussed above. Comet 67P/C-G went through all these three activity stages during the *Rosetta* mission (Hansen et al., 2016; Läuter et al., 2019). Though the spacecraft remained at roughly the same distance from the nucleus of 67P/C-G, changes in the cometary activity allowed various solar wind-cometary plasma interaction regions to pass over *Rosetta* (Mandt et al., 2016).

1.3 Composition of Comets

Comets have been observed remotely from ground and space based telescopes, over a wide range of wavelengths. This has resulted in the detection of highly charged solar wind ions in the X-ray regime, while molecules undergoing electronic, vibrational and rotational transitions have been detected in the ultraviolet to visible range, the infrared range and the sub-millimeter to millimeter range, respectively (Bockelée-Morvan et al., 2004; Lisse et al., 2004; Dello Russo et al., 2016a; Bodewits et al., 2022). Powerful interferometers, such as the Atacama Large Millimeter/submillimeter Array (ALMA) has resulted in a steady increase in the number of known cometary molecules observed remotely (Biver et al., 2015). In addition to remote observations, in situ investigations are a powerful tool to analyze the cometary volatiles and refractory dust. Apart from the flyby missions to 1P/Halley, other comets have also been visited by spacecrafts, including the *Giotto* flyby of 26P/Grigg-Skjellerup (Coates et al., 1997), the Deep Space 1 mission to 19P/Borrelly (Soderblom et al., 2002), the Deep Impact probe that deployed an impactor onto 9P/Tempel (A'Hearn et al., 2005), and the EPOXI flyby of 103P/Hartley (A'Hearn et al., 2011). NASA's Stardust mission to the comet Wild 2 was the first sample return mission to a comet (Brownlee et al., 2006). The most significant of all cometary spacecraft missions has been ESA's Rosetta mission that followed comet 67P/C-G along its orbit for more than two years, carrying out extensive investigations (Glassmeier et al., 2007; Schulz, 2009), including the deployment of the *Philae* lander onto its surface (Biele et al., 2015).

Numerous volatiles have been detected in comets till the present time, either remotely or in situ. Here, volatiles are those species that sublimate in the temperature regime of comet 67P/C-G, ranging from tens of Kelvin in the subsurface (Gulkis et al., 2015) to several hundred Kelvin on hot grains that may release semivolatiles in the coma (Lien, 1990). The long and extensive investigation of 67P/C-G, by mass spectrometers and other instruments carried by *Rosetta*, led to the detection of many species for the first time (Altwegg et al., 2019). At present, the number of parent volatile species (i.e. those species that are present in the cometary ices), detected at least tentatively, either remotely or in situ, stands at 72, out of which 37 are complex organic molecules (Rubin et al., 2019). In the context of the interstellar medium, complex organic molecules (COMs) are those species that contain six or more atoms, including one or more carbon atoms (Herbst & van Dishoeck, 2009). A similar definition can be used for organic molecules in comets (Rubin et al., 2019). Some of the cometary species may also be present as isomers, indistinguishable by mass spectrometry, and this may increase molecular diversity even more. Table 1.1 shows a list of molecules detected remotely in comets, and their abundances relative to water.

1.3.1 Main Constituents

In most of the Solar System comets, H₂O is the dominant constituent and can form up to ~ 90% of the cometary volatile composition at heliocentric distances < 2.5 AU (Combi et al., 2004). Its production rate is used to quantify cometary activity and the abundances of other volatiles. The vibrational bands of water, especially ν_3 near 2.7 μ m, cannot be observed directly from the ground due to strong telluric absorption, though this limitation is overcome by space based observatories such as the *Hubble Space Telescope* and the *James Webb Space Telescope*. The observations of H and OH, with velocities and spatial distributions consistent with their production in the coma from the photolysis of H₂O, established the presence of water in comets (Festou et al., 1993).

The next important parent volatiles in terms of abundance are CO and CO₂. The average abundance of CO with respect to H₂O is ~ 5%, though some comets may show high levels of CO at large heliocentric distances due to its low sublimation temperature (Dello Russo et al., 2016a; Womack et al., 2017). The range of abundance for CO₂ is a few up to ~ 30% of H₂O, with a median value of 17% (Ootsubo et al., 2012). Trace amounts of other species such as NH₃, H₂S, HCN are present, to name a few, whose abundance with respect to H₂O is at the percent level or less (Mumma & Charnley, 2011). Solar System comets exhibit chemical diversity in terms of their volatile composition, with the range of species abundances varying by a factor of a few up to several tens (Bockelée-Morvan,

Species	Abundance (%)	Observed	Species	Abundance (%)	Observed
C-O bearing					
СО	0.2 - 23	U, I, R	$\rm CO_2$	2.5 - 30	U, I
Hydrocarbons					
CH ₄	0.12 - 1.5	Ι	C_2H_6	0.14 - 2.0	Ι
C_2H_2	0.04 - 0.5	Ι			
CHO-bearing					
CH ₃ OH	0.6 - 6.2	I, R	H ₂ CO	0.13 - 1.4	I, R
НСООН	0.028 - 0.18	R	$(CH_2OH)_2$	0.07 - 0.35	R
HCOOCH ₃	0.07 - 0.08	R	CH_3CHO	0.047 - 0.08	R
CH ₂ OHCHO	0.016	R	$\rm C_2H_5OH$	0.12	R
N-bearing					
HCN	0.08 - 0.25	I, R	HNC	0.002 - 0.035	R
HNCO	0.009 - 0.08	R	$\rm CH_3 CN$	0.008 - 0.036	R
HC ₃ N	0.002 - 0.068	R	$\rm NH_2CHO$	0.008 - 0.021	R
NH ₃	0.3 - 0.7	I, R			
S-bearing					
H ₂ S	0.13 - 1.5	R	OCS	0.03 - 0.40	I, R
H_2CS	0.009 - 0.09	R	CS	0.02 - 0.2	U, R
SO	0.04 - 0.30	R	NS	0.006 - 0.012	R
S ₂	0.001 - 0.25	U	S_2	0.2	R

Table 1.1: Relative abundance (%) with respect to water, of cometary volatiles from remote spectroscopic observations. The wavelength regime in which the molecules are detected are ultraviolet (U), infrared (I) and radio (R, submillimeter to millimeter). Adapted from Bockelée-Morvan & Biver (2017).

2011; Dello Russo et al., 2016a).

1.3.2 Hydrocarbons

The first detection of the symmetric hydrocarbon C_2H_6 was reported in the comet C/1996 B2 (Hyakutake), and this molecule has bright cometary emission bands in the near-infrared wavelength regime (Mumma et al., 1996). Since C_2H_6 is a symmetric molecule with no permanent dipole moment, it is not observable at submillimeter wavelengths. It is one of the trace volatiles that has a relatively high abundance, with the average abundance with respect to H_2O being 0.55%.

 CH_4 is another symmetric hydrocarbon and like C_2H_6 , it is only observable through its IR rovibrational transitions. However, the CH_4 lines are intrinsically weaker than C_2H_6 emissions, making it a harder molecule to detect. In addition, due to telluric absorptions, ground-based detections of CH_4 is possible only at certain observing geometries, such that the geocentric velocity is sufficient to cause a Doppler-shift in the cometary CH_4 emissions away from the corresponding telluric absorptions. Space-based observations do not have this limitation, though most of the cometary CH_4 observations have been made from groundbased facilities, since space-instruments lacked the desired spectral resolution before JWST (Dello Russo et al., 2016a). The average CH_4 abundance is 0.78%, which is similar to that of C_2H_6 .

Yet another symmetric hydrocarbon observed in cometary comae at IR wavelengths is C_2H_2 . Though its emission lines do not suffer from telluric absorptions like CH_4 , the lines of C_2H_2 are weak, and it also has a mean abundance of 0.13% with respect to H_2O , which is lower than that of C_2H_6 and CH_4 . The *Rosetta* mission has detected CH_4 through the VIRTIS instrument (Bockelée-Morvan et al., 2016), and both CH_4 and C_2H_2 through mass spectrometry by ROSINA (Le Roy et al., 2015). ROSINA also identified a number of other saturated aliphatic hydrocarbons and the aromatic compounds benzene and toluene (Schuhmann et al., 2019).

1.3.3 CH_3OH and H_2CO

Methanol (CH₃OH), the simplest alcohol, was first detected in comets at millimeter wavelengths (Bockelée-Morvan et al., 1994), and has since been measured in many comets at sub-millimeter/millimeter and near-infrared wavelengths (Dello Russo et al., 2016b; Bockelée-Morvan & Biver, 2017). CH₃OH is mainly associated with direct release from the nucleus, though measurements on the hyperactive comet 103P/Hartley indicated its production by sublimation from icy coma grains (Dello Russo et al., 2011). CH₃OH is one of the more abundant cometary volatiles, with an abundance range of 0.6 - 6.2% relative to H₂O.

 (H_2CO) Formaldehyde can also be measured at both submillimeter/millimeter and NIR wavelengths. Observations of comets C/1990 V (Austin) and C/1990 XX (Levy) resulted in the first unambiguous detection of H₂CO (Bockelée-Morvan et al., 1991; Colom et al., 1992), although tentative detections were claimed for 1P/Halley. Observational results show that cometary H_2CO can result from nucleus sublimation as well as from unknown sources in the coma (known as distributed sources; Cottin & Fray, 2008). Organic macromolecular material, detected by the VIRTIS instrument onboard Rosetta, has been suggested as a likely coma source of H_2CO (Capaccioni et al., 2015).

1.3.4 Complex Organics

Rotational transitions of complex organic molecules has resulted in their detection in comets at millimeter and sub-millimeter wavelengths, particularly in those comets with high activity such as C/1995 O1 (Hale-Bopp) and C/2014Q2 (Lovejoy). The organics that have been detected include CHO-bearing molecules such as formic acid (HCOOH), methyl formate (HCOOCH₃), ethylene glycol $(CH_2OH)_2$, acetaldehyde (CH_3CHO) , ethanol (C_2H_5OH) , and the simplest monosaccharide sugar, glycolaldehyde (CH₂OHCHO), as well as nitrogenbearing species such as isocyanic acid (HNCO), cyanoacteylene (HC_3N), acetonitrile (CH₃CN), and formamide (NH₂CHO) (Bockelée-Morvan et al., 2000; Crovisier et al., 2004; Biver et al., 2014, 2015). In situ measurements by the ROSINA mass spectrometer aboard Rosetta and by COSAC and Ptolemy on the Philae lander revealed a suite of organic molecules that were previously undetected in comets (Goesmann et al., 2015; Altwegg et al., 2017). The simplest amino acid, glycine was detected in the samples returned from Wild 2 (Elsila et al., 2009), and also in situ by *Rosetta* (Altwegg et al., 2016). Though the abundances of these molecules are poorly constrained owing to very few cometary measurements, yet their detection is an indication of the chemical complexity stored in cometary nuclei.

The origin of organic molecules in comets can be traced to the interstellar

medium (ISM), partially. Over 250 molecules have been detected in the ISM, including organic molecular species and COMs (Herbst & van Dishoeck, 2009). The detection of COMs near protostars is an indication that they are building blocks for planetary systems and can be incorporated into comets. Besides, the D, ¹³C and ¹⁵N isotopic measurements in organic molecules are an indication of the survival of organics from the prestellar core and their condensation as cometary volatiles (Rubin et al., 2019). The ISM contains different environments that show densities varying over $10^2 - 10^8$ H atoms per cubic centimeter. The density of the coma is higher (~ $10^{12} - 10^{13}$ molecules cm⁻³ in the inner regions), which may aid in the formation of complex organic molecules through gas-phase collisional reactions.

1.3.5 Interstellar Comet Composition

The arrival of interstellar objects in the Solar System had been anticipated for many years (Sekanina, 1976). Simulation studies have suggested that the migration of the giant planets in the early formation and evolution stages resulted in the ejection of upto 99% of the planetesimals from the Solar System into the interstellar space (for example, Charnoz & Morbidelli, 2003; Bottke et al., 2005). 2I/Borisov is the first active interstellar comet, which was discovered in the Solar System by G. Borisov on 30 August 2019. Since comets contain largely unprocessed material frozen in at the time of planet formation, interstellar comets offer a unique opportunity to deduce the possible composition of a distant protoplanetary disk. Before the arrival of 2I/Borisov, the knowledge of extrasolar comets was limited to the deductions that could be made from distant, unresolved observations of regions around stars that show exocometary signatures, with only a single detection of carbon monoxide (Matrà et al., 2017).

Measurements of the production rates of various volatiles resulted in the characterization of 2I/Borisov as significantly rich in CO (Bodewits et al., 2020; Cordiner et al., 2020). The range of the CO/H₂O ratio for this comet is 35-105%(Cordiner et al., 2020), but it can also be as high as 173% (Bodewits et al., 2020). Volatile CO ice may begin to sublimate from the nucleus of a comet at heliocentric distances as far out as 120 AU (Meech & Svoren, 2004), while the sublimation of water ice efficiently occurs only at heliocentric distances < 2.5 AU. CO is an important driver of cometary activity at large distances (Senay & Jewitt, 1994; Womack et al., 2017), and measurements of cometary CO production exceeding water production at distances beyond 2.5 AU have been reported (Ootsubo et al., 2012). However, the CO/H₂O ratio measured in 2I/Borisov is substantially higher than what has been observed in other comets that came within a heliocentric distance of 2.5 AU (Bodewits et al., 2020; Cordiner et al., 2020). The production rates of other trace volatile species in 2I/Borisov was found to be similar to that of Solar System comets (Cordiner et al., 2020).

1.4 Comet Classifications

1.4.1 Dynamical Classification

1.4.1.1 Periodicity

Comets can be classified on the basis of their orbital properties. In terms of periodicity, comets are divided into two categories, namely periodic and nonperiodic. Periodic comets orbit the sun in a stable elliptical orbit, with an orbital eccentricity e < 1, while nonperiodic comets have a nonstable trajectory, which can be parabolic (e = 1) or hyperbolic (e > 1). Nonperiodic comets having hyperbolic orbits do not re-approach the sun, but pass through the inner Solar System only once, before being ejected out into the interstellar space. Recently, a new class of interstellar objects have been discovered in the Solar System, which are 1I/'Oumuamua and 2I/Borisov, with the latter exhibiting cometary activity. Both these objects have a high hyperbolic excess velocity, indicating their origin from outside the Solar System (Meech et al., 2017a; Jewitt & Luu, 2019).

1.4.1.2 Orbital Period

Comets also show a great deal of variation in their orbital periods, and can thus be classified as long-period and short-period comets (Oort, 1990). Long-period comets are those that have an orbital period P ranging from 200 years to as high as 100 million years, and an orbital eccentricity $e \leq 1$. Orbital eccentricities slightly greater than 1, indicating hyperbolic orbits, have been observed as well, though this is rare and is a result of perturbations from giant planets. Long-period comets are thought to originate mainly in the Oort cloud, which is a region of space beyond the outer Solar System extending from $2 \times 10^3 - 1.5 \times 10^5$ AU (Oort, 1950; A'Hearn, 2006). In fact, the existence of the Oort cloud was proposed to explain the origin of long-period comets with semi-major axes a > 40AU. Oort (1950) argued that the distribution of 1/a shows a spike for $a > 10^4$ AU, and the orbital elements $\cos i$, ω and Ω are isotropic, which can be explained by a spherical reservoir of objects around the sun. These comets evolve dynamically under the influence of perturbations from stellar passages and the galactic gravitational tidal field. Most of the long-period comets have been observed only once in recorded history, due to their large orbital period. Although the Oort cloud extends about halfway to the nearest star alpha Centauri, the comets residing here belong to the Solar System and are not interstellar objects (Brandt & Chapman, 2004). The number of comets in the Oort cloud was earlier estimated to be ~ 10^{11} (Oort, 1950). More recent estimates based on numerical simulations distinguish between a disk-like inner Oort cloud containing $\sim 10^{13}$ comets, and an outer Oort cloud housing $\sim 10^{12}$ comets (Weissman, 1991; Levison et al., 2001). The boundary between the two is estimated to be at $\sim 2 \times 10^4$ AU (Brandt & Chapman, 2004). Long-period comets can enter the inner Solar System either in the same direction of circulation of planets (prograde comets) or in the inverse direction (retrograde comets). The giant planets, particularly Jupiter, often influence the trajectory of long-period comets once they enter the inner Solar System. Such influence may cause the comets to be either ejected into the interstellar space or get captured into more tightly bound orbits and become short-period comets.

Short-period comets are those that have a periodicity P < 200 years. Nearly 60% of the short-period comets have periods between 5 and 6.5 years (Oort, 1990). They mainly originate from the Kuiper belt (also known as the Edgeworth-Kuiper belt), which is a disk of minor bodies located beyond the orbit of Neptune, extending at 30 – 50 AU from the sun (Edgeworth, 1949; Kuiper, 1951). The orbital inclination of these comets is up to $\sim 13^{\circ}$ and hence they are close to the ecliptic, and their aphelion is generally $\sim 5 - 6$ AU.

The short-period comets are further subdivided into two groups, namely Jupiter Family comets (orbital period less than 20 years) and Halley Type comets (orbital period lying between 20 and 200 years). A distinction is made between these two subcategories based on the Tisserand parameter T, which is calculated on the basis of the semi-major axes of the orbits of Jupiter and the comet, and also the cometary orbital inclination and eccentricity (Carusi & Valsecchi, 1987). The Jupiter Family comets have T > 2 while long-period and Halley Type comets have T < 2. More precisely, the Jupiter Family comets may be transition type (2.0 < T < 2.5), loosely bound (2.5 < T < 2.8) or tightly bound ($T \ge 2.8$) (Horner et al., 2003). It is to be noted that the three families of comets namely long-period comets, Jupiter Family comets and Halley Type comets can have their origin in either the Oort cloud or the Kuiper belt (Brandt & Chapman, 2004). The orbital period of a comet does not necessarily indicate its origin. Most comets may have dynamical lifetimes that transition between Jupiter Family and Halley Type orbits many times (Levison & Duncan, 1994).

1.4.2 Compositional Classification

1.4.2.1 Carbon-Chain Species Abundances

The photometric survey of a sample of 85 comets, conducted from 1976 to 1992, resulted in the identification of distinct compositional groups of comets based on the abundance of the carbon-chain species C_2 and C_3 (A'Hearn et al., 1995). These comets are classified as 'typical' and 'depleted' in C_2 and C_3 , with most of the depleted class of comets being Jupiter Family comets. However, not all Jupiter Family comets that were surveyed belong to the depleted class, while the percentage of Oort cloud comets showing such depletion is comparatively smaller. The correlation of CN, C_2 and C_3 abundances with each other is stronger than with either OH or NH, in typical comets. This classification was later extended to more than 191 comets (Schleicher & Bair, 2016), which are further divided into seven compositional classes, and some of these classes are subgroups of the original carbon-chain depleted class defined by A'Hearn et al. (1995). It is indicated that the depletion in carbon-chain species abundances is a reflection of the primordial composition at the location and time of cometary accretion. Schleicher & Bair (2016) also identify a new class of comets depleted in NH_3 but not depleted in carbon-chain species. In a spectroscopic survey, Cochran et al. (2012) found that the depleted comets make up 37% of JFCs, while 18.5% of long-period comets belong to the depleted class, which is in agreement with A'Hearn et al. (1995).

Fink (2009) presented the spectroscopic survey of 92 comets from 1985 to 2002, out of which 50 comets showed good emissions, enabling the calculation of the abundances of C_2 , CN and NH₂, with respect to water. Fink (2009) identified four compositional groups of comets: (1) typical composition, that exhibit typical abundance of C_2 , CN and NH₂; (2) Tempel 1 type, that show deficiency in C_2 abundance but normal NH₂ abundance; (3) G-Z type, that have low abundance of C_2 and NH₂; (4) the unusual object Yanaka (1988r), that shows no detectable C_2 and CN but normal NH₂ abundance. The Oort cloud comets in this survey do not show low C_2 abundance, and they generally exhibit higher C_2/CN ratios. On the other hand, nearly half of the Jupiter Family comets exhibit deficiency in the abundance of C_2 . This is in agreement with the characterization obtained by A'Hearn et al. (1995).

1.4.2.2 CO₂ and CO Abundances

Reach et al. (2013) classified comets as 'rich' and 'poor' in CO_2 and CO, based on an infrared survey of 23 comets by the *Spitzer* Space Telescope. There were multiple observations for many of the comets, at different heliocentric distances. However, in most cases, this did not alter the compositional class of the comet. While there is no one-on-one correlation between this classification and the compositional grouping by A'Hearn et al. (1995), more comets belonging to the CO_2 -poor class are also depleted in carbon-chain species. This is intuitively expected, since both depleted and CO_2 -poor classifications indicate lower cometary abundances of carbon-bearing molecules.

1.4.2.3 Organic Abundances

Mumma & Charnley (2011) identified three principal compositional groups namely, organics-normal, organics-enriched, and organics-depleted, based on the organic abundances in a sample of 13 comets. The abundance ratios with respect to water for 12 comets are compared by Mumma & Charnley (2011) with in situ abundance measurements of the comet 1P/Halley. A positive correlation is seen in the abundances of ethane and methanol, i.e. if a comet belonging to this sample is enriched in ethane, it is also enriched in methanol, and so on. The hypervolatile species methane and carbon monoxide are only coarsely correlated in this sample.

1.4.2.4 Comet Taxonomy

Dello Russo et al. (2016a) analyzed the abundance mixing ratios with respect to water for eight cometary volatiles, namely CO, CH₄, C₂H₆, C₂H₂, H₂CO, CH₃OH, HCN and NH₃, measured with infrared spectroscopy in 30 comets. They noted at least one order of magnitude variation in the mixing ratios for the observed species. The mixing ratios of HCN, CH₄ and C₂H₆ exhibit high correlation with each other, while NH₃, C₂H₂ and H₂CO are moderately correlated with each other and poor to uncorrelated with other species. The abundance of CO is mostly uncorrelated with that of the other species. Jupiter Family comets show an average depletion in mixing ratios as compared to Oort cloud comets, with the most volatile species showing the highest relative depletion. Dello Russo et al. (2016a) employed cluster analysis to create a hiearchical tree classification system, dividing the comets into four groups and eleven subgroups.

1.5 Coma Modeling

The primary source of knowledge about the structure and composition of comets comes from studies of the cometary atmosphere or the coma. As mentioned before, the coma expands to very large distances, that are greater than the size of the nucleus by many orders of magnitude. Astronomical measurements of the coma can be made directly because the spectral emission lines of the volatile species can be observed remotely. Modeling of the chemical and thermodynamical processes of the coma is significant in expanding our understanding of the coma gas-dynamics and interpreting cometary observations.

1.5.1 Coma Collisional Region

When talking about the physical and chemical processes occurring in the coma, the collisional coma is particularly interesting in terms of the creation of new molecules and ions. The collisional coma is the inner cometary region where particle collisions drive the gas-phase chemistry. The size of the collisional region can roughly be estimated as the cometocentric distance r such that the mean free path of a particle becomes equal to r. The collisional region is proportional in size to the total gas production rate from the nucleus, and its size generally increases with a decrease in the heliocentric distance. The size of this region for a Halley-type comet at a distance of 1 AU from the sun is nearly several thousand kilometers for neutral-neutral collisions. For ion-neutral collisions, this can be upto one order of magnitude larger, due to higher cross sections for ion-neutral reactions.

We can also loosely describe a "molecular coma", which is the region where most of the molecules have not yet undergone photodissociation. This region will have different sizes for different molecules, due to variations in the species lifetimes. The size of the molecular coma for water and most other species is ~ 10^5 km for the solar radiation field at 1 AU and a typical outflow velocity ~ 1 km s⁻¹. Species such as formaldehyde and ammonia are destroyed much faster and the size of the molecular coma will be smaller by an order of magnitude, while more stable species such as carbon monoxide and carbon dioxide will survive up to more than 10^6 km. The approach of the comet towards the sun will shrink the molecular coma because most of the coma is optically thin and the stronger radiation field will increase the photodissociation rates.

1.5.2 Physical and Chemical Processes in the Coma

The solar radiation field initiates most of the processes occurring in the inner coma. Ultraviolet radiation causes the photodissociation and ionization of the parent molecules, resulting in the production of "second-generation" ions, radicals and electrons. These further react with each other or with the parent species to form "third-generation" species. Many of the ions thus created have been detected in 1P/Halley by the ion mass spectrometer aboard the *Giotto* space probe (Geiss et al., 1991). The densities of the various species in the coma are large enough such that the gaseous coma can reasonably be considered as a fluid. Integration of standard fluid flow conservation equations can be used to describe the thermodynamics of the coma, as long as the initial boundary values on the nucleus surface are known or can be estimated to a certain degree of accuracy. With an increase in the cometocentric distance, there is a decrease in the coma density which results in an increase of the mean free path, so that the fluid description cannot be applied. This is the region where there is a transition to free molecular flow and processes affecting a particular molecule does not necessarily affect the entire gas, and the outflowing gas has attributes that are "frozen in" from the earlier collisional region (Crifo, 1991).

Apart from the gaseous species, there is also a population of dust grains in the coma. The entrained dust and the coma gas interact, which has an effect on the chemistry and dynamics of the coma. For example, the gas-dust drag may decelerate the outflowing gas close to the nucleus, such that the gas velocity attains subsonic levels (Marconi & Mendis, 1983). The dust grains, though not strictly a fluid, can be described using the hydrodynamic variables, namely, temperature and velocity. Some molecules have "extended sources" in the coma and dust grains may account for this. Molecules having low volatility may have delayed sublimation from the hot dust grains, or the grains may themselves break up, thus accounting for the extended sources.

1.5.3 Historical Overview of Coma Modeling

Haser (1957) proposed the first analytical model to find the distribution of vari-

ous molecules in the coma. This model only considered the escape of molecules radially outwards at a constant velocity without undergoing collisions. Subsequently, the vectorial model by Festou (1981) allowed for the photodissociated products (daughter species) to move non-radially in the coma. O'dell et al. (1988) gave the expression for the column density profile of a three generation Haser-type model by considering the scale lengths of the granddaughter species, the intermediate daughter and the original parent. This was necessitated by observations of C_2 in 1P/Halley, since Wyckoff et al. (1988) suggested that C_2 is produced as a granddaughter species or by grains.

Apart from photolytic dissociation and ionization, it was realized that chemical reactions that are important in other astrophysical environments, are of significant importance in comets as well, due to the high density conditions of the coma (number density $\sim 10^{13}$ cm⁻³ near the nucleus). In addition, the development of better computational technology resulted in the development of detailed chemical models (for example, Oppenheimer, 1975; Giguere & Huebner, 1978; Huebner & Giguere, 1980; Mitchell et al., 1981; Biermann et al., 1982). These earlier models made many assumptions to reduce complexity, which included the use of constant temperature and velocity profiles. However, these models established the importance of ion-neutral reactions in the inner coma, particularly the formation of protonated species by proton transfer reactions, and the subsequent dissociative recombination of the protonated molecule. These models also demonstrated that the solar UV radiation field cannot penetrate into the inner regions of the coma, and optical depth calculations need to be taken into account for more accurate chemical models.

Coma hydrodynamic models that were developed susbsequently illustrated the non-viable nature of the assumptions of constant temperature and velocity (for example, Marconi & Mendis, 1982a, 1983, 1986; Ip, 1983; Gombosi et al., 1985, 1986; Combi & Smyth, 1988). The initial expansion of the gas outwards from the nucleus is adiabatic, resulting in temperatures as low as ~ 10 K in the inner regions of the coma. Further outwards in the coma, the dominance of photochemical reactions leads to an increase in the temperature, particularly of the electrons. The rates of the recombination reactions of electrons with ions is thus reduced in the outer coma, due to the high temperature of the electrons. Hence, the chemistry and physics of the coma is intimately linked, and a complete description of the coma requires a combined chemicalhydrodynamical model (for example, Huebner, 1985; Körösmezey et al., 1987; Wegmann et al., 1987; Schmidt et al., 1988; Rodgers & Charnley, 2002; Weiler, 2012). Most of these later models include an extensive chemical network, that includes additional reactions such as radiative association and electron impact processes. Modeling studies have also been done for extended CO and H₂CO sources in the coma (Boice et al., 1990; Cottin et al., 2001), and for a dusty gas cometary atmosphere (for example, Marconi & Mendis, 1982b; Gombosi & Körösmezey, 1989).

The coma can also be modeled using Monte Carlo techniques, which describe the coma more accurately, since the fluid assumption is neglected (Combi & Smyth, 1988; Hodges, 1990). However, they are computationally very expensive, and it is not feasible to use detailed chemistry in such coma models. In the inner collisional coma, the coma properties derived from Monte Carlo models and fluid models are sufficiently well-matched, and thus Monte Carlo methods do not need to be employed in modeling the coma chemistry (Combi et al., 2004; Rodgers et al., 2004).

1.6 Importance of Studying Comets

Comets are interesting and fascinating objects that merit scientific investigations for various interdisciplinary reasons, some of which are listed below (Huebner & McKay, 1990).

• Comets are generally believed to be pristine and largely unaltered objects of the Solar System (Altwegg, 2008; Mumma & Charnley, 2011). Hence, their study can give insights into the formation history and evolution of matter in the early Solar System (Mumma et al., 1993; Irvine et al., 2000; Bockelée-Morvan et al., 2004). Cometary compositions and structures can provide clues about the thermodynamic conditions and the chemical composition of the comet-forming regions of the solar nebula, and the formation of planetesimals from the agglomeration of cometary subbodies.

- Comets can also reveal information about the evolution of planets and their atmospheres since impact processes may have led to the enrichment of volatiles in the inner Solar System. Cometary impacts may have also delivered organic molecules to the Earth, which are necessary for creating molecules of biological interest (Chyba et al., 1990; Ehrenfreund et al., 2002), and cometary studies can give indications about the chemical evolution that led to the molecular origins of life (Rubin et al., 2019).
- It is seen that the molecular abundances in comets show notable similarities when compared with interstellar abundances (Mumma & Charnley, 2011). A comparative study of the chemical composition of comets with protostars can be used to investigate the building blocks required to form planetary systems similar to ours. The midplane ices of the protoplanetary disk are inherited in comets, and comets can be used to probe the midplane composition (Drozdovskaya et al., 2016).
- The regions of interaction of the solar wind with the cometary coma and tails can be regarded as an exceptionally large laboratory of plasma physics for the study of processes, instabilities and waves that cannot be created under terrestrial laboratory conditions. The plasma structures in comets can be used as natural laboratories to investigate regions of the interplanetary medium where in situ measurements are difficult.

1.7 Work Objectives

The application of combined hydrodynamical and chemical simulations to the coma helps in a quantitative understanding of the physics and chemistry occurring in the coma gas. As has been established from observational studies, most of the Solar System comets within a heliocentric distance of 2.5 AU have cometary comae that are dominated by the outgassing of water molecules from the nucleus. CO is an important driver of cometary activity at large heliocentric distances

(Senay & Jewitt, 1994; Womack et al., 2017; Jewitt et al., 2019) and there have been measurements of CO/H₂O \gg 1, such as in 29P/Schwassman-Wachmann 1 (Ootsubo et al., 2012) and C/2016 R2 (PanSTARRS) (McKay et al., 2019), though such observations do not exist for distances less than 2.5 AU from the sun. Thus, previous modeling studies have simulated the atmosphere of comets where H₂O is the most abundant species. On the other hand, the high CO/H₂O ratio observed in the interstellar comet 2I/Borisov makes it a notable exception when compared with the Solar System comets. This alters the chemistry and dynamics of the coma, and the changes can be understood with the help of a numerical model for the coma gas. There are only a few coma-modeling studies on comets that have a CO abundance comparable to or more than that of water.

Improvements in observational capabilities and the discovery of Solar System comets exhibiting high activity has resulted in the detection of many new organic species in comets. While organic species can originate from the nucleus, comets showing moderate to high activity can reach sufficient coma densities for organic molecules to form by active gas-phase coma chemistry. The formation of organic molecules in the coma has been the focus of only a handful of modeling studies, and a quantitative description of the rates of formation and the resultant organic abundances can be obtained through coma modeling. The objectives of this thesis work are thus defined as follows:

• To build a chemical-hydrodynamical model for the coma, with emphasis on a CO rich coma, and the formation of organics

The first objective of this work is to build a numerically robust coma model that can be used to study the physico-chemical propeties of the comae of comets having wide range of volatile compositions. The model built in this work is based on the application of fluid conservation equations to a spherically symmetric coma in the steady state. This model involves collisiondominated flow, a multifluid treatment of the coma-gas, a chemical reaction network, and heating and cooling mechanisms. The model employs an extensive chemical network, including chemical reactions involving organic molecules and ions. Cooling mechanisms due to vibrational excitation of CO molecules have also been added, which was not considered in previous models due to the lesser relative abundance of CO with respect to H_2O .

• To study the effect of high CO/H_2O ratio on the coma of 2I/Borisov

The second objective is to simulate the coma of 2I/Borisov, using the coma model that is built, and see how the high CO/H₂O ratio will affect the chemistry and dynamics of the coma, and how the abundances of secondary and tertiary species are affected when the production rate of CO is comparable to or more than that of water. In addition, another aim is to see the differences in the abundances of organic neutrals and ions in the interstellar comet as compared to a typical Solar System comet.

• To study organic formation in the comae of assorted Solar System comets

The third objective is to use the coma model to study the gas-phase formation pathways in the comae of assorted Solar System comets, and how successful the proposed formation pathways are for producing organic molecules and COMs in the cometary atmosphere. Besides, another goal is to see how the organic formation rates get altered when there are changes in the relative abundances of volatile species with respect to water, from one comet to another.

1.8 Thesis Overview

The following is a brief description of the organization of this thesis.

Chapter 2: Chemical Network and Reaction Pathways

This chapter contains a description of the chemical reaction network that is employed by the gas phase coma model. Details of the different types of chemical reactions are given, along with the relevant formulae to calculate the reaction rates, and the databases where these rates are available. In addition, a brief description of the reaction scheme for the formation of organic species in the coma is given in this chapter.

Chapter 3: Gas Phase Coma Model

This chapter contains a complete description of the combined chemical and hydrodynamical model that has been built as part of this thesis work. The model equations are a set of coupled first order differential equations. The equations are described, the methods used to calculate the requisite paramters are explained, and the numerical integration scheme is also discussed.

Chapter 4: Study of the Interstellar Comet 2I/Borisov

This chapter contains the modeling results of the interstellar comet 2I/Borisov. The simulation results include the temperature profile, the species abundances, and the formation/destruction rates of major ions. A comparison of the results are made with a Solar System comet of the Halley-type composition, and the effect of large CO abundance in 2I/Borisov is examined.

Chapter 5: Study of the Formation of Organics in the Coma

This chapter contains the modeling results on the formation of organics in the comets C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy) and C/2014 Q2 (Lovejoy). The different mechanisms for the formation of neutral organic molecules and organic ions in the coma are discussed, and the resulting abundances of these species in the coma is described.

Chapter 6: Cometary Organics: Efficiency of Coma Chemistry

This chapter contains a discussion on the efficiency of the formation of organic molecules in the coma, as opposed to their outgassing rate from the nucleus, in the comets C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy)

and C/2014 Q2 (Lovejoy). The role of the various types of gas-phase reactions towards the formation of cometary organics in these comets is discussed.

Chapter 7: Conclusions, Implications and Future Work

This chapter contains the concluding remarks and implications of the work that has been done in this thesis, and a brief description of future projects to be undertaken.

Chapter 2

Chemical Network and Reaction Pathways

Understanding the molecular complexity that exists in the cometary atmosphere requires an understanding of the formation and destruction pathways of molecular species in the coma. This requires the use of an extensive chemical network. The chemistry occurring in the coma can be described by a number of two-body reactions and photolytic processes, which are used to build the reaction network. In addition, the rates at which these reactions occur in the gas phase are also required, for the relevant temperature range. Thus, the chemical behavior of the coma is modeled by constructing a comprehensive network of collisional and photolytic gas-phase reactions involving a large number of species, and the associated parameters required to calculate the reaction rates.

2.1 Types of Chemical Reactions

2.1.1 Photolytic Processes

The general equations for the photolytic processes, caused by solar radiation, are as follows:

Photodissociation:
$$A + h\nu \rightarrow B + C$$

 $A + h\nu \rightarrow B + C + D$ (2.1)

Photoionization:
$$A + h\nu \rightarrow A^+ + e^-$$
 (2.2)

Photodissociative ionization:
$$A + h\nu \rightarrow B + C^+ + e^-$$
(2.3)

$$A + h\nu \to B + B' + C^+ + e^-.$$

The photodissociation and photoionization of parent molecules sublimating from the nucleus results in the creation of highly reactive radicals and ions, intitiating the chemical reactions in the coma. Another important photolytic process is photodissociative ionization in which extreme UV photons ionize a neutral molecule into an excited state, and this is followed by the dissociation of the molecular ion into a lighter ion and one or more neutral species. A molecular species in the coma can undergo one or all of these processes, with different branching ratios.

Photolytic reactions can be regarded as unimolecular processes, and their rates are dependent on the strength of the UV radiation field, which itself is dependent on the heliocentric distance and on the solar cycle for $\lambda < 200$ nm. In addition, photolysis can only occur when the UV photons possess a minimum energy that is equal to the dissociation or ionization threshold (i.e., the binding energy). The excess energy above this threshold is converted into kinetic energy of the photo products. Due to the light mass of electrons, the excess energy that results from ionization is almost entirely in the form of kinetic energy of the photoelectrons.

Water, the most abundant volatile molecule in a majority of comets, undergoes photolysis via a number of channels, some of which are as follows (Huebner et al., 1992; Combi et al., 2004):

$$H_2O + h\nu \rightarrow OH + H$$

$$\rightarrow O(^1D) + H_2 \qquad (2.4)$$

$$\rightarrow H_2O^+ + e^-.$$

The major dissociative process for H_2O is the formation of OH and H, and the threshold wavelength for this process to take place is 1860 Å. Since the ionization energy for H_2O is higher than the dissociation energy, photons possessing higher energies are required for the photoionization of water, and the threshold wavelength for this process that creates H_2O^+ ions is 984 Å. Photolytic reactions may lead to the creation of species in their metastable states, an example of which is the creation of $O(^1D)$ by the photodissociation of water. H_2O also undergoes photodissociative ionization with comparatively lower branching ratios, and this leads to the creation of H^+ , O^+ and OH^+ ions.

2.1.2 Electron Impact and Recombination Processes

The energetic electrons that are created due to photolytic processes can undergo impact processes in the coma, as given below.

Electron impact ionization:
$$A + e^- \rightarrow A^+ + e^- + e^-$$
 (2.5)

Electron impact dissociation: $A + e^- \rightarrow B + C + e^ A + e^- \rightarrow B + C + D + e^-$ (2.6)

$$\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{B} + \mathrm{C} + \mathrm{D} + \mathrm{E} + \mathrm{e}^-$$

Electron impact dissociative ionization:
$$A + e^- \rightarrow B + C^+ + e^- + e^-$$

 $A + e^- \rightarrow B + B' + C^+ + e^- + e^-$ (2.7)

Electron impact excitation:
$$A + e^- \rightarrow A^* + e^-$$
. (2.8)

Electron impacts with neutral molecules can result in secondary ionization, dissociation, and excitation. Dissociative ionization by electron impacts can be regarded as a two-step process, in which the first step involves the creation of ions of unbound states, while the second step involves the dissociation of these unbound states. Excitation of neutral molecules to higher electronic states can also occur due to electron impacts, an example of which is the excitation of CO molecules, as follows:

$$CO + e^{-} \rightarrow CO(^{1}\Pi) + e^{-}.$$

$$(2.9)$$

For impact ionization processes to take place, the electrons need to have energy greater than the ionization potential of the neutral molecule, which is generally in the range of $\sim 10 - 20$ eV. Apart from impact processes, electrons also participate in recombination reactions, which require lower collisional energy, and the general equations for these reactions are as follows:

Dissociative recombination:
$$A^+ + e^- \rightarrow B + C$$

 $A^+ + e^- \rightarrow B + C + D$ (2.10)
 $A^+ + e^- \rightarrow B + C + D + E$

Radiative recombination:
$$A^+ + e^- \rightarrow A + h\nu$$
. (2.11)

Positive ions in the coma capture electrons, combining with them to form neutral species. Dissociative recombination occurs when an ion recombines with an electron to form a neutral intermediate, which subsequently dissociates into two or more fragments. This process is generally exothermic, and has a large cross section since Coulomb interactions are long-range in nature. Radiative recombination processes also occur in the coma, whereby an ion recombines with an electron, by capturing the electron into an excited state, and then radiating the excess energy as photons.

2.1.3 Radiative Processes

In addition to the radiative recombination of ions with electrons, other radiative processes that occur in the coma are collisional de-excitation (quenching) and radiative association, and the general formulae for these reactions are as follows:

Collisional de-excitation:
$$A^* \to A + h\nu$$
 (2.12)

Radiative association of neutrals:
$$A + B \rightarrow C + h\nu$$
 (2.13)

Radiative association of ions & neutrals: $A + B^+ \rightarrow C^+ + h\nu$. (2.14)

Similar to photolytic reactions, radiative de-excitation is also a unimolecular process. Neutral molecules that get excited to higher electronic states by electron impact or other processes, release their excess energy radiatively. Photolytic reactions may lead to the creation of atoms in their metastable states, such as the creation of $O(^{1}D)$ by the photodissociation of water (Equation 2.4). The radiative de-excitation of these metastable states generally leads to forbidden

emission lines in the optical region of cometary spectra. For example, the O(¹D) state has a lifetime ~ 110 s, leading to emissions at wavelengths 6300 Å and 6364 Å, popularly known as the red doublet.

Radiative association involves two species (neutral or ion) combining to form a new molecule, which is stabilized by emitting a photon. These processes are important, particularly in the creation of organic species, because they result in the growth of species from smaller fragments. The mechanism of radiative association involves the reacting species combining to form an energized complex, which then loses energy by spontaneous emissions, so that it does not have sufficient internal energy to re-dissociate.

2.1.4 Reactions of Ions and Neutrals

The general equations for chemical reactions involving ions and neutral species are given below.

Neutral-neutral:
$$A + B \rightarrow C + D$$

 $A + B \rightarrow C + D + E$ (2.15)

Associative ionization:
$$A + B \rightarrow C^+ + e^-$$
 (2.16)

Ion-neutral:
$$A + B^+ \rightarrow C + D^+$$

 $A + B^+ \rightarrow C + C' + D^+$ (2.17)
 $A + B^+ \rightarrow C + C' + C'' + D^+.$

A large number of neutral-neutral bimolecular reactions in the gas-phase possess an activation energy barrier, and these reactions were earlier thought to be unimportant at low temperatures. The CRESU (cinétique de réaction en ecoulement supersonique uniforme, meaning kinetics of reactions in uniform supersonic flow) technique is a method that has been used to measure reaction rates at temperatures as low as 20 K (Rowe et al., 1984a,b). A variety of experiments, especially those that employ the CRESU technique, provide sufficient evidence that many neutral-neutral reactions do not have activation energy barriers, and can proceed at a rapid rate at low temperatures (Smith et al., 2004; Wakelam et al., 2010). These reactions include both radical-radical systems, as well as processes involving a radical/atom and a stable molecule. Two neutral species may also undergo associative ionization, which occurs when one or both of the neutrals are in the excited state, and the sum of their energies is sufficient to create a single additive ionic product and an electron.

Besides neutral-neutral reactions, a significant part of the chemical network is made up of ion-neutral reactions, that are responsible for the formation

Name	Formula	Proton Affinity
		$(kJ mol^{-1})$
Ammonia	NH_3	853.6
Formamide	$\rm NH_2 CHO$	822.2
Ethylene glycol	$(CH_2OH)_2$	815.9
Methyl formate	HCOOCH_3	782.5
Acetonitrile	$\rm CH_3 CN$	779.2
Ethanol	C_2H_5OH	776.4
Amino radical	NH_2	773.4
Acetaldehyde	CH_3CHO	768.5
Methanol	$\rm CH_3OH$	754.3
Cyanoacetylene	$\mathrm{HC}_3\mathrm{N}$	751.2
Formic acid	НСООН	742.0
Hydrogen cyanide	HCN	712.9
Formaldehyde	H_2CO	712.9
Water	H_2O	691.0
Ethylene	C_2H_4	680.5
Acetylene	C_2H_2	641.4
Ethane	C_2H_6	596.3
Carbon monoxide	CO	594.0
Hydroxyl radical	ОН	593.2
Methane	CH_4	543.5
Carbon dioxide	$\rm CO_2$	540.5
Hydrogen	H_2	422.3

Table 2.1: Data on the proton affinity of some neutral cometary species, evaluated and compiled by Hunter & Lias (1998). The species are arranged in decreasing order of their proton affinities.

of a wealth of new species in the coma. The experimental database of laboratory measured gas-phase ion-neutral reactions is also quite extensive, which is of significant advantage in modeling the ion and neutral abundances in the coma. Many of the reactive ions originate from photoionization and photodissociative ionization of parent species. Another abundant class of ions are protonated species, that form when a hydrogen cation attaches to a neutral molecule. Further collisional reaction of the H⁺-bearing protonated species with a neutral molecule having higher proton affinity results in the transfer of the hydrogen cation to the neutral molecule. This sets up a proton transfer "chain", whereby protonated species are created by the successive transfer of the H⁺ ion from one molecule to another, moving in the direction of increasing proton affinity. This is a significant feature of the coma chemistry.

Table 2.1 is a list of some of the major cometary volatiles, arranged in decreasing order of their respective proton affinities. Molecules that are high up on the chart, such as NH_3 and CH_3OH , have a tendency to get protonated and form NH_4^+ and $CH_3OH_2^+$ respectively, since they have higher proton affinities. On the other hand, ions such as H_3O^+ and HCO^+ that are created due to protonation of H_2O and CO respectively, will have a tendency to transfer their protons to the molecules that lie above them. An example of the proton transfer chain that is set up in the coma is as follows:

$$H_2O + H_2O^+ \to H_3O^+ + OH \tag{2.18}$$

$$H_2CO + H_3O^+ \to H_2COH^+ + H_2O$$

$$(2.19)$$

$$\mathrm{NH}_3 + \mathrm{H}_2\mathrm{COH}^+ \to \mathrm{NH}_4^+ + \mathrm{H}_2\mathrm{CO}$$
 (2.20)

$$NH_3 + H_3O^+ \to NH_4^+ + H_2O.$$
 (2.21)

The ion-neutral reactions also include charge exchange reactions between ions and neutral species, which are of the form

$$A + B^+ \to A^+ + B. \tag{2.22}$$

Negative ions and multiply ionized species are not considered in the present network, since they do not have high enough densities to be chemically important.

2.2 Reaction Rates

Type of Reaction	Rate Coefficient
Photo Reactions	$10^{-3} - 10^{-9} \text{ s}^{-1}$
Electron Impact Reactions	$10^{-10} - 10^{-15} \text{ cm}^3 \text{ s}^{-1}$
Dissociative Recombination	$10^{-7} - 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
Collisional De-Excitation	$10^{-4} - 10^7 \text{ cm}^3 \text{ s}^{-1}$
Radiative Association	$10^{-10} - 10^{-15} \text{ cm}^3 \text{ s}^{-1}$
Neutral-Neutral Reactions	$10^{-10} - 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
Ion-Neutral Reactions	$10^{-9} - 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

Table 2.2: Typical range of rate coefficients for the different types of chemical reactions in the cometary atmosphere. The values are appropriate for the solar UV radiation field at a heliocentric distance of 1 AU, and temperatures of 300 K for the ion and neutral species, and 10^4 K for the electrons.

The rate coefficients of the chemical reactions in the current network are stored in the form of three parameters, namely α , β and γ . These parameters are used to calculate the rate coefficients using different formulae, depending upon the chemical process and the temperature range. The rate coefficients of unimolecular reactions have units of s⁻¹, and the reaction rate is computed by multiplying this with the density (in cm⁻³) of the reactant. Bimolecular reaction rate coefficients have units of cm³ s⁻¹, and when this is multiplied by the densities (in cm⁻³) of the two reacting species, the reaction rate can be obtained.

Table 2.2 lists the typical range of values of the rate coefficients for the various chemical reactions occurring in the coma. These ranges are calculated using the values of the rate parameters α , β and γ listed in different databases and literature. For photo reactions, the values of the rate parameters given by Huebner & Mukherjee, 2015 appropriate for a quiet sun are used. For the other reactions, the rate parameter values listed in the KIDA database (Wakelam et al., 2015; http://kida.astrophy.u-bordeaux.fr/) are used. The formulae that are used to calculate the rate coefficients are discussed in the following
subsections.

It can be seen that the rate coefficients for different types of processes vary over many orders of magnitude. However, it is to be noted that these ranges are for representational purposes, and the rate coefficients for all reactions do not necessarily lie in this range. The coma shows significant temperature variation in its different regions, which may alter the rates considerably (Weiler, 2006; Rubin et al., 2014). This is in addition to changes in the photolytic rates due to variations in the UV flux.

2.2.1 Photolytic Rates

In the wavelength interval λ_i and $\lambda_i + \Delta \lambda_i$, the photolytic rate coefficient can be written as:

$$k_i(\tau_i) = \int_{\lambda_i}^{\lambda_i + \Delta \lambda_i} \sigma(\lambda) \phi(\lambda) e^{-\tau(\lambda)} d\lambda.$$
(2.23)

This equation takes into account the UV optical depth τ_i in the same wavelength interval. $\sigma(\lambda)$ and $\phi(\lambda)$ are respectively the photolytic cross section and the unattenuated solar UV flux at wavelength λ . In general, since $\sigma(\lambda)$ and $\phi(\lambda)$ are not known as continuous functions of the wavelength, the rate coefficients can approximately be written as

$$k_i(\tau_i) = \sigma_i \phi_i(\tau_i). \tag{2.24}$$

Here, σ_i is the wavelength-averaged photo cross section in the *i*-th wavelength bin that has a width of $\Delta \lambda_i$, and $\phi_i(\tau_i)$ is the attenuated spectral photon flux integrated over the same wavelength bin:

$$\phi_i(\tau_i) = \int_{\lambda_i}^{\lambda_i + \Delta\lambda_i} \phi(\lambda) e^{-\tau(\lambda)} d\lambda.$$
(2.25)

The total rate coefficient for any photolytic process can then obtained by summing over all the wavelength bins:

$$k(\tau) = \sum_{i} k_i(\tau_i). \tag{2.26}$$

2.2.2 Bimolecular Reaction Rates

The rate coefficients of bimolecular reactions at a temperature T can be written in the form of a modified Arrhenius formula:

$$k(T) = \alpha \left(\frac{T}{300 \text{ K}}\right)^{\beta} e^{-\gamma/T}, \qquad (2.27)$$

where α , β and γ are parameters whose values for various reactions are available in literature and reaction databases. The Arrhenius form does not have a strict theoretical background, and is an empirical relation at best, though it is suitable for fitting the variation of the rate coefficients with temperature. The term $\left(\frac{T}{300 \text{ K}}\right)^{\beta}$ is a description of the dependence of the reaction rate on the impact energy. The term $e^{-\gamma/T}$ accounts for the possible existence of an activation energy barrier. γ can be written in terms of the activation energy E_a and the Boltzmann constant k_B as $\gamma = E_a/k_B$ (in temperature units). Then, e^{-E_a/k_BT} denotes the fraction of molecules with energy $\geq E_a$ for a Maxwellian distribution.

2.2.3 Ion-dipole Reaction Rates

Many of the reactions that are employed in chemical model networks are unmeasured in the laboratory, or have been studied only at limited temperature ranges. Those reactions that have been studied experimentally are between singly charged cations and neutral molecules that can be synthesized or purchased quite easily. However, these neutral species only form a fraction of the possible reactants, while many significant ion-neutral reactions involve radicals as the neutral reactant. Studying these reactions introduces experimental difficulties as the radicals have to be created by flow-discharge techniques and their steadystate concentration estimated. The rates for unmeasured reactions between ions and neutral species possessing a dipole moment can be estimated using the Su-Chesnavich capture approach (Su & Chesnavich, 1982). This method can be employed to calculate the reaction rates for low and high temperature ranges (Woon & Herbst, 2009; Wakelam et al., 2010, 2012). For ion-neutral reactions in which the neutral species is non-polar, the rate coefficient is given by the Langevin expression k_L :

$$k_L = 2\pi e \sqrt{\frac{\alpha_P}{\mu}}.$$
(2.28)

In this expression, e is the electronic charge, α_P is the average dipole polarizability of the neutral species, and μ is the reduced mass $(1/\mu = 1/m_{\rm ion} + 1/m_{\rm neutral}, m_{\rm ion}$ and $m_{\rm neutral}$ being the masses of the ion and neutral species, respectively), and cgs-esu units are employed, such that the rate coefficient has the unit cm³ s⁻¹.

For neutral species possessing a dipole moment μ_D , a unitless parameter x is defined to delineate the temperature ranges, such that

$$x = \frac{\mu_D}{\sqrt{2\alpha_P k_B T}},\tag{2.29}$$

where k_B is the Boltzmann constant and T is the temperature. If all the quantities are in cgs-esu units, then the low temperature range is defined by the region for which $x \ge 2$, while x < 2 corresponds to the high temperature range. The temperature-dependent rate coefficients for ion-dipole collisional reactions in the low and high temperature ranges can be written in terms of the parameters xand k_L as:

$$\frac{k(T)}{k_L} = 0.4767x + 0.62 \quad \text{if } x \ge 2 \tag{2.30}$$

$$\frac{k(T)}{k_L} = \frac{(x+0.5090)^2}{10.526} + 0.9754 \quad \text{if } x < 2.$$
(2.31)

For x = 0, the rate coefficient reduces to the Langevin expression given by Equation 2.28. The rate coefficients for reactions that proceed via more than a single channel need to be multiplied by the branching ratio. Equations 2.30 and 2.31 can be re-written using the parameters α , β and γ , as Equations 2.32 and 2.33, respectively.

$$k(T) = \alpha \beta \left[0.62 + 0.4767 \gamma \left(\frac{300 \text{ K}}{T} \right)^{0.5} \right]$$
 (2.32)

$$k(T) = \alpha \beta \left[1 + 0.0967 \gamma \left(\frac{300 \text{ K}}{T} \right)^{0.5} + \frac{\gamma^2}{10.526} \frac{300 \text{ K}}{T} \right].$$
 (2.33)

Here, α is the branching ratio of the reaction, β is the Langevin rate and γ is the value of x at 300 K. The accuracy of this approach depends on the values of the dipole moments and dipole polarizabilities. Woon & Herbst (2009) find that for the dipole moment, the overall rms difference between theory and experiment is 0.094 D, while for the dipole polarizability, it is 0.268 Å³.

2.3 Formation Pathways of Organic Species

Gas-phase chemistry in the cometary atmosphere leads to the formation of organic molecular species, with varying degrees of complexity. An important mechanism for the formation of neutral organic molecules is by the corresponding protonated organic species undergoing proton transfer reactions, and transferring H^+ ions to molecules with higher proton affinity. Dissociative recombination of the protonated species into neutral unprotonated molecules is another dominant mechanism in the synthesis of organic neutrals. The protonated species are themselves created by a series of ion-neutral or radiative association reactions. The major reactions that are responsible for the formation of organic ions and neutral molecules in the coma are discussed in the following sections.

2.3.1 Formation Pathways Starting from Alcohols

2.3.1.1 Formation from CH₃OH

Figure 2.1 shows the formation routes of organic molecular neutrals and ionic species starting from methanol. Due to its high proton affinity, methanol forms $CH_3OH_2^+$ or protonated methanol when proton transfer takes place from H_3O^+ and HCO^+ ions to neutral CH_3OH . Ion-neutral reactions of $CH_3OH_2^+$ with H_2CO and HCOOH form protonated methyl formate or $HCOOCH_4^+$ (Woon & Herbst, 2009; Cole et al., 2012), and methyl cation transfer reaction of $CH_3OH_2^+$ with CH_3OH creates protonated dimethyl ether or $CH_3OCH_4^+$ (Wakelam et al., 2015). These protonated ions then undergo dissociative recombination to form the re-

spective neutral molecules, namely HCOOCH_3 and CH_3OCH_3 (Hamberg et al., 2010; Wakelam et al., 2015). The dissociative recombination of HCOOCH_4^+ and $\text{CH}_3\text{OCH}_4^+$ proceeds via two and three channels respectively, and in both cases, one of the channels produce methanol.



Figure 2.1: Schematic showing the gas-phase formation of species, starting from methanol.

CH₃OH also undergoes bimolecular reactions with photo produced radicals and atoms such as OH, O, H, CN and C₂H. This leads to H-abstraction or the removal of an H-atom from CH₃OH, and the creation of hydroxymethyl (CH₂OH) radicals (Hebrard et al., 2009; Ruaud et al., 2015). CH₂OH combines with itself to form (CH₂OH)₂ or ethylene glycol (Tsang, 1987).

 $CH_3OH_2^+$ can also form by the protonation of methanol by CH^+ and CH_4^+ ions (Woon & Herbst, 2009), that have lesser abundance, or by the radiative association of H_2O with CH_3^+ (Luca et al., 2002), which is a slower process compared to protonation.

2.3.1.2 Formation from C₂H₅OH

Figure 2.2 shows the formation routes of organic neutrals starting from ethanol. Similar to CH_3OH , ethanol also undergoes H-abstraction by reacting with OH, O and H, resulting in the formation of the radicals CH_2CH_2OH and CH_3CHOH (Wu et al., 2007; Sivaramakrishnan et al., 2010; Skouteris et al., 2018). CH_2CH_2OH radicals further react with atomic oxygen to create formaldehyde (H₂CO) and glycolaldehyde (CH₂OHCHO), while the reaction of CH₃CHOH with O atoms creates formic acid (HCOOH), acetaldehyde (CH₃CHO) and acetic acid (CH₃COOH).



Figure 2.2: Schematic showing the gas-phase formation of species, starting from ethanol.

 C_2H_5OH itself forms in the gas phase when protonated ethanol or $C_2H_5OH_2^+$ participates in a proton transfer reaction with ammonia (Feng & Lifshitz, 1995), or undergoes dissociative recombination (Wakelam et al., 2015). The dissociative recombination of $C_2H_5OH_2^+$ proceeds via three branches with equal branching ratios, and the other two branches form C_2H_4 and CH_3CHO molecules. $C_2H_5OH_2^+$ forms by the radiative association of H_2O with $C_2H_5^+$, and of C_2H_4 with H_3O^+ (Herbst, 1987), or by the protonation of C_2H_5OH by H_3O^+ and HCO^+ ions.

2.3.2 Formation of Aliphatic Diols

The aliphatic diols whose gas-phase formation is added in the present network are $(CH_2OH)_2$ and CH_2OHCHO . Besides forming in the coma from radicals created by the H-abstraction of CH_3OH and C_2H_5OH , they are also created by the dissociative recombination of their corresponding protonated forms, namely $(CH_2OH)_2H^+$ and $CH_2OHCHOH^+$. These protonated species are themselves created when $(CH_2OH)_2$ and CH_2OHCHO undergo protonation reactions with H_3O^+ and HCO^+ ions (Garrod et al., 2007).

2.3.3 Formation of Acids and Aldehydes

2.3.3.1 Formic Acid

Apart from the neutral-neutral reaction of $\text{CH}_2\text{CH}_2\text{OH}$ and O, formic acid or HCOOH forms when protonated formic acid (HCOOH₂⁺) undergoes proton transfer reactions with CH₃OH, CH₃CN, CH₃CHO and NH₃, or by the dissociative recombination of HCOOH₂⁺. Radiative recombination of H₂O and HCO⁺, and the ion-neutral reaction of CH₄ and O₂⁺ forms HCOOH₂⁺ in the coma (Herbst, 1985; Wakelam et al., 2015).

$$H_2O + HCO^+ \rightarrow HCOOH_2^+ + h\nu$$
 (2.34)

$$CH_4 + O_2^+ \to HCOOH_2^+ + H.$$
(2.35)

2.3.3.2 Acetaldehyde

As already seen, acetaldehyde or CH_3CHO forms by the neutral-neutral reaction of atomic oxygen with the H-abstracted ethanol radical CH_3CHOH . Other neutral-neutral reactions forming CH_3CHO in the coma are (McElroy et al., 2013; Wakelam et al., 2015):

$$O + C_2 H_5 \to H + C H_3 C H O \tag{2.36}$$

$$CH + CH_3OH \rightarrow H + CH_3CHO.$$
 (2.37)

In addition, the dissociative recombination of several ions namely $C_2H_5OH_2^+$, $C_2H_5OH^+$ and CH_3CHOH^+ (protonated acetaldehyde) results in the creation of CH_3CHO (Wakelam et al., 2015). CH_3CHOH^+ forms by the ion-neutral reaction of H_2CO^+ and CH_4 (Wakelam et al., 2015), the methyl cation transfer reaction of $CH_3OH_2^+$ with H_2CO (Karpas & Mautner, 1989), and the protonation of CH_3CHO by H_3O^+ , HCO^+ and $HCOOH_2^+$. In addition, C_2H_5OH reacts with C^+ , H^+ and H_3^+ ions (Sung Lee et al., 1992; Wakelam et al., 2015), while the H-abstracted ethanol radicals undergo charge exchange with H^+ ions (Skouteris et al., 2018), creating CH_3CHOH^+ .

2.3.4 Formation of N-bearing Organics

2.3.4.1 Acetonitrile

Acetonitrile or CH_3CN forms via bimolecular reactions of saturated and unsaturated hydrocarbons with N-bearing radicals or ions (Anicich, 2003; Hebrard et al., 2009):

$$CH_4 + CN \rightarrow H + CH_3CN$$
 (2.38)

$$C_2H_4 + N(^2D) \rightarrow H + CH_3CN \qquad (2.39)$$

$$C_2H_6 + CNC^+ \rightarrow C_2H_3^+ + CH_3CN.$$
(2.40)

Dissociative recombination of protonated acetonitrile or CH_3CNH^+ also creates CH_3CN (Loison et al., 2014), where CH_3CNH^+ forms by the following radiative association (Herbst, 1985; Loison et al., 2014) and methyl cation transfer reactions (Plessis et al., 2010):

$$HCN + CH_3^+ \to CH_3CNH^+ + h\nu \tag{2.41}$$

$$HNC + CH_3^+ \to CH_3CNH^+ + h\nu$$
(2.42)

$$HCN + CH_4^+ \to CH_3CNH^+ + H.$$
(2.43)

2.3.4.2 Formamide

The nitrogen-bearing species NH_2CHO (formamide) can be produced in the gasphase via neutral-neutral reaction of the NH_2 radical (created due to photodissociation of ammonia) with H_2CO (Wakelam et al., 2015). NH_2CHO undergoes proton transfer reactions with H_3^+ , H_3O^+ , HCO^+ and N_2H^+ to form NH_2CHOH^+ or protonated formamide (Woon & Herbst, 2009), and NH_2CHOH^+ undergoes dissociative recombination to get converted back into NH_2CHO (Wakelam et al., 2015).

2.3.4.3 Cyanopolyynes

Cyanopolyynes ($HC_{2n+1}N$) form in the gas phase through neutral-neutral reactions, and dissociative recombination of protonated species. Cyanoacetylene or HC_3N forms in the gas phase when C_2H reacts with HCN or HNC (Hebrard et al., 2009; Loison et al., 2014), or by the reaction of CN with C_2H_2 (Wakelam et al., 2015). C_3N reacts with hydrocarbons namely CH_4 , C_2H_2 and C_2H_6 , and with the carbon-chain radicals C_2H_3 and C_2H_5 (Hebrard et al., 2009) to create HC_3N . The reaction of C_2H_2 with the radicals C_3N and C_5N leads to the gas-phase formation of HC_5N (Hebrard et al., 2009; Harada et al., 2010). Other neutral-neutral reactions that form HC_5N are the following (Wakelam et al., 2015):

$$C_4H_2 + CN \to HC_5N + H, \qquad (2.44)$$

$$\mathrm{HC}_{3}\mathrm{N} + \mathrm{C}_{2}\mathrm{H} \to \mathrm{HC}_{5}\mathrm{N} + \mathrm{H}.$$
 (2.45)

Additionally, the dissociative recombination of the protonated cyanopolyynes HC_3NH^+ and HC_5NH^+ can produce HC_3N in the coma, while HC_5N forms by the dissociative recombination of HC_5NH^+ and $C_5H_4N^+$ (Wakelam et al., 2015).

2.4 Reaction Databases and Other Sources

The Kinetic Database for Astrochemistry or KIDA (Wakelam et al., 2015, http: //kida.astrophy.u-bordeaux.fr/) contains gas-phase chemical reactions, and updated parameters for calculating rate coefficients using Equations 2.27, 2.32 and 2.33. Most of the reactions in the present chemical network are taken from the KIDA database. Additional reactions involving organics are taken from Skouteris et al. (2018), Garrod et al. (2007), the UMIST Database for Astrochemistry (McElroy et al., 2013, http://udfa.ajmarkwick.net/index.php) and the NIST Chemical Kinetics Database (Manion et al., 2008, https://kinetics. nist.gov/). The reaction rates for the electron impact excitation and radiative de-excitation of the electronic states of CO are taken from Schmidt et al. (1988). The reactions involving the metastable excited states of oxygen, carbon, and nitrogen are taken from Raghuram & Bhardwaj (2013) and Raghuram et al. (2020). The photochemical reactions are taken from Huebner et al. (1992), with updates from Weiler (2006) and Huebner & Mukherjee (2015).

The present chemical reaction scheme consists of 486 species linked by over 5000 reactions. This is a comprehensive network, with chemical reaction rates compiled from various sources, and it includes most of the parent H-C-N-O neutral molecules (containing upto 10 carbon atoms) that have been detected in comets either in situ or by remote observations (Rubin et al. 2019; also Altwegg 2017, Table 2). However, gas phase reactions and reaction rates are not available in literature for some of the molecules, and these have been excluded from the chemical network. Second and third generation species that are created by the ionization/dissociation of these neutrals are also included. These products of ionization/dissociation react with one another and with the parent species, and the species thus created are included in the network, along with the relevant formation and destruction reactions. A list of the major reactions for the formation of the cometary organics studied in this work, and the parameters to calculate their rate coefficients is included in the Appendix.

Chapter 3

Gas Phase Coma Model

The chemistry and dynamics of the gas phase cometary atmosphere or the coma can be described with the help of a numerical model. The parent volatile species sublimating from the cometary nucleus undergo photolytic reactions, resulting in the formation of neutral radicals, ions and photoelectrons. This triggers an active gas-phase chemistry in the coma, whereby the species interact with each other by a host of processes, including neutral-neutral and ion-neutral bimolecular reactions, recombination reactions and electron impact reactions. In addition to considering the coma chemistry, a dynamical evolution of the coma gas is also included. This is done because many of the chemical reaction rates are dependent on the gas temperature and previous hydrodynamical models have found that the temperature varies strongly with cometocentric distance (Ip, 1983; Marconi & Mendis, 1983, 1986; Gombosi et al., 1986; Körösmezey et al., 1987; Schmidt et al., 1988; Crifo, 1991). Furthermore, the energy released due to chemical reactions is generally distributed non-uniformly amongst the species, resulting in unequal heating and thus, different temperatures of the species involved. Hence a multifluid approach is adopted, and the neutrals, ions, and electrons are considered to be three different fluids.

3.1 Hydrodynamical Description

The governing model equations for the coma are arrived at from the principles of conservation of number density, mass, momentum and energy, and cgs units are employed. Considering a single inviscid fluid, the continuity equation for the particle flux, $n\mathbf{v}$ is

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{v}) = N, \qquad (3.1)$$

where $n \text{ (in cm}^{-3})$ is the particle number density, $\mathbf{v} \text{ (in cm s}^{-1})$ is the fluid velocity and $N \text{ (in cm}^{-3} \text{ s}^{-1})$ is the number density source term. The corresponding equation for the conservation of mass, with mass density $\rho \text{ (in g cm}^{-3})$ and mass source term $M \text{ (in g cm}^{-3} \text{ s}^{-1})$, is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = M. \tag{3.2}$$

Alternatively, the mass density can be computed from the number density as $\rho = \mu n$, where μ is the mean molecular mass. The momentum conservation equation is vector in nature and can be written as

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla p = \mathbf{F}.$$
(3.3)

This equation represents the acceleration of a fluid element under a pressure gradient ∇p and an external force density \mathbf{F} (in dyne cm⁻³). The term $\nabla \cdot (\rho \mathbf{v} \otimes$ $\mathbf{v}) + \nabla p$ can be written as $\nabla \cdot \Pi$, where Π is the momentum flux tensor that has the components $\Pi_{ij} = \rho v_i v_j + \delta_{ij} p$ in Cartesian coordinates (Landau & Lifshitz, 1987). The energy conservation equation can be written in terms of the specific energy e, the energy flux density \mathbf{j}_e , and the energy source term Q (in erg cm⁻³ s⁻¹), as follows:

$$\frac{\partial \rho e}{\partial t} + \nabla \cdot \mathbf{j}_e = Q. \tag{3.4}$$

The specific energy (in erg g⁻¹) of a fluid element is related to the specific internal energy ϵ by the relation:

$$e = \epsilon + v^2/2, \tag{3.5}$$

while the energy flux density (in erg $\text{cm}^{-2} \text{ s}^{-1}$) is given by:

$$\mathbf{j}_e = \rho \mathbf{v} (v^2/2 + h), \tag{3.6}$$

where h is the specific enthalpy. If V is the specific volume, given by $V = 1/\rho$, then h can be written as the sum of the specific internal energy and the work done by expansion, giving $h = \epsilon + pV$.

The coma is assumed to be in the steady state, which causes the partial time derivatives in Equations 3.1-3.4 to become zero. Spherical symmetry is also assumed for the coma, and a transformation of the divergence into spherical coordinates results in the radial components being the only non-zero derivatives. The conservation equations then take the following form (Rodgers & Charnley, 2002):

$$\frac{1}{r^2}\frac{d}{dr}(r^2nv) = N,\tag{3.7}$$

$$\frac{1}{r^2}\frac{d}{dr}(r^2\rho v) = M,\tag{3.8}$$

$$\frac{1}{r^2}\frac{d}{dr}(r^2\rho v^2) + \frac{d}{dr}(nk_BT) = F,$$
(3.9)

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\rho v\left(\frac{v^2}{2} + \frac{\gamma}{\gamma - 1}\frac{k_BT}{\mu}\right)\right] = Q.$$
(3.10)

In the above equations, r (in cm) is the cometocentric distance, and the source terms N, M, F and Q represent the net rate per unit volume for the generation of species number density, mass, momentum and energy respectively. The equation of state for the coma is generally assumed to follow that of an ideal gas, such that the pressure is written as:

$$p = nk_BT, (3.11)$$

while the specific internal energy can be written as:

$$\epsilon = \frac{p}{\rho(\gamma - 1)},\tag{3.12}$$

where k_B is the Boltzmann constant and γ is the adiabatic exponent. Using these relations, the specific enthalpy term in Equation 3.10 is

$$h = \frac{\gamma}{\gamma - 1} pV = \frac{\gamma}{\gamma - 1} \frac{k_B T}{\mu}.$$
(3.13)

The energy source term Q in Equation 3.10 can be replaced by the thermal energy source term G, such that

$$G = Q - Fv + \frac{1}{2}Mv^2.$$
 (3.14)

3.2 Model Equations

Every species in the coma can be described using the set of Equations 3.7-3.10, that is, each species can be treated as a separate fluid. However, such a treatment is computationally expensive, and the species are divided into three categories of fluids, namely the neutral, ion and electron fluids. These three fluids have separate temperatures and a common expansion velocity. Equations 3.7-3.10 are re-written as a set of coupled first-order differential equations in number density, velocity and temperature, as follows.

$$\frac{dn_j}{dr} = \frac{N_j}{v} - \frac{n_j}{v}\frac{dv}{dr} - \frac{2n_j}{r},\tag{3.15}$$

$$\frac{dv}{dr} = \sum_{k} \left[\frac{1}{\rho_{k}v^{2} - \gamma_{k}n_{k}k_{B}T_{k}} \left(F_{k}v - (\gamma_{k} - 1)G_{k} - M_{k}v^{2} + \frac{2v}{r}\gamma_{k}n_{k}k_{B}T_{k} \right) \right],$$

$$\frac{dT_{k}}{dr} = \frac{(\gamma_{k} - 1)T_{k}}{v} \left(\frac{G_{k}}{n_{k}k_{B}T_{k}} - \frac{2v}{r} - \frac{dv}{dr} - \frac{N_{k}}{(\gamma_{k} - 1)n_{k}} \right).$$
(3.16)
(3.17)

In the above differential equations, the subscript j (Equation 3.15) stands for any particular chemical species, while the subscript k = n, i, e (Equations 3.16 and 3.17) indicates the three fluids namely neutral, ion and electron, respectively. Thus, in this system of coupled differential equations, there are as many ODEs in number density as there are species in the coma, three ODEs in temperature, for the three different fluids, and a single ODE for the common velocity. A summation of the number densities and number density source terms of the species that belong to the fluid k gives the terms n_k and N_k , respectively. Similarly, the mass density ρ_k of the fluid k is obtained by summing over the densities of all the species corresponding to the fluid k, such that

$$\rho_k = \sum_l m_l n_l, \tag{3.18}$$

where m is the molecular weight of a species. γ_k for the fluid k is computed as a weighted average of the adiabatic exponents γ of all the species that belong to the fluid k, where the weights are the species number densities:

$$\gamma_k = \frac{\sum_l \gamma_l n_l}{\sum_l n_l}.$$
(3.19)

The value of γ for most species is listed in Schmidt et al. (1988).

3.2.1 Simplifications

The present model employs a large chemical network to study the coma chemistry and certain simplifications and assumptions are made to reduce complexity and computational time. The following is an overview of these assumptions and the justification of their validity.

Hydrodynamic Flow

The model assumes a hydrodynamic flow of the cometary atmosphere, which is true for a collisionally dominated coma. The model also assumes an isotopically active comet and sublimation takes place from the entire surface of the nucleus. When the gas expands in space, the flow is collisionally dominated only in the inner coma, and there is strong dilution and a transition to free molecular flow in the outer coma. This transition region is roughly at a distance $\sim 10^4$ km from the nucleus, for a moderately active comet at 1 AU (Rodgers et al., 2004). A Monte Carlo treatment of the gas is more apt for free molecular flow, though it has been shown that a hydrodynamical description can reasonably reproduce observed number densities and temperatures (Marconi & Mendis, 1986).

Steady State and Spherically Symmetric Flow

The model is valid for a cometary atmosphere in the steady state, and does not take transient phenomena into account, such as sudden outgassing due to outbursts, or periodic variations due to a rotating cometary nucleus. Changes in the heliocentric distance also causes variations in cometary activity, though this occurs at a timescale that is much larger than the timescale for fluid flow within the coma. At 1 AU, the lifetime of H_2O is $\sim 8.5 \times 10^4$ s, and for a cometary gas expansion velocity of 1 km s⁻¹, the density of the coma at 10⁵ km is reduced to < 35% of the near-nucleus density. There is negligible change in the heliocentric distance in this timescale.

The nucleus of the comet is expected to show higher activity in the sunward direction, and there is day-night asymmetry in the outgassing of parent species (cf. Le Roy et al., 2015). A more detailed coma model would thus require a multi-dimensional approach. There are shape models which exist from in situ observations. However, it is not possible to deduce the shape of the nucleus from ground based observations. Due to lack of data on the shape of the cometary nucleus for the comets studied in this work, the assumption of spherical symmetry is practicable.

Common Fluid Velocity

The ions and the electrons are coupled due to Coulomb interactions, which ensures charge neutrality in the coma. Thus it is reasonable to assume that the plasma velocity for the ion and electron fluids is the same. The sonic speed of the plasma, containing ions of an average mass μ_i is given by

$$c_p = \sqrt{\frac{k_B(\gamma_i T_i + \gamma_e T_e)}{\mu_i}}.$$
(3.20)

The electron temperature can attain very high values in the outer coma (> 10^4 K or > 1 eV), causing the plasma velocity to become subsonic. At the sonic point, Equation 3.16 for the plasma velocity would become singular. To ensure a smooth transition through the sonic point, a separate numerical treatment would

be required. This can be avoided if the plasma velocity is assumed to be the same as the velocity of the neutral species, so that all of the fluids move with a single bulk velocity.

Neglect of Suprathermal Species

Neutral hydrogen atoms are produced by the photodissociation of water, and other reactions. Due to their low mass, hydrogen atoms created by chemical reactions will receive most of the excess energy (cf. Combi et al., 2004). They can thus trigger chemical reactions that have high activation energies, that cannot otherwise occur under the temperature conditions of the coma. These reactions are H-abstraction reactions, and have effects that are chemically similar to photodissociation i.e., the destruction of parent molecules and the creation of reactive radicals. However, Rodgers & Charnley (2005) showed that this effect is weak since the reactions proceed at a much slower rate as compared to photodissociation, and the non-inclusion of suprathermal species does not significantly alter the coma chemistry.

Approximations for Dust

Cometary volatiles may sublimate from dust grains present in the coma, leading to volatile production from distributed or extended sources (for example, DiSanti et al., 2001, 2003). The detection of a number of complex organics is associated with dust activity in the coma, which suggests that they originate from dust grains (for example, Altwegg et al., 2020; Hänni et al., 2022). Volatiles released from dust grains should initially follow a directed outward flow, and if they are released closer to the nucleus where the collision rates are higher, their flow becomes nearly isotropic. In this model, it is assumed that the distributed sources lie near the surface of the nucleus, and volatile production from distributed sources is approximated as the sublimation of that volatile from the nucleus. In addition, previous models have shown that the presence of dust does not significantly affect the temperature and velocity of the outflowing gas (for example, Marconi & Mendis, 1982a). Weiler (2006) showed for 67P/C-G that a dust-to-gas mass ratio as high as 8.5 has negligible influence on the coma gas flow, and in situ measurements estimate a lower dust-to-gas mass ratio for 67P/C-G (Choukroun et al., 2020).

Approximations for Magnetic Fields

The solar wind interacts with the cometary plasma outside the diamagnetic cavity, the size of which is affected by the gas production rate of the nucleus (see Section 1.2.5). For weakly and intermediately active comets, the contact surface lies close to the nucleus (Benna & Mahaffy, 2006; Koenders et al., 2016) and the solar wind interacts with the coma gas even at low cometocentric distances. Charge exchange and electron impact ionization reactions are included in the chemical network to account for this interaction. For comets with higher activity, the contact surface and plasma interaction regions lie further away from the nucleus, at distances $\geq 10^4$ km. In this case, ionization effects due to the solar wind do not necessarily increase the accuracy of the modeling of the inner regions. A more detailed treatment of the magnetic field effects on the cometary plasma flow requires a three-dimensional magnetohydrodynamic treatement. This would be computationally expensive in the present model that employs a large chemical network and beyond the scope of the current work.

3.3 Initial Conditions

The initial gas velocity at the nuclear surface is assumed to be equal to the local sonic speed (Weiler, 2006) given by:

$$v_0 = \sqrt{\gamma R_g T_0},\tag{3.21}$$

where γ is the adiabatic exponent, R_g is the specific gas constant and T_0 is the initial temperature of the coma gas. This temperature can be calculated from the surface ice temperature T_s . A Maxwellian velocity distribution of the outflowing gas is reached only after several molecular collisions, after which T_0 and T_s are related as:

$$T_0 = \frac{T_s}{1 + \frac{1}{2}(\gamma - 1)}.$$
(3.22)

The initial temperature of all the three fluids is set in this manner. In order to find the surface temperature, the energy balance equation is solved, and for a pure icy surface, this equation can be written as:

$$\frac{F_{\odot}(1-A_v)}{r_h^2} \left\langle \cos\theta\cos\phi \right\rangle = \epsilon_{\rm IR}\sigma_B T_s^4 + HZ(T), \qquad (3.23)$$

where F_{\odot} is the incident solar flux, which is scaled by the heliocentric distance r_h , A_v is the visual albedo, θ and ϕ are the local hour angle and the latitude, $\epsilon_{\rm IR}$ is the infrared emissivity, σ_B is the Stefan-Boltzmann constant, H is the latent heat of sublimation of the ice, and Z(T) is the surface sublimation rate. If $Q_{0,\rm pri}$ is the production rate of a parent volatile from the nucleus and r_0 is the nuclear radius, then the number density of that volatile near the surface is

$$n_{0,\text{pri}} = \frac{Q_{0,\text{pri}}}{4\pi r_0^2 v_0}.$$
(3.24)

3.4 Source Terms

3.4.1 Number Density Source Term

The number density source term N_j for a species j is calculated by adding or subtracting together the rate coefficients of the reactions that contribute to the creation or destruction of that species.

$$N_j = \sum_{j\prime} \nu_{j\prime} \mathcal{R}_{j\prime}.$$
(3.25)

 ν is the number of molecules of the species created in a particular reaction, \mathcal{R} is the reaction rate in cm⁻³ s⁻¹, and the summation index $j\prime$ runs over all those reactions in which the species j is a product or a reactant. Since the different fluids considered in this model have separate temperatures, the temperature dependent collisional reaction rates are calculated at an effective temperature

 $T_{\rm eff}$ (Flower et al., 1985), such that

$$T_{\rm eff} = \frac{m_k T_l + m_l T_k}{m_l + m_k}.$$
 (3.26)

 T_l and T_k are the fluid temperatures to which the reacting species having masses m_l and m_k belong. For reactions involving collisions with electrons, $T_{\text{eff}} \approx T_e$, since the mass of the electron is much less than the mass of the other reacting species.

The reaction rate per unit volume \mathcal{R}_{ij} (cm⁻³ s⁻¹) of the *j*-th chemical reaction forming the *i*-th species is calculated by multiplying the rate coefficient of the process obtained from the relevant rate equation (Equations 2.26, 2.27, 2.32 or 2.33), by the number densities of the reacting species. The reaction rate thus depends upon the abundance of the reacting species, the fluid temperature, and the cometocentric distance (for photolytic processes). The net coma formation rate per unit volume P_i for the *i*-th species is obtained by summing the reaction rates per unit volume of all the chemical processes contributing to the formation of that species, such that

$$P_i = \sum_j \mathcal{R}_{ij}.$$
(3.27)

The relative reaction rate for each chemical process can be calculated as \mathcal{R}_{ij}/P_i . The relative reaction rate is a measure of the fractional contribution of each chemical process towards the net creation rate per unit volume of a species in the coma. The loss rate per unit volume L_i for the *i*-th species can be calculated in a similar manner.

The total mass and momentum source terms are conserved, that is

$$\sum_{k} M_k = 0, \tag{3.28}$$

$$\sum_{k} F_k = 0. \tag{3.29}$$

Since these terms appear only as summations in Equation 3.16, they need not be calculated individually for each fluid. The thermal energy source terms G_k for each fluid are a sum of different components, which are discussed in the next section.

3.4.2 Thermal Energy Source Terms

The thermal energy source terms for the neutral, ion and electron fluids, respectively are defined as:

$$G_n = G_n^{\text{chem}} + G_{i,n}^{\text{elas}} + G_{e,n}^{\text{elas}} + G_{e,n}^{\text{inel}} - G_n^{\text{rad}}, \qquad (3.30)$$

$$G_i = G_i^{\text{chem}} - G_{i,n}^{\text{elas}} - G_{e,i}^{\text{elas}}, \qquad (3.31)$$

$$G_e = G_e^{\text{chem}} + G_{e,i}^{\text{elas}} - G_{e,n}^{\text{elas}} - G_{e,n}^{\text{inel}}.$$
 (3.32)

These components arise due to chemical reactions, exchange of energy due to elastic and inelastic scattering processes, and radiative losses.

3.4.2.1 Chemical Reactions

The components G_n^{chem} , G_i^{chem} and G_e^{chem} denote the contribution to the thermal energy source terms of the neutral, ion and electron fluids, respectively, arising due to chemical reactions. Production or loss of a chemical species results in the addition or removal of the kinetic energy of that species from the fluid that it belongs to. If a species j is created (or destroyed) by the reaction α , then its rate of increase (or decrease) of energy per unit volume is (Draine, 1986):

$$G_{j,\alpha} = \mathcal{R}_{j,\alpha} \left(\frac{1}{2} m_j |\vec{v}_j - \vec{w}_{j,\alpha}|^2 + \frac{1}{2} m_j \zeta_{j,\alpha}^2 \right).$$
(3.33)

Here, $\mathcal{R}_{j,\alpha}$ is the creation or destruction rate of species j by the reaction α , m_j is the mass and \vec{v}_j is the mean velocity of species j, $\vec{w}_{j,\alpha}$ is the mean velocity of the particles of species j emerging from or being used up by the reaction α and $\zeta_{j,\alpha}$ is the random velocity of the particles of species j involved in the reaction α . Since the bulk velocity is assumed to be the same for all the species, $\vec{v}_j - \vec{w}_{j,\alpha} = \vec{0}$, and only the internal energy $\frac{1}{2}m_j\zeta_{j,\alpha}^2$ is required to compute $G_{j,\alpha}$. Chemical reactions also increase or decrease the energy of the system, depending on whether they are exothermic or endothermic, and this is the excess energy ΔE . The fraction of the excess energy received by the products is computed from energy-momentum conservation in the reference frame of the center of momentum of the reactants. Electrons that are created as products receive all of the excess energy since their mass is negligible in comparison with that of the other species.

The thermal energy source terms for the different reaction types were computed by Draine (1986) and extended by Rodgers & Charnley (2002) and Weiler (2006). Table 3.1 lists the source terms \hat{G}_k , k = n, i, e for the species belonging respectively to the neutral, ion and electron fluids, for the 15 generic types of reactions that are included in the current network. \hat{G}_k , when multiplied by the appropriate reaction rate \mathcal{R} and summed over all the chemical reactions in the network, gives the net component G_k^{chem} , k = n, i, e.

3.4.2.2 Elastic Scattering

Elastic scattering occurs between each of the fluids, resulting in three types of scattering processes, namely ion-neutral, electron-neutral and electron-ion, for which the rates of exchange of energy per unit volume are $G_{i,n}^{\text{elas}}$, $G_{e,n}^{\text{elas}}$ and $G_{e,i}^{\text{elas}}$ respectively.

The ion-neutral elastic scattering is a special case of the ion-neutral reaction A + B⁺ \rightarrow C + D⁺ given in Table 3.1, with $m_{\rm A} = m_{\rm C}$, $m_{\rm B} = m_{\rm D}$ and $\Delta E = 0$. The most abundant neutral species in the coma are the parent molecules H₂O, CO and CO₂, and the most abundant ions with which these do not undergo chemical reactions are H₃O⁺, NH₄⁺, CH₃OH⁺, CH₃OH₂⁺ and HCNH⁺. Thus, ion-neutral elastic collisions can be modeled as 'pseudo-reactions' of the kind

$$A + B^+ \to A + B^+, \tag{3.34}$$

where there is only exchange of energy and no change in the number densities of A and B⁺. The rates for these reactions are calculated using Equation 2.27, with the Arrhenius coefficients $\alpha_j \approx 10^{-10}$ cm³ s⁻¹, $\beta_j = 0.5$ and $\gamma_j = 0$. The net change in energy for each collision is:

$$\hat{G}_{i,n}^{\text{elas}} = \frac{2m_n m_i}{(m_n + m_i)^2} \left(\Theta_i - \Theta_n\right),$$
(3.35)

Reaction type	Formula	\hat{G}_n	\hat{G}_i	\hat{G}_e
Photodissociation ^[1]	$\mathbf{A} + h\nu \to \mathbf{B} + \mathbf{C}$	ΔE	0	0
Photoionization ^[2]	${ m A} + h u ightarrow { m A}^+ + { m e}^-$	$-\Theta_n$	Θ_n	ΔE
Photodissociative ionization ^{[2],[3]}	$A + h\nu \rightarrow B + C^+ + e^-$	$-\frac{m_{C}}{m}\Theta_{n}$	$\frac{m_{\rm C}}{m}\Theta_n$	ΔE
	$A + h\nu \rightarrow B + B' + C^+ + e^-$	$-\frac{m_{\text{CA}}^{\text{AA}}}{m_{\text{C}}}\Theta_n$	$\overset{\text{m.r.}}{\underset{m}{\overset{m}{}{}{}{}{}{$	ΔE
Neutral-neutral ^{[2],[3]}	$A+B \to C+D$	ΔE	0. 0	0
	$A + B \rightarrow C + D + E$	ΔE	0	0
Ion-neutral [†] ^[1] , ^[3]	$A + B^+ \rightarrow C + D^+$	$\frac{m_{\rm A}m_{\rm D}+m_{\rm B}m_{\rm C}}{m_{\rm Z}^2}(\Theta_i-\Theta_n)+\frac{m_{\rm D}}{m_{\rm T}}\Delta E$	$\frac{m_{A}m_{D}+m_{B}m_{C}}{m_{Z}^{2}}(\Theta_{n}-\Theta_{i})+\frac{m_{C}}{m_{T}}\Delta E$	0
	$A + B^+ \rightarrow C + C' + D^+$	$\frac{m_{\rm A}m_{\rm D}+1}{m_{\rm M}^2}m_{\rm CC'}(\Theta_i-\Theta_n)+\frac{m_{\rm D}}{m_{\rm T}}\Delta E$	$\frac{m_{\text{A}}m_{\text{D}}+^{\text{H}}m_{\text{CC}'}}{m_2}(\Theta_n - \Theta_i) + \frac{m_{\text{CC}'}}{m_{\text{T}}}\Delta E$	0
	$A+B^+ \rightarrow C+C'+C''+D^+$	$\frac{m_{\rm A}m_{\rm D}+m_{\rm B}m_{\rm CC'C''}}{m_{\rm A}^2}(\Theta_i-\Theta_n)+\frac{m_{\rm D}}{m_{\rm T}}\Delta E$	$\frac{m_{\mathrm{A}}m_{\mathrm{D}}+\hat{m}_{\mathrm{B}}m_{\mathrm{CC}'\mathrm{C}'}}{m_{\mathrm{Z}}^{2}}(\Theta_{n}-\Theta_{i})+\frac{m_{\mathrm{CC}'\mathrm{C}'}}{m_{\mathrm{T}}}\Delta E$	0
Radiative association of neutrals ^[2]	$\mathbf{A} + \mathbf{B} \to \mathbf{C} + h\nu$	$-\Theta_n$	0	0
Radiative association of ions & neutrals $^{[2]}$	$A + B^+ \rightarrow C^+ + h\nu$	$-\Theta_n$	$rac{m_A}{m_C}(\Theta_n-\Theta_i)$	0
Associative ionization ^[3]	$\rm A + B \rightarrow \rm C^{+} + e^{-}$	$-2\Theta_n$	$2\Theta_n$	ΔE
Radiative de-excitation ^[3]	$\mathbf{A}^* \to \mathbf{A} + h\nu$	0	0	0
Radiative recombination ^[1]	${ m A}^+ + { m e}^- ightarrow { m A} + h u$	Θ_i	$-\Theta_i$	$-\Theta_e$
Dissociative recombination ^{[1],[3]}	$\rm A^+ + e^- \rightarrow B + C$	$\Theta_i + \Theta_e + \Delta E$	$-\Theta_i$	$-\Theta_e$
	$\rm A^+ + e^- \rightarrow B + C + D$	$\Theta_i + \Theta_e + \Delta E$	$-\Theta_i$	$-\Theta_{e}$
	$A^+ + e^- \rightarrow B + C + D + E$	$\Theta_i + \Theta_e + \Delta E$	$-\Theta_i$	$-\Theta_e$
Electron impact ionization ^[2]	$\rm A + e^- \rightarrow A^+ + e^- + e^-$	$-\Theta_n$	Θ_n	ΔE
Electron impact dissociative ionization ^[3]	$\rm A + e^- \rightarrow B + C^+ + e^- + e^-$	$-\frac{m_{C}}{m_{A}}\Theta_{n}$	$\frac{m_{\mathrm{C}}}{m_{\mathrm{A}}}\Theta_n$	ΔE
	$A + e^- \rightarrow B + B' + C^+ + e^- + e^-$	$-\frac{m_{C}}{m_{A}}\Theta_{n}$	$\frac{mc}{m}\Theta_n$	ΔE
Electron impact dissociation ^[2]	$\rm A + e^- \rightarrow \rm B + \rm C$	0	0	ΔE
	$\rm A + e^- \rightarrow B + C + D$	0	0	ΔE
	$\rm A + e^- \rightarrow B + C + D + E$	0	0	ΔE
Electron impact excitation ^[3]	$A + e^- \rightarrow A^* + e^-$	0	0	ΔE

 Θ_k is the mean kinetic energy of a particle belonging to the fluid k such that $\Theta_n = \frac{3}{2}k_BT_n$, $\Theta_i = \frac{3}{2}k_BT_i$ and $\Theta_e = k_BT_e$. ΔE is the mean exo/endo-thermicity of the chemical reaction. [†] $m_{\rm T}$ is the sum of the masses of the reactants, $m_{\rm CC'} = m_{\rm C} + m_{\rm C'}$, and $m_{\rm CC'C''} = m_{\rm C} + m_{\rm C'} + m_{\rm C''}$. References: [1] Draine (1986), [2] Rodgers & Charnley (2002), [3] Weiler (2006). Table 3.1: The thermal energy source terms \hat{G}_k , k = n, i, e due to the different types of chemical reactions included in the model.

where m_n and m_i are the respective masses of the neutral and ionic species participating in the scattering process. $G_{i,n}^{\text{elas}}$ is found by multiplying the energy change given by Equation 3.35 with the collision rate per unit volume, and summing over all ion-neutral elastic collision reactions.

Similar to the case of ion-neutral scattering, the elastic scattering between electrons and neutrals is dominated by scattering from H_2O , CO and CO_2 molecules, such that

$$G_{e,n}^{\text{elas}} \approx G_{e,n}^{\text{elas,H}_2\text{O}} + G_{e,n}^{\text{elas,CO}} + G_{e,n}^{\text{elas,CO}_2}, \qquad (3.36)$$

where $G_{e,n}^{\text{elas},\text{H}_2\text{O}}$, $G_{e,n}^{\text{elas},\text{CO}}$ and $G_{e,n}^{\text{elas},\text{CO}_2}$ are the rates of exchange of energy per unit volume due to elastic scattering of electrons from H₂O, CO and CO₂ molecules, respectively. The momentum transfer collision cross sections of electrons in these neutral gases has been compiled by Itikawa (2002; 2015) and Itikawa & Mason (2005), over a wide range of electron energies. To find the collision rate per unit volume of electrons with a neutral species, the relevant cross sections are averaged over a Maxwellian velocity distribution, and then multiplied by the number densities of electrons and the colliding neutral species. The average change in energy per collision $\hat{G}_{e,n}^{\text{elas}}$ can be found from Equation 3.35, by replacing the mass of the ion by the electron mass, and Θ_i by Θ_e . $G_{e,n}^{\text{elas}}$ is then calculated by multiplying $\hat{G}_{e,n}^{\text{elas}}$ with the corresponding collision rate, and then summing over the three neutral species.

Elastic scattering between ions and electrons due to Coulomb interactions results in the following rate of energy change per unit volume (Draine, 1980):

$$G_{e,i}^{\text{elas}} = 1.37 \times 10^{-42} \frac{n_i^2}{\mu_i} T_e^{-1.5} (T_i - T_e) \ln\left(1.24 \times 10^4 \sqrt{\frac{T_e^3}{n_i}}\right) \quad (\text{erg cm}^{-3} \text{ s}^{-1}),$$
(3.37)

where n_i is the total number density of all ions and μ_i is the mean ionic molecular mass.

3.4.2.3 Inelastic Scattering

For inelastic electron-neutral scattering, H_2O and CO are the only neutral species that are considered. The per unit volume rate of cooling of the electron fluid due to these types of collisions is thus given by

$$G_{e,n}^{\text{inel}} \approx G_{e,n}^{\text{inel},\text{H}_2\text{O}} + G_{e,n}^{\text{inel},\text{CO}}.$$
 (3.38)

Inelastic collisions of H_2O molecules with electrons results in rotational and vibrational excitation of the molecules. The net cooling rate per unit volume of electrons due to inelastic scattering with H_2O is:

$$G_{e,n}^{\text{inel},\text{H}_2\text{O}} = G_{\text{rot},\text{H}_2\text{O}} + G_{\nu 1,\text{H}_2\text{O}} + G_{\nu 2,\text{H}_2\text{O}}.$$
(3.39)

The first term on the right is the cooling due to rotational excitation of H_2O and the second and third terms are due to vibrational excitations. The analytical expressions for these were derived by Cravens & Korosmezey (1986) and are given below.

$$G_{\rm rot,H_2O} = \left[a + b \ln\left(\frac{T_e}{T_n}\right)\right] (T_e - T_n) T_e^{-5/4} n_{\rm H_2O} n_e \quad (eV \ cm^{-3} \ s^{-1}).$$
(3.40)

$$G_{\nu j, \mathrm{H}_{2}\mathrm{O}} = 8.37 \times 10^{13} W_{j} T_{e}^{-3/2} \left[1 - \exp\left\{ W_{j} / k_{B} (T_{e}^{-1} - T_{n}^{-1}) \right\} \right]$$

$$\times I_{j} T_{e} n_{\mathrm{H}_{2}\mathrm{O}} n_{e} \quad (\mathrm{eV \ cm}^{-3} \ \mathrm{s}^{-1}).$$
(3.41)

 $n_{\rm H_2O}$ and n_e are the number densities of water molecules and electrons, j = 1 corresponds to the vibrational transition (000) \rightarrow (010) and j = 2 stands for the sum of the transitions (000) \rightarrow (100) and (000) \rightarrow (001). The values of a, b, W_j and I_j in the above expressions are given by Cravens & Korosmezey (1986).

Vibrational and electronic transitions of CO due to inelastic collisions with electrons are considered to calculate the term $G_{e,n}^{\text{inel,CO}}$. The rotational excitation of CO is ignored, because the cross sections for these transitions due to inelastic collisions with electrons is less than that of H₂O by up to four orders of magnitude. The vibrational cooling rate per unit volume for $0 \rightarrow j$ vibrational excitation of CO can be calculated in the manner given by Waite & Cravens (1981) for molecular hydrogen:

$$G_{\nu j,\rm CO} = n_{\rm CO} n_e \int_0^\infty L(E, T_n) v f_e(E, T_e) dE \quad (\rm eV \ cm^{-3} \ s^{-1}). \tag{3.42}$$

Here, $n_{\rm CO}$ and n_e are the CO and electron number densities, $L(E, T_n)$ is the loss function for vibrational excitation and de-excitation, $v = (2E/m_e)^{1/2}$ is the electron thermal velocity and $f_e(E, T_e)$ is the normalized Maxwellian electron energy distribution function. The loss function for the transition $0 \rightarrow j$ is

$$L_{\nu j}(E,T_n) = W_j \{\sigma_j(E) - \exp(-W_j/kT_n) \left(\frac{E+W_j}{E}\right) \sigma_j(E+W_j)\}, \quad (3.43)$$

where W_j is the threshold for transition j and T_n is the neutral temperature. $\sigma_j(E)$ is the energy-dependent cross section for transition j, taken from Itikawa (2015). The transitions j = 1, 2, 3 are considered; higher transitions are ignored because of reduced cross sections.

The reactions for the electronic excitation of CO by electron impact and its subsequent de-excitation are shown in Table 3.2. These reactions are included in the network, and the energy change \hat{G}_k is calculated as described in Section 3.4.2.1.

Neutral molecules with a permanent dipole moment can be excited to higher rotational states due to self-collisions. Energy can be lost from the neutral fluid (mainly H_2O) due to infrared rotational emission, resulting in the cooling of the neutral fluid, such that

$$G_n^{\mathrm{rad}} \approx G_n^{\mathrm{rad},\mathrm{H_2O}}.$$
 (3.44)

An empirical formula for the energy loss due to H₂O-H₂O collisions was given by

Reaction	α	β	γ	$\Delta E \ (eV)$
Electron impact excitation				
$\rm CO + e^- \rightarrow \rm CO(^1\Pi) + e^-$	4.46(-9)	2.03(-1)	9.494(+4)	-8.09
$\rm CO + e^- \rightarrow \rm CO(^3\Pi) + e^-$	1.63(-7)	-4.18(-1)	8.384(+4)	-6.00
$\rm CO + e^- \rightarrow \rm CO(^3\Sigma) + e^-$	2.89(-9)	1.07(-1)	9.100(+4)	-6.90
$\rm CO + e^- \rightarrow \rm CO(^3\Delta) + e^-$	8.22(-10)	-4.00(-2)	9.985(+4)	-7.70
Radiative de-excitation				
$\mathrm{CO}(^{1}\Pi) \to \mathrm{CO} + h\nu$	9.70(7)	0	0	0
$\mathrm{CO}(^{3}\Pi) \to \mathrm{CO} + h\nu$	1.26(2)	0	0	0
$\mathrm{CO}(^{3}\Sigma) \to \mathrm{CO} + h\nu$	1.00(5)	0	0	0
$\operatorname{CO}(^{3}\Sigma) \to \operatorname{CO}(^{3}\Pi) + h\nu$	1.00(5)	0	0	0
$\mathrm{CO}(^{3}\Delta) \to \mathrm{CO} + h\nu$	1.00(-5)	0	0	0
$\operatorname{CO}(^{3}\Delta) \to \operatorname{CO}(^{3}\Pi) + h\nu$	2.37(5)	0	0	0

Table 3.2: Reactions showing the excitation and de-excitation of the electronic states of CO, resulting in the cooling of the electron fluid (Schmidt et al., 1988).

Shimizu (1976):

$$G_n^{\text{rad},\text{H}_2\text{O}} = \frac{8.5 \times 10^{-19} T_n^2 n_{\text{H}_2\text{O}}^2}{n_{\text{H}_2\text{O}} + 2.7 \times 10^7 T_n} \quad (\text{erg cm}^{-3} \text{ s}^{-1}).$$
(3.45)

Since optical depth effects cause radiation trapping in the inner regions of the coma, the radiation cooling rates are scaled by $\exp(-\tau_{\rm IR})$ (Schmidt et al., 1988), where

$$\tau_{\rm IR}(r) \approx 0.4 \times n(r_0) r_0^2 \frac{\sigma_{\rm IR}}{r}.$$
(3.46)

 r_0 is the nuclear radius, n is the number density of H₂O and $\sigma_{IR} = 4 \times 10^{-15} \text{ cm}^2$ is the average infrared absorption cross section per molecule.

3.5 Photochemistry

Solar UV radiation causes photodissociation, photoionization and photodissociative ionization of the gaseous cometary species. The absorption of the UV radiation in the coma causes attenuation of the UV flux, resulting in optical depth effects. In Chapter 2, a general description of the photolytic rate calculation while accounting for the optical depth is given. A more specific description for the cometary case is given here.

If $\phi_{i,\infty}$ is the unattenuated flux corresponding to the wavelength λ_i , then the UV flux at a cometocentric distance r is given by

$$\phi_i(r) = \phi_{i,\infty} e^{-\tau_i(r)},\tag{3.47}$$

where τ_i is the optical depth at wavelength λ_i , and can be calculated from the wavelength dependent photochemical reaction cross sections and species number densities. For a cometary species denoted by j, if n_j is its number density and $\sigma_{ij,\text{tot}}$ is its total photolytic cross section in λ_i , then the contribution of this species to the optical depth is:

$$\tau_{ij}(r) = \int_{r}^{\infty} \sigma_{ij,\text{tot}} n_j(r) dr \qquad (3.48)$$

The total optical depth at distance r can be obtained by summing over j, such that $\tau_i(r) = \sum_j \tau_{ij}(r)$. Once the fluxes are known, the photolytic rate coefficient in the wavelength interval λ_i and $\lambda_i + \Delta \lambda_i$, and at a distance r can be found out using the relation

$$k_i(r) = \int_{\lambda_i}^{\lambda_i + \Delta\lambda_i} \sigma(\lambda)\phi(\lambda, r)d\lambda.$$
(3.49)

This can be approximated as $k_i(r) = \sigma_i \Phi_i(r)$, where σ_i is the wavelengthaveraged photo cross section in the *i*-th bin that has a width of $\Delta \lambda_i$, and $\Phi_i(r)$ is the attenuated spectral photon flux integrated over the same wavelength bin. The total rate coefficient for any photolytic process can then be written as :

$$k(r) = \sum_{i} k_i(r).$$
 (3.50)

The excess photon energy above the dissociation or ionization threshold is converted into kinetic energy of the photo-products. The mean excess energy of the photolytic products at a distance r is given by:

$$E(r) = \frac{\int_{0}^{\lambda_{th}} hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_{th}}\right) \sigma(\lambda)\phi(\lambda, r)d\lambda}{\int_{0}^{\lambda_{th}} \sigma(\lambda)\phi(\lambda, r)d\lambda}, \quad (\lambda \le \lambda_{th})$$

$$\approx \sum_{i} hc\left[\frac{\lambda_{i} + \Delta\lambda_{i}/2}{\lambda_{i}(\lambda_{i} + \Delta\lambda_{i})} - \frac{1}{\lambda_{th}}\right] \frac{k_{i}(r)}{k(r)},$$
(3.51)

where the summation is done over all wavelength bins and λ_{th} is the threshold wavelength. In case of photoionization, the excess energy is almost entirely converted to kinetic energy of the photoelectrons, giving the photoelectron energy spectrum.

3.5.1 Photo Cross Section and UV Flux Data

The cross sections that are required for calculating the photolytic rates are taken from the PHIDRATES database. The Photo Ionization/Dissociation Rates (PHIDRATES) database, available at https://phidrates.space.swri.edu/#, contains wavelength dependent photolytic cross sections for atomic and molecular species that have been identified or may exist in planetary and cometary atmospheres. This database is based on the publications on solar photorates by Huebner & Carpenter (1979), Huebner et al. (1992) and Huebner & Mukherjee (2015).

The UV flux used to calculate the photolytic rate coefficients is derived from the FISM2 model in the wavelength interval 0.1-190 nm, and the NRLSSI2 model for wavelengths > 190 nm. The datasets (explained below) are available for a heliocentric distance of 1 AU. The scaling to some other heliocentric distance r_h is done by using the multiplicative factor r_h^{-2} .

The LASP Interactive Solar Irradiance Data Center (LISIRD; https://lasp.colorado.edu/lisird/) is a comprehensive set of solar datasets, including the solar spectral irradiance, total solar irradiance, sunspots, and so on. These datasets are compiled in the wavelength range from soft X-ray to near infrared, obtained from models and measurements by various missions, instruments and laboratories.

The Flare Irradiance Spectral Model (FISM) is an empirical model to

estimate variations in the solar ultraviolet irradiance due to solar rotation, solar flares and the solar cycle (Chamberlin et al., 2007, 2008). This model is used to fill the spectral and temporal gaps in measurements of the solar UV radiation, in the wavelength interval 0.1 - 190 nm. Since the release of FISM, several new and improved instruments have been launched for measuring solar irradiance. These include the Solar Stellar Irradiance Comparison Experiment (SOLSTICE; McClintock et al., 2005) and the XUV Photometer System (XPS; Woods et al., 2005) aboard the Solar Radiation and Climate Experiment (SORCE; Rottman, 2005), and the Extreme ultraviolet Variability Experiment (EVE; Woods et al., 2012) onboard the Solar Dynamics Observatory (SDO; Pesnell et al., 2012). Thus, version 2 of FISM, or FISM2 is the updated version of this model that incorporates the new measurements having greater accuracy and higher cadence (Chamberlin et al., 2020). The wavelength ranges of the new base datasets are 0.1 - 6 nm (SORCE/XPS), 6 - 105 nm (SDO/EVE) and 115 - 190nm (SORCE/SOLSTICE).

NRLSSI2 is the daily climate record of the solar spectral irradiance (SSI) from 1882 to the present day, constructed using the solar variability model developed jointly by the Laboratory for Atmospheric and Space Physics (LASP) and the Naval Research Laboratory (NRL) (Coddington et al., 2016). This data record is a part of the National Oceanic and Atmospheric Administration's (NOAA) Climate Data Record (CDR) program. NRLSSI2 uses the irradiance observations from SORCE to compute the solar spectral irradiance.

3.6 Interaction with the Solar Wind

The solar wind can penetrate upto low cometocentric distances in weakly and intermediately active comets, where the contact surface lies close to the nucleus. Ionization of cometary neutrals initiates the solar wind cometary interaction process. Though photoionization is the main source of creation of ions, previous modeling studies have suggested that charge exchange with solar wind protons and electron impact processes also create ions in the cometary environment (for example, Cravens et al., 1987; Benna & Mahaffy, 2007; Rubin et al., 2014; Koenders et al., 2015). Hence, the relevant reactions and their rates are included in the reaction network for weakly and intermediately active comets.

3.6.1 Charge Exchange

One of the processes in the collisional interaction between the cometary environment and the solar wind is charge exchange. H^+ ions in the solar wind undergo charge exchange reactions with neutral target molecules M (such as H₂O, CO, OH and so on) in the coma resulting in the ionization of the neutral molecules and the creation of a neutral hydrogen atom:

$$\mathrm{H}^{+} + \mathrm{M} \to \mathrm{H} + \mathrm{M}^{+}. \tag{3.52}$$

In order to save large computational time and for the sake of simplicity, Koenders et al. (2015) assumed a velocity independent collision rate of the solar wind protons with the cometary neutral gas. A constant collision rate of 10^{-8} cm³ s⁻¹ is used, according to Kriegel et al. (2014).

3.6.2 Electron Impact

Collisional impact of neutral species with solar wind electrons results in the occurence of ionization reactions, as described in Section 2.1.2 of Chapter 2, when the energy of the incident electron exceeds the ionization potential of the neutral species. Assuming a Maxwellian distribution function f(v) (normalized to unity) for solar wind electrons having number density n_e , the ionization frequency R_{sk} for a species s attaining an ionized state k can be calculated as

$$R_{sk} = n_e \int_{v_{sk}}^{\infty} v \sigma_{sk}(v) f(v) 4\pi v^2 dv, \qquad (3.53)$$

where v_{sk} is the velocity corresponding to the ionization potential I_{sk} and σ_{sk} is the cross section. R_{sk} can be multiplied with the neutral species number density n_s to get the ionization rate R_{sk}^* . The Maxwellian distribution function for electrons at a temperature T_e is

$$f(v) = [m_e/2\pi k_B T_e]^{3/2} \exp\{-m_e v^2/2k_B T_e\},$$
(3.54)

where m_e is the electron mass and k_B is the Boltzmann constant. The ionization frequencies R_{sk} for major neutral species found in the cometary atmosphere have been calculated by Cravens et al. (1987) at a number of discrete points for electron temperatures between $10^4 - 10^7$ K. A polynomial fit is obtained to this discrete data set so that the ionization rate at any temperature can be estimated.

3.7 Numerical Approach

The chemical reaction network contains rate coefficients that vary over many orders of magnitude. As a result, the system of differential equations used to model the coma are stiff, and numerical solutions require an implicit/semi-implicit integration method. A set of ordinary differential equations of the first order are given as

$$y'(x) = f(x, y(x)), \quad x \in [x_0, x_n].$$
 (3.55)

The condition for the initial value is prescribed as

$$y_0 = y(x_0). (3.56)$$

The system is said to be autonomous if there is no explicit dependence of f on x, and is non-autonomous otherwise. These equations may be solved by using iterative implicit methods, though this may result in a problem of convergence due to nonlinear implicit equations. Rosenbrock (1963) presented a class of methods, whereby stable formulae were derived by involving the Jacobian matrix. The exact solution of the system of Equations given by 3.55 is denoted by y(t), $x_0 \leq t \leq x_n$. The non-autonomous form of Equation 3.55 can be converted to the autonomous form by adding y'(x) = 1. For an autonomous system and an

exact Jacobian, an s-stage Rosenbrock method is defined as:

$$(I - h\gamma_{ii}J)k_i = hf\left(y_n + \sum_{j=1}^{i-1} \alpha_{ij}k_j\right) + hJ\sum_{j=1}^{i-1} \gamma_{ij}k_j, \quad i = 1, ..., s$$
(3.57)

$$y_{n+1} = y_n + \sum_{j=1}^s b_j k_j, \qquad (3.58)$$

where h > 0 is the stepsize for the integration, α_{ij} , γ_{ij} and b_j are the determining coefficients and $\gamma_{ii} = \gamma$. *I* is the identity matrix, $J = \partial f(x, y) / \partial y$ is the Jacobian matrix and y_n is an approximation to $y(t_n)$ with $t_n = x_0 + nh$. Each k_i is an approximation to some information about the exact solution given by y(t). Comparing Equations 3.15 and 3.55, $x \equiv r, y \equiv n_j$, and

$$\frac{\partial f_{j'}}{\partial n_j} = \frac{1}{v} \frac{\partial N_{j'}}{\partial n_j} - \frac{\delta_{j'j}}{v} \frac{dv}{dr} - \frac{2\delta_{j'j}}{r},\tag{3.59}$$

where j' and j run over all the species, and $\delta_{j'j}$ is the Kronecker delta. The Jacobian matrix is written as:

$$J = \frac{\partial(f_1, \cdots, f_m)}{\partial(n_1, \cdots, n_m)} = \begin{pmatrix} \frac{\partial f_1}{\partial n_1} & \frac{\partial f_1}{\partial n_2} & \cdots & \frac{\partial f_1}{\partial n_m} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_m}{\partial n_1} & \frac{\partial f_m}{\partial n_2} & \cdots & \frac{\partial f_m}{\partial n_m} \end{pmatrix}$$
(3.60)

where the subscript m denotes the total number of species in the network.

The fourth-order Rosenbrock method is used to arrive at a solution for the number densities, the differential equations for which are the set of Equations given by 3.15. The first practical application of Rosenbrock methods was done by Kaps & Rentrop (1979), so they are also known as Kaps-Rentrop methods. The Fortran stiff integrator based on the Kaps-Rentrop algorithm is adopted as the numerical scheme (Press et al., 1992).

Chapter 4

Study of the Interstellar Comet 2I/Borisov

The modeling studies of the first interstellar comet 2I/Borisov, done as part of this thesis work, is discussed in this chapter. The large CO abundance of 2I/Borisov can potentially alter the physical and chemical properties of the coma, as compared to a typical water dominated Solar System comet. The modeling results of 2I/Borisov are presented, along with a comparison of the coma properties with a Solar System comet of the Halley-type composition.

Comet 2I/Borisov was discovered by G. Borisov on 30 August 2019 UT, when it was at a heliocentric distance of about 3 AU. This was the second interstellar object to have been discovered in the Solar System, after 1I/'Oumuamua. It exhibited comet-like activity and outgassing at the time of its discovery, and was observable for many months. This was quite different from 1I/'Oumuamua, which was a considerably fainter object and observable only for a few weeks, without showing any detectable quantities of gas and dust ('Oumuamua ISSI Team et al., 2019). Initial physical characterization of 2I/Borisov revealed it to have a very high hyperbolic excess velocity of $-33.8^{+0.6}_{-0.5}$ km s⁻¹, which was calculated by de León et al. (2019) using the prescription given by de la Fuente Marcos & de la Fuente Marcos (2019). A high orbital eccentricity of 3.38 ± 0.02 , and an orbital inclination of $44.00 \pm 0.04^{\circ}$ was also calculated for 2I/Borisov (Guzik et al., 2020). Since this comet was traveling at a large angle from the ecliptic plane, gravitational perturbations from the giant planets could not account for the strongly hyperbolic orbit, and the only likely explanation was its arrival from outside the Solar System. It crossed perihelion on 8 December 2019 UT at a heliocentric distance of 2.006 AU (Jewitt et al., 2020).



Figure 4.1: Volatile production rates for the interstellar comet 2I/Borisov. The uncertainties in measurements are shown by the vertical error bars, while the downward pointing arrows indicate upper limits on the measurements. Reference: Fitzsimmons et al., 2019 (CN, C₂); Opitom et al., 2019 (H₂O, CN, C₂, C₃); Bannister et al., 2020 (CN, C₂, NH₂); Bodewits et al., 2020 (H₂O, CO); Cordiner et al., 2020 (CO, HCN, CH₃OH, CS); de León et al., 2020 (CN, C₂); Lin et al., 2020 (CN, C₂, C₃); Kareta et al., 2020 (CN, C₂); McKay et al., 2020 (H₂O); Xing et al., 2020 (H₂O); Aravind et al., 2021 (CN, C₂, C₃); Opitom et al., 2021 (H₂O).
4.1 Observations of 2I/Borisov

Figure 4.1 shows the volatile production rates of comet 2I/Borisov, obtained from measurements by various remote observation facilities. Based on OH measurements, water production rates are reported by Opitom et al. (2019) from observations obtained using the 4.2 m William Herschel Telescope (WHT), by Xing et al. (2020) from observations acquired from the UltraViolet/Optical Telescope (UVOT) on the Neil Gehrels Swift Observatory, and by Opitom et al. (2021) from observations made by the Ultraviolet-Visual Echelle Spectrograph (UVES) mounted on the ESO 8.2 m Very Large Telescope (VLT). In addition, McKay et al. (2020) report on the water production rates derived from measuring the [O I] 6300 Å line observed by the ARCES instrument at Apache Point Observatory. The peak value of the water production rate $(Q_{\rm H_2O})$ of 2I/Borisov is $10.7 \pm 1.2 \times 10^{26}$ mol s⁻¹. Xing et al. (2020) compared the temporal evolution of the water production rate of 2I/Borisov and found that before perihelion, the rate of increase of $Q_{\rm H_2O}$ with heliocentric distance is greater than that in the dynamically new comets reported by Combi et al. (2018). Post perihelion, the decrease is faster than all the previously detected comets reported by Combi et al. (2018). An empirical relation for the water production rate (in mol s^{-1}) was derived by Bodewits et al. (2020), which is given by Equations 4.1 and 4.2, for pre-perihelion and post-perihelion periods respectively.

$$Q_{\rm H_{2O}} = 1.77 \times 10^{23} \times \Delta T^2 + 2.01 \times 10^{25} \times \Delta T + 1.2 \times 10^{27}, \qquad (4.1)$$

$$Q_{\rm H_{2}O} = \exp(62.42184 - 0.0964962 \times \Delta T), \tag{4.2}$$

where ΔT is the number of days from perihelion, which is negative for preperihelion and positive for post-perihelion.

CO abundances of 2I/Borisov are reported by Bodewits et al. (2020), measured using the Cosmic Origins Spectrograph (COS) on the Hubble Space Telescope (HST), and by Cordiner et al. (2020) from observations obtained by the Atacama Large Millimeter/submillimeter Array (ALMA). From these measurements, the CO production rate is found to be between $4.4 \pm 0.7 \times 10^{26}$ mol s^{-1} and $10.7 \pm 6.4 \times 10^{26}$ mol s⁻¹. The measured CO/H₂O ratio lies in the range 35 - 105% (Cordiner et al., 2020), but can also be as high as 173% (Bodewits et al., 2020). The relative abundance of CO with respect to water in Solar System comets is found to lie in the range $\sim 0.2 - 23\%$ (Bockelée-Morvan & Biver, 2017), while the average abundance is $\sim 5\%$ (Dello Russo et al., 2016a). Thus 2I/Borisov is significantly rich in CO, with an unusually high CO abundance than has been measured in any Solar System comet that reached a heliocentric distance < 2.5 AU.

Besides H₂O and CO, the abundances of HCN, CN, C₂, and NH₂ are also measured conclusively. The relative abundance of HCN with respect to water is in the range of 0.06 – 0.16% (Cordiner et al., 2020), which is similar to an average abundance of 0.12% observed in typical Solar System comets (Bockelée-Morvan & Biver, 2017). The CN production rate from various observations lies in between $1.6 \pm 0.5 \times 10^{24}$ mol s⁻¹ to $9.5 \pm 0.2 \times 10^{24}$ mol s⁻¹ (Fitzsimmons et al., 2019; Opitom et al., 2019; de León et al., 2020; Kareta et al., 2020; Aravind et al., 2021). The C₂ production rate (Q_{C_2}) was reported to be 1.1×10^{24} mol s⁻¹ by Bannister et al. (2020), while Lin et al. (2020) reported a value of $5.5 \pm$ 0.4×10^{23} mol s⁻¹, and a number of other authors provide an upper limit for Q_{C_2} (Fitzsimmons et al., 2019; Opitom et al., 2019; de León et al., 2020; Kareta et al., 2020). A power-law variation of Q_{C_2} as a function of the heliocentric distance r_h was fitted by Lin et al. (2020), such that its slope is given by

$$\gamma = \frac{\log Q(r_{h_1}) - \log Q(r_{h_0})}{\log r_{h_1} - \log r_{h_0}}.$$
(4.3)

The slope γ is found to be steeper than that of other Solar System comets, suggesting that the production of C₂ may be comparatively more sensitive to changes in the heliocentric distance. In addition it is found that in terms of the C₂ abundance, 2I/Borisov is carbon-chain depleted (Bannister et al., 2020), according to the definition given by A'Hearn et al. (1995). NH₂ was measured by Bannister et al. (2020) with a production rate of 4.8×10^{24} mol s⁻¹, and 2I/Borisov was found to be enriched in NH₂ as compared to the bulk of Solar System comets. Upper limits for the C₃ production rate are estimated by Opitom et al. (2019) and Lin et al. (2020). Cordiner et al. (2020) report on the upper limits for the production of CH_3OH and CS, which are consistent with previously reported abundances of these volatiles in Solar System comets (Bockelée-Morvan & Biver, 2017).

4.2 Model Inputs

The coma of 2I/Borisov is modeled at a heliocentric distance of 2.01 AU postperihelion, that was achieved on 15–16 December 2019 UT. Cordiner et al. (2020) report on the production rates of several volatiles derived from observations made on these dates. There are several other volatiles whose production rates are not available for these dates. In these cases, either the production rates derived from observations made on other dates are used, or the production rate is estimated from some fitted relation. Additional model runs are also obtained for a typical Solar System comet, namely comet 1P/Halley, for comparing the properties of the coma of the interstellar comet as opposed to the Solar System comet. The input conditions for the model runs are described in this section.

4.2.1 Input Volatile Production Rate of 2I/Borisov

The molecular production rates for the different volatiles that are used as the initial inputs in the gas phase coma model for 2I/Borisov are given in Table 4.1. The CO production rate ($Q_{\rm CO}$) is derived by Cordiner et al. (2020) as $Q_{\rm CO} = (4.4 \pm 0.7) \times 10^{26}$ mol s⁻¹ from the interferometric spectra and $Q_{\rm CO} = (5.0 \pm 0.5) \times 10^{26}$ mol s⁻¹ using the autocorrelation (total power) spectra. Bodewits et al. (2020) report $Q_{\rm CO} = (6.4 \pm 1.4) \times 10^{26}$ mol s⁻¹ for the observational epoch 19 – 22 December 2019 UT. A conservative value of $Q_{\rm CO} = 5.0 \times 10^{26}$ mol s⁻¹ is used, and this is within the measured error limits. The empirical fitting derived by Bodewits et al. (2020) for $Q_{\rm H_{2O}}$ post-perihelion (Equation 4.2) is used to estimate the water production rate around 15 December 2019.

The production rate of HCN and the upper limit on the production rates of CS as obtained by Cordiner et al. (2020) are used as the initial values for these species. The initial abundance of CH₃OH is taken to be 2% of H₂O. This is a conservative value, which is roughly the average abundance of CH₃OH with respect to H₂O in Solar System comets (Dello Russo et al., 2016a). Using the relation for the power law variation of Q_{C_2} (Equation 4.3), and $Q_{C_2} = (5.5 \pm 0.4) \times 10^{23}$ mol s⁻¹ at 2.145 AU (Lin et al., 2020), Q_{C_2} is calculated at 2.01 AU for the model run. The production rate of NH₂ was estimated by Bannister et al. (2020) from observations made in late November 2020 at a distance of 2.03 AU pre-perihelion, and the reported value is used as the model input for the initial production rate of NH₂.

CS, C_2 and NH₂ are product species that are formed in the coma directly or indirectly by the photodissociation of parent species. The CS radical is most likely to trace the parent molecule CS₂ (Bockelée-Morvan et al., 2004). C₂ may be produced from several sources, though the photodissociation chain $C_2H_2 \rightarrow$ $C_2H \rightarrow C_2$, producing C₂ as a granddaughter species, is suggested to be the most likely one (Jackson et al., 1996; Sorkhabi et al., 1997; Feldman et al., 2004). The most probable candidate for the formation of NH₂ in comets is the short lived parent species NH₃, and the abundance of NH₂ is a direct measurement of the NH₃ abundance (Wyckoff et al., 1989). NH₃ is also likely to be present in the form of ammonium salts, though these salts sublimate only at low heliocentric distances < 0.5 AU (Altwegg et al., 2020). The initial production rates of CS, C₂ and NH₂ are converted into their respective parent species abundances, as suggested by Fink & Disanti (1990), from the photodissociation branching ratios given by Huebner & Mukherjee (2015).

4.2.2 Inputs: Volatile Abundance of H_2O -Rich Comet and Nucleus Size

The abundance percentage of volatiles with respect to H₂O for comet 1P/Halley near perihelion, as compiled by Bockelée-Morvan et al. (2004), is listed in Table 4.2. Using a net gas production rate of $Q = 10^{29}$ mol s⁻¹ from the nucleus, these abundances are converted to production rates, and used as inputs to model the Halley-type comet.

Species	Production rate (mol s^{-1})
H ₂ O	5.4×10^{26}
CO	5.0×10^{26}
HCN	7.0×10^{23}
CS_2^\dagger	6.5×10^{23}
CH ₃ OH	1.1×10^{25}
$C_2 H_2^{\dagger}$	3.0×10^{23}
$\mathrm{NH_3}^\dagger$	5.0×10^{24}

Table 4.1: Input volatile production rates used as model inputs for 2I/Borisov at 2.01 AU. The production rates for CS_2 , C_2H_2 and NH_3 are calculated from the photodissociation branching ratios of their respective product species.

Species	Relative Abundance (%)
CO	3.5
CO_2	3
CH_4	0.8
C_2H_2	0.3
C_2H_6	0.4
CH ₃ OH	1.8
H ₂ CO	4
NH ₃	1.5
HCN	0.1
H_2S	0.4
CS_2	0.2

Table 4.2: Relative abundance percentage with respect to water, for the Solar System comet 1P/Halley (Bockelée-Morvan et al., 2004).

Several estimates on the size of the nucleus of 2I/Borisov are available in literature. Lee et al. (2020) used infrared imaging to infer an upper limit of 0.58 km for the radius r_n of the nucleus of 2I/Borisov. Assuming an albedo of 0.04, Jewitt et al. (2020) constrained the radius to be ≤ 0.5 km from the surface brightness profile measurements, obtained from HST. Guzik et al. (2020) estimated $r_n \sim 1$ km from the observed water production rate and an active fraction of 30%. A value of 1 km is assumed as the radius of the nucleus of 2I/Borisov, in the present model. The model is also tested for few other sizes of 2I/Borisov, in the range $\sim 0.5 - 1$ km, while keeping other input parameters constant, and no significant changes in the results are seen. The radius of the nucleus of the Halley-type comet is assumed to be 2.5 km, since several modeling studies on 1P/Halley have assumed this value (Marconi & Mendis, 1983, 1986).

In order to derive the photolytic rates, the daily average solar spectral irradiance, as given by the FISM2 and NRLSSI2 flux models, are collected for the entire month of December 2019, from the LISIRD database. These are used to find the average spectral fluxes for December 2019, scaled to a heliocentric distance of 2.01 AU. These scaled fluxes are used to derive the photorates as described in Section 3.5.

4.3 Results

The model is run for two different comets: (a) comet 2I/Borisov, and (b) Halleytype comet, with input parameters as described in the previous section. The results of the model runs are shown in this section.

4.3.1 Temperature Profile

The temperature profiles, i.e. the variation of the temperature of the neutral, electron, and ion fluids with cometocentric distance, for 2I/Borisov and Halley-type comet are shown in Figure 4.2. The major heating and cooling rates per unit volume for the neutral and electron fluid are shown in Figure 4.3. The neutral temperature profiles shown in Figure 4.2(a) and Figure 4.2(b) are qualitatively alike, with an initial dip and then a temperature inversion at a cometocentric distance ~ 200 km. However, the neutral fluid temperature near inversion for 2I/Borisov is ~ 6 K, which is lower in comparison with an inversion temperature ~ 18 K for the Halley-type comet. In fact, it is to be noted that the neutral comet, for all cometocentric distances. This is because the heating rate per unit volume of the neutral fluid due to chemical reactions is higher in the Halley-type comet, as seen from Figure 4.3. Photodissociation is one of the primary chemical reaction mechanisms which heat the neutral fluid. The main branch for the



Figure 4.2: Temperature profiles for (a) comet 2I/Borisov and (b) Halley-type comet. T_n , T_e and T_i denote the temperatures of the neutral, electron and ion fluids respectively.

photodissociation of H_2O into OH and H generates 3.41 eV of energy, while the photodissociation of CO to form C and O produces 2.56 eV of energy (Huebner & Mukherjee, 2015). Additionally, the branching ratio for the production of OH from H_2O is nearly 85% while it is ~ 50% for the production of C and O from CO, and the dissociation rate of H_2O is also higher. Thus, the net rate of heat energy released per unit volume due to photodissociation is higher in the Halley-type comet because of a greater relative abundance of H_2O . Besides, the higher production rate of the Halley-type comet results in higher coma density and more number of molecules that undergo photodissociation. This causes the net heating rate of the neutral fluid per unit volume from chemical reactions to be larger.

It is seen that there exists an initial coupling between the electron and neutral temperatures. This coupling is relatively weak for 2I/Borisov, and the electron and neutral temperatures decouple at a shorter distance (~ 20 km) from the nucleus, as compared to the Halley-type comet. This coupling is due to inelastic collisions between the electrons and the water molecules, leading to rotational excitation of the water molecules. The energy exchange rate per unit volume due to collisional scattering depends on the collision cross section as well



Figure 4.3: Variation of the heating and cooling rates per unit volume for the neutral and electron fluids for (a) comet 2I/Borisov and (b) Halley-type comet. The labels 'Chem-n' and 'Chem-e' denote the net energy gained due to chemical reactions by the neutral and electron fluids, respectively. The other labels denote the energy lost by the electrons due to elastic scattering from H₂O and CO molecules ('e-H₂O elas' and 'e-CO elas') and inelastic scattering from H₂O and CO molecules leading to the rotational and vibrational excitation of H₂O and the vibrational excitation of CO ('e-H₂O rot', 'e-H₂O vib' and 'e-CO vib').

as the number densities of the colliding species. The lower coma density for 2I/Borisov implies that the frequency of such collisions is reduced. In addition, the dominant neutral species in the coma of the Halley-type comet is H_2O , while 2I/Borisov has nearly equal abundances of both H_2O and CO. This means that the relative number of H_2O molecules available for rotational excitation is lesser in the interstellar comet. Therefore, the rate of energy exchange between the neutral and electron fluids is reduced in the innermost coma regions of 2I/Borisov when compared to that of the Halley-type comet, as can be seen from Figure 4.3. Hence, the electron fluid loses less of its energy to the neutral fluid in 2I/Borisov, and its temperature decouples closer to the nucleus. In the outer part of the coma, the electron temperature is high and the dominant cooling mechanism for electrons in this region is inelastic scattering with H_2O and CO molecules, resulting in their vibrational excitation. It is seen from Figure 4.3 that while the cooling of electrons due to vibrational excitation of CO is comparable to or even higher than water for 2I/Borisov, it is lesser in the Halley-type comet

by atleast an order of magnitude. This is again due to the dependence of the cooling rate on the collisional cross section and the abundances of the colliding species. The vibrational excitation cross section of CO is generally higher than that of H_2O (Itikawa & Mason, 2005; Itikawa, 2015), while the abundance of H_2O and CO molecules is similar in 2I/Borisov. This results in a higher cooling rate of the electrons due to vibrational excitation collisions with CO as compared to H_2O , in 2I/Borisov. On the other hand, the Halley-type comet has a dominant H_2O abundance, resulting in a higher electron cooling rate due to vibrational excitation of H_2O as compared to CO. Finally, it is also seen from Figure 4.3 that the energy loss rate per unit volume for electrons due to elastic scattering from the neutral species is several orders of magnitude less than the loss due to inelastic collisions, due to lower elastic scattering cross sections.

4.3.2 Coma Chemistry

2I/Borisov is unique in the sense that it contains H₂O and CO in nearly equal proportions. This has a considerable bearing on the coma composition and chemistry, including the abundances of ionic species.

4.3.2.1 Species Abundances

The variation of the flux of parent volatiles, electrons and assorted ions, as a function of cometocentric distance in 2I/Borisov, is shown in Figure 4.4. The flux is calculated as $4\pi r^2 vn$, where r is the cometocentric distance, v is the velocity and n is the species number density. Plotting the flux removes the r^{-2} dependence of the number density, and a rise or fall in the flux of any particular species indicates its creation or destruction by chemical reactions.

 $\rm H_2O$ and CO together account for nearly 99% of the outgassing from the nucleus. Most of the parent species survive up to 10^5 km, which is consistent with an outflow velocity of ~ 1 km s⁻¹ and an average photolytic reaction rate $\leq 10^{-5}$ s⁻¹, leading to nearly constant flux of the parent volatiles throughout the modeled region of the coma. Exceptions to this are NH₃ and CS₂, which are destroyed by photolytic processes at a higher rate. It is also to be noted

that since the number density is low, optical depth effects are nearly absent in the coma. Thus, the rates for the photolytic processes remain nearly constant throughout the entire region of the coma.

The ions H_3O^+ , HCO^+ , NH_4^+ , $HCNH^+$ and $CH_3OH_2^+$ that are formed by the protonation of the parent species, show an initial sharp rise in their fluxes, as they form rapidly. The curves gradually become flatter on moving outwards in the coma, since the timescale for the formation of these species becomes more than the dynamical timescale, as the density of the coma decreases at large distances. The flux of ions formed by the photoionization or photodissociative



Figure 4.4: Variation of the flux of (a) parent volatiles, and (b), (c), (d) electrons and assorted ions, with cometocentric distance in 2I/Borisov.

ionization of parent species keeps rising in the outer coma as well, since photolytic processes continue to occur even in the outer regions.

4.3.2.2 CO⁺ and HCO⁺

The variation of the flux of the ions $\rm CO^+$ and $\rm HCO^+$ with cometocentric distance, in 2I/Borisov is shown in Figure 4.4(b). The major gas phase formation and destruction mechanisms of these two ions are shown in Figure 4.5. The most important mechanism that creates $\rm CO^+$ in the coma is the photoionization of CO. As can be seen from Figure 4.5(a), the relative rate of this process is ~ 100%. implying that nearly all of the $\rm CO^+$ is created by this process. $\rm CO^+$ is destroyed in the coma either through charge exchange or bimolecular reactions with neutral species. The destruction of $\rm CO^+$ by H₂O takes place via two channels, and the sum of these two channels accounts for up to 99% of the total loss rate of $\rm CO^+$ up to ~ 5000 km. Beyond this distance, destruction by dissociative recombination increases on moving outwards, changing from ~ 1% at 5000 km, to > 20% in the outermost regions.

 $\rm HCO^+$ forms when CO undergoes protonation, and also when H₂O undergoes bimolecular reactions with ions such as CO⁺ and C⁺. The relative contribution to $\rm HCO^+$ formation by protonation reactions is slightly more than bimolecular reactions up to 500 km; the trend reverses beyond this distance. Photodissociative ionization of H₂CO also creates $\rm HCO^+$ ions, and the rate for this process rises sharply beyond ~ 1000 km. In the region of the coma > 10⁴ km, the relative contribution to the creation of $\rm HCO^+$ from ion-neutral reactions falls, and the photo-process contributes to most of the $\rm HCO^+$ ion formation. $\rm HCO^+$ is destroyed in the coma by proton transfer reactions with the parent species H₂O, CH₃OH and NH₃, and by dissociative recombination. As in the case of CO⁺, the relative dissociative recombination reaction rates become important in the outer regions, accounting for up to 10% of the loss rate.

The presence of a large amount of CO in 2I/Borisov results in high abundance of these two ions. A higher CO abundance implies that the density of CO^+ ions will also be higher. HCO⁺ forms by the reactions that involve CO molecules and CO⁺ ions as the reacting species, and its resultant abundance is also larger.



Figure 4.5: Major formation (solid lines) and destruction (dashed/dotted lines) pathways of (a) CO^+ (b) HCO^+ , in 2I/Borisov.

4.3.2.3 H_2O^+ and H_3O^+

The variation of the flux of the ions H_2O^+ and H_3O^+ with cometocentric distance is shown in Figure 4.4(b) and their major formation and destruction pathways are shown in Figure 4.6. H_2O^+ is produced by the photoionization of H_2O , and by charge exchange reactions of H_2O with ions present in the coma. CO^+ is the most abundant ion with which H_2O undergoes charge exchange, and this reaction accounts for 30 - 35% of the net production of H_2O^+ within 100 km. Other ions with which H_2O undergoes charge exchange include OH^+ , H^+ and O^+ , and their combined relative contribution towards the formation of H_2O^+ is < 10% within 100 km, and reduces on moving further outwards, as indicated by the line labeled ' H_2O + ion \rightarrow neutral + H_2O^+ ' in Figure 4.6(a). H_2O^+ is mainly destroyed when it participates in proton transfer reactions with H_2O and CO, and also with OH beyond ~ 500 km. As with CO^+ and HCO^+ , dissociative recombination reactions become steadily more important, and their contribution to the loss of H_2O^+ can rise up to 20 - 25% in the outer regions.

 $\rm H_3O^+$ is one of the more abundant ions in the coma, and it forms mostly by the protonation of H₂O by ions such as H₂O⁺, HCO⁺ and OH⁺. The ionneutral reaction of OH radicals with H₂O⁺ ions can form up to ~ 10% of H₃O⁺ in the outer coma regions. Proton transfer reactions of H₃O⁺ with the parent species CH₃OH, NH₃ and HCN account for most of the loss of H₃O⁺ within ~ 10³ km. The relative rate for the destruction of H₃O⁺ by dissociative recombination is much more than that of other ions such as H₂O⁺, HCO⁺ and CO⁺. In the outer regions beyond 10⁴ km, proton transfer reactions lose importance, and dissociative recombination is the most efficient loss mechanism for H₃O⁺.

4.3.2.4 N-bearing ions

The variation of flux as a function of cometocentric distance for major N-bearing ionic species is shown in Figure 4.4(c) and the reaction pathways in Figure 4.7. Most of the NH_2^+ in the coma is formed by the photodissociative ionization of NH₃, and a very small amount ~ 2% by charge exchange reactions between NH₂ and abundant ions such as H₂O⁺, CO⁺ and OH⁺. NH₃⁺ is formed by the photoionization of NH₃ and the charge exchange of NH₃ with ions (mainly CO⁺ and H₂O⁺). Photoionization and charge exchange contribute nearly equally to NH₃⁺ ion formation near the nucleus, but beyond 50 km, the charge exchange reaction rates begin to fall. The destruction of both NH₂⁺ and NH₃⁺ is primarily



Figure 4.6: Major formation (solid lines) and destruction (dashed/dotted lines) pathways of (a) H_2O^+ (b) H_3O^+ , in 2I/Borisov.

caused by H_2O molecules. NH_2^+ reacts with H_2O via multiple branches, and the most dominant of these branches is proton transfer, leading to the formation of the protonated species H_3O^+ . NH_2^+ also reacts with H_2O at slower rates to form

 NH_3^+ and NH_4^+ ions. NH_3^+ reacts with H_2O , and also with NH_3 and OH to form NH_4^+ . Similar to previously discussed ions, dissociative recombination rates of NH_2^+ and NH_3^+ increase on moving outwards in the coma.

Since NH_3 has a higher proton affinity, it undergoes proton transfer reaction with many of the ions such as H_3O^+ , H_2O^+ and HCO^+ , accepting H^+ ions to form NH_4^+ . Apart from this, neutral species (mainly H_2O and NH_3) undergo bimolecular reactions with NH_3^+ , and form NH_4^+ by breaking of the hydrogen bond. NH_4^+ is mainly destroyed by dissociative recombination, that proceeds via three channels.

 $\rm HCN^+$ forms by the photoionization of the parent molecule HCN and is destroyed by proton transfer and charge exchange reactions with the parent species CO and H₂O. HCN undergoes protonation by ions such as H₃O⁺, H₂O⁺ and HCO⁺ to form HCNH⁺, and HCNH⁺ then successively causes protonation of the neutral molecules H₂O, NH₃ and H₂CO.

4.3.2.5 Complex ions

The flux of assorted bigger organic ions is shown in Figure 4.4(d). CH_3OH^+ and H_2COH^+ are mainly formed by the photoionization and photodissociative ionization of CH_3OH , and small quantities of these ions are also formed when CH_3OH respectively undergoes charge exchange and ion-neutral bimolecular reactions with the atomic ions H^+ , C^+ , O^+ and N^+ . $CH_3OH_2^+$ is formed by the protonation of CH_3OH by the ions HCO^+ and H_3O^+ . $CH_3OCH_4^+$ forms when a methyl cation transfer takes place from $CH_3OH_2^+$ to CH_3OH . H_2CO^+ is a product of photoionization and photodissociative ionization undergone by H_2CO and CH_3OH respectively.

The major loss mechanisms for CH_3OH^+ , $CH_3OH_2^+$ and $CH_3OCH_4^+$ are dissociative recombination reactions. The major loss mechanism for both H_2CO^+ and H_2COH^+ are proton transfer reactions with H_2O , while dissociative recombination reactions also destroy these two ions in the outer regions.



Figure 4.7: Major formation (solid lines) and destruction (dashed/dotted lines) pathways of (a) $\rm NH_2^+$ (b) $\rm NH_3^+$ (c) $\rm NH_4^+$, in 2I/Borisov.

4.4 Discussions

The focus of previous hydrodynamical and chemical models has been to study cometary comae dominated by H_2O outgassing from the nucleus, though there have been few model studies for CO-dominated coma, for example, Ip & Mendis (1977); Crifo et al. (1999); Raghuram et al. (2021). In this section, the differences seen in the modeled coma of 2I/Borisov is discussed, as compared to waterdominated Solar System comets.

4.4.1 Effect of CO Abundance on Energy Exchange Rates

The electrons that are created due to photoionization and photodissociative ionization processes gain most of the excess energy released from the corresponding photochemical reaction because of their lighter mass. A dominant heat loss mechanism for electrons is inelastic scattering from neutral species, leading to the excitation of the neutrals to higher rotational and vibrational energy levels. H₂O is a highly polar molecule and in a water dominated coma, inelastic scattering from this molecule is the primary reason for cooling of the electron fluid. Previous hydrodynamical models have only considered electron cooling due to water molecules because of lesser abundance of other neutral species and high $e^- - H_2O$ collision cross section. In the case of the interstellar comet 2I/Borisov, where the CO abundance can be as high as or even higher than the H₂O abundance, $e^- - CO$ inelastic collision cannot be ignored. It is shown in the present work that in the high electron temperature and lower density region of the coma, $e^- - CO$ vibrational collisions are an important cooling mechanism.

Electron-neutral temperature coupling exists up to some distance from the nucleus because the energetic photoelectrons efficiently lose their energy to the neutral fluid by rotationally exciting water molecules. This coupling that is observed in a water-dominated coma is also seen in the interstellar comet, though the coupling is weaker because of reduced density, resulting from lower production rate. The presence of a large amount of CO also reduces the net relative abundance of H_2O , thereby reducing the cooling efficiency. If the CO abundance is increased even more, e.g. in comet C/2016 R2 (Biver et al., 2018; Wierzchos & Womack, 2018; McKay et al., 2019), coupling may be lost altogether. However, it should be kept in mind that only the vibrational excitation of CO (due to $e^- - CO$ inelastic collisions) is considered, and the rotational excitation of CO resulting from $e^- - CO$ inelastic collisions has not been considered in the present model. Since the $e^- - CO$ collision cross section for rotational excitation is nearly four orders of magnitude less than that of $e^- - H_2O$ collision, the net effect of including rotational excitation of CO may cause only a fractional change in the temperature profile of 2I/Borisov.

4.4.2 Effect of CO Abundance on Reaction Rates

Many types of chemical reactions occur in the coma, but two particularly important processes that drive ion chemistry in the coma in terms of creating new ions are photolytic reactions and proton transfer reactions. The dominant ions in the coma are the protonated parent species, and the products of photoionization and photodissociative ionization of the parent molecules. The protonated molecules are more abundant within ~ 100 km, while the abundance of ions created as photo products takes over in the outer regions. The abundant ions H_3O^+ and HCO^+ , formed by the protonation of H_2O and CO, in turn cause protonation of other parent species to produce other ions namely NH_4^+ , $HCNH^+$ and $CH_3OH_2^+$. Hence, an important feature of the coma chemistry is a protonation "chain" whereby successive protonated species are created.

Ions in the coma undergo dissociative recombination reactions, which are dependent on the temperature of the electrons. The rates for these reactions are determined by Equation 2.27 (see Chapter 2), where T is the electron temperature and typically, the parameters $\beta \sim -0.5$ and $\gamma = 0$. Thus, these reaction rates decrease with an increase in the electron temperature and vice versa. From Figures 4.5 - 4.7, it is seen that all the dissociative recombination reaction rates show an inversion at ~ 30 km, and the relative loss of ions by these processes slows down sharply. This happens because there is an electron temperature inversion, followed by a sudden increase in the electron temperature at this distance. The primary mechanism by which electrons lose heat in the coma is due to in-

elastic collisions with the neutral species. The electron temperature decouples from the neutral temperature once the frequency of such collisions is reduced (Section 4.3.1). Subsequently, the heating rate of the electrons per unit volume due to chemical reactions becomes more than the cooling rate, resulting in the temperature inversion. On moving outward in the coma, the relative rates of the dissociative recombination reactions again increase, due to the continuous increase in the flux of photoelectrons. This inversion in the dissociative recombination rate is also seen in the Halley-type comet, though it occurs further out from the nucleus, at a distance ~ 1300 km, due to the delay in the electron fluid decoupling and temperature inversion. Besides, the relative reaction rates reduce at most by a factor of 2 in the Halley-type comet, whereas they can reduce by up to a factor of 4 in the interstellar comet. The reduction in the rate coefficients is compensated by the enhanced electron flux, resulting in a lower net reduction for the Halley-type comet. The rates at which the chemical reactions occur in the coma depend on a host of factors such as the temperature dependence of the reaction rates, the availability of the reacting species and the optical depth effects (for photochemical reactions). In general, it is seen that the relative rates for the reactions involved in forming or destroying a particular species do not necessarily stay constant throughout. The dominant process by which a species is created or destroyed gets altered in different regions of the coma.

4.4.3 Effect of CO Abundance on Ionic Composition

The production of H_2O^+ ions generally occurs by the photoionization of H_2O in water dominated comets. However for 2I/Borisov, which has a large amount of CO, the CO⁺ abundance is high and charge exchange of H_2O with CO⁺ is also an important formation mechanism of H_2O^+ . A large amount of HCO⁺ is also present in the modeled coma of 2I/Borisov because of high CO and CO⁺ abundance. Such high quantities of HCO⁺ would not be seen in water dominated comets because of lesser amount of CO. HCO⁺ is an important ion that causes protonation of neutral species. The approximate contribution of HCO⁺ to the formation rate of H_3O^+ , NH_4^+ and $CH_3OH_2^+$ is up to 30-40%, ~ 5% and up to 20% respectively.

The flux profiles of H_2O^+ and CO^+ ions for comet 2I/Borisov are nearly alike and this can be explained as follows. These two ions are primarily produced by photoionization at similar rates. In terms of loss processes, H_2O^+ is destroyed mainly by proton transfer reactions with H_2O and CO while CO⁺ is destroyed by charge exchange and ion-neutral reactions with H_2O . The Arrhenius rate coefficients (Equation 2.27) for the loss processes of H_2O^+ and CO⁺ are similar. The production and loss rates also depend on the number densities of H_2O and CO, which again, are almost alike.

4.4.4 Effect of CO Abundance on Organic Composition

CH₃OH is not conclusively detected in 2I/Borisov, and an upper limit of 4.4×10^{26} mol s⁻¹ is reported on its production rate (Cordiner et al., 2020). Laboratory studies on low temperature ices have demonstrated that the successive hydrogenation of CO can lead to the formation CH₃OH in CO-rich ices, while H₂CO forms as an intermediate product (Hiraoka et al., 1994; Watanabe & Kouchi, 2002; Fuchs et al., 2009). Thus, CH₃OH is quite likely to be present in the CO-rich icey nucleus of 2I/Borisov, though it was not conclusively detected possibly due to lower activity. Since 2I/Borisov shows similarities to other Solar System comets in terms of the composition of some of the volatiles, the initial CH₃OH abundance with respect to H₂O in the coma model of 2I/Borisov is taken to be 2% (Table 4.1), which is the average value estimated by Dello Russo et al. (2016a) for Solar System comets.

To investigate the effect of large CO outgassing from the nucleus, as in the case of 2I/Borisov, on the abundances of different species created in the coma, two additional models are run for a 2I-type comet composition. In the first model, the input volatile production rates given in Table 4.1 is multiplied by a factor of 10^2 , so that the net gas production rate from the nucleus is $\sim 10^{29}$ mol s⁻¹. This aids in comparing the abundances to the Halley-type comet that also has a similar production rate, but the outgassing is dominated by H₂O. The hydrogenation of CO ices may form some amount of H₂CO as an intermediate product. Thus,



Figure 4.8: Flux of large organic ions and neutrals for 2I-type (solid lines) and Halley-type abundances (dashed lines). The species show (a) higher abundance for the 2I-type composition (b) nearly equal abundances, and (c) higher abundance for the Halley-type composition, while (d) shows the abundances of species when H_2CO is added to the 2I-type comet composition.

in the second model of the 2I-type composition, the volatile abundances have a higher production rate (i.e., net outgassing ~ 10^{29} mol s⁻¹), and H₂CO is added as a parent volatile. The relative abundance of H₂CO with respect to H₂O is taken to be 4% for this model, which is also the H₂CO abundance in the Halley-type comet composition.

Figure 4.8 shows the flux variation of some of the larger organic ions and neutrals for the 2I-type and Halley-type cometary compositions. The species shown in Figure 4.8(a) exhibit higher abundance in the coma for the 2I-type comet as compared to the Halley-type comet, by nearly one order of magnitude. This can be understood from the reaction pathways discussed previously. $CH_3OH_2^+$ forms when H_3O^+ and HCO^+ ions cause protonation of CH_3OH . There is considerably higher abundance of HCO^+ ions in the coma of the 2I-type comet as opposed to the Halley-type comet, which increases the net protonation reaction rate of CH_3OH and results in a higher $CH_3OH_2^+$ abundance. An increased density of $CH_3OH_2^+$ will result in a higher abundance of $CH_3OCH_4^+$ (formed by methyl cation transfer from $CH_3OH_2^+$ to CH_3OH). Dissociative recombination of $CH_3OCH_4^+$ then leads to the formation of CH_3OCH_3 . The radiative association of H_2O and HCO^+ leads to the formation of $HCOOH_2^+$, and this ion then undergoes dissociative recombination to form HCOOH. Thus, it is seen that a high HCO^+ abundance (resulting from high CO abundance) is key to the increased abundance of these species in a 2I-type comet composition. Therefore, the presence of large quantities of CO accelerates the formation of some of the organic ions and neutrals in the gas-phase.

 CH_3OH undergoes photoionization to form CH_3OH^+ and neutral-neutral collision reactions to form CH_2OH and CH_3O . Since there is a nearly equal abundance of CH_3OH in the 2I-type and Halley-type comet compositions, these product species also show near similar abundances, as seen in Figure 4.8(b). CH_3O and CH_2OH show a sharp fall in the outermost region as they are destroyed by H_2O in this region. The energy barrier for the destruction reactions is high, and this barrier is crossed in the high temperatures that are achieved in the outer coma.

Figures 4.8(c) and 4.8(d) show the abundance of assorted species, with and without H₂CO added to the 2I-type comet composition, respectively. H₂CO⁺ forms by the photoionization of H₂CO, the photodissociative ionization of CH₃OH, and charge-exchange reactions of H₂CO with ions such as H₂O⁺ and CO⁺. H₂COH⁺ forms by the protonation of H₂CO, and also from CH₃OH undergoing photodissociative ionization or ion-neutral reactions. HCOOCH₄⁺ forms when H₂CO undergoes an ion-neutral reaction with CH₃OH₂⁺, and the dissociative recombination of HCOOCH₄⁺ successively forms HCOOCH₃. Thus, the presence of H₂CO as a parent increases the formation rate of the ions shown in Figure 4.8(c), and they are seen in larger quantities in the Halley-type comet. When H_2CO is not present as a parent species in the 2I-type composition, some amount of H_2CO forms in the coma by the photodissociation of CH_3OH . However, this is not sufficient to match the abundances of H_2CO^+ , H_2COH^+ , $HCOOCH_4^+$ and $HCOOCH_3$ seen in the Halley-type comet.

On the other hand, the abundance of these species increases in the coma of a 2I-type composition when H_2CO is added as a parent, and the abundance is even greater than the Halley-type comet, as is evident from Figure 4.8(d). This is because of higher availability of HCO^+ and $CH_3OH_2^+$ ions in the 2I-type comet composition. HCO^+ causes protonation of H_2CO to form H_2COH^+ , and $CH_3OH_2^+$ reacts with H_2CO to form the successive species, as discussed. The higher abundance of CO^+ ions also leads to higher amounts of H_2CO^+ forming due to charge-exchange of CO^+ with H_2CO . Thus, if any organic molecule is present as a parent species in a comet, then the ions and neutrals produced from this molecule will have high abundance in the coma. In addition, the abundance of these product species will be more in a comet where there is enhanced CO outgassing.

4.4.5 Effect of Solar Wind on Ionic Composition

From Table 4.1, it is seen that the net volatile production rate for the coma model of 2I/Borisov is ~ 10^{27} mol s⁻¹. This falls under the category of an intermediately active comet, as defined in Chapter 1. Thus, in order to assess the effect of solar wind on the ionic composition of the coma, an additional model was run. In this model, the production rates from Table 4.1 and the solar wind parameters from Table 4.3 are used as inputs.

A comparison of the major ions whose abundances get altered with and without the solar wind effects is shown in Figure 4.9. The solid lines in the figure denote the variation with cometocentric distance of the ion number densities when taking into consideration the impact ionization and charge exchange reactions of the coma gas with the solar wind. The dashed lines show the ion densities when solar wind is not considered in the model. It can be seen that the addition of processes due to the solar wind can increase the number density of ions, though the percentage increase is variable for different ions.

The ionization of neutral CO and H_2O molecules by the solar wind leads to an increase in the density of CO⁺ and H_2O^+ ions by ~ 30-40%. The increase in the density of OH⁺ ions is lower as compared to the increase in H_2O^+ , since the cross section of its formation by dissociative electron impact ionization is lower. From the formation processes discussed in Section 4.3.2, it can be seen that an increase in the density of CO⁺ and H_2O^+ ions results in higher abundance of HCO^+ and H_3O^+ ions.

NH₃, CH₃OH and HCN have proton affinities that are higher than that of H₂O and CO. Thus, an increase in the abundance of HCO⁺ and H₃O⁺ will result in an increase in the abundance of their respective protonated species namely NH_4^+ , $CH_3OH_2^+$ and $HCNH^+$, due to successive proton transfer reactions. Methyl cation transfer reaction of $CH_3OH_2^+$ with CH_3OH creates $CH_3OCH_4^+$, and an increase in the $CH_3OH_2^+$ abundance explains the increase in the density of $CH_3OCH_4^+$.

There are a number of factors that affect the impact ionization rates, including the neutral outgassing rate, and the density and temperature of the solar wind electrons. In the present case, the electron impact ionization rate of H₂O due to solar wind electrons is ~ 14% of the photoionization rate, while this value is ~ 7% for CO. Cravens et al. (1987) estimated that under solar minimum conditions at 1 AU, the ionization frequency of H₂O is less than 20% of the photoionization rate, for solar wind electrons having density 5 cm⁻³ and temperature 1.5×10^5 K. Heating of electrons behind the bow shock can cause the temperature to reach 3×10^5 K, leading to an ionization frequency that is about 50%

Quantity	Value
Solar wind number density $n_{\rm SW}$	$2.5~{\rm cm}^{-3}$
Solar wind mean molecular mass $m_{\rm SW}$	1 amu
Solar wind electron temperature $T_{\rm e,SW}$	$10^5 { m K}$
Solar wind proton temperature $T_{\rm p,SW}$	$5 \times 10^4 {\rm ~K}$

Table 4.3: Solar wind parameters used at 2.01 AU, taken from Hansen et al. (2007).



Figure 4.9: The solid lines show the variation of the number density with cometocentric distance for major cometary ions in 2I/Borisov when ionization due to solar wind is considered. The dashed lines show the number density of ions when solar wind is not considered.

of the photoionization rate. The outgassing activity of 2I/Borisov is such that well-defined plasma boundaries do not form (see Section 1.2.5). Thus, it is assumed that the solar wind electrons remain unshocked, leading to a lower impact ionization frequency. However, 67P/C-G does exhibit an infant bow shock at an outgassing rate similar to 2I/Borisov (Gunell et al., 2018; Goetz et al., 2021). If a similar feature exists in 2I/Borisov, then heating of solar wind electrons may occur downstream of the shock, and calculating the impact ionization frequecy in this case would require a more detailed treatment, which is beyond the scope of this work. Cravens et al. (1987) also report that charge exchange with solar wind protons is approximately as important as photoionization, though in the modeled coma of 2I/Borisov, the charge exchange frequency is lower than the photoionization rate due to reduced solar wind proton number density at 2.01 AU.

The interaction of 2I/Borisov with the solar wind can also be compared with the ionization processes at comet 67P/C-G, which had similar outgassing activity as 2I/Borisov for some part of the *Rosetta* mission. At heliocentric distances > 3 AU, the solar wind has access to the nucleus, though it does not cause any ionization processes (Fuselier et al., 2015; Galand et al., 2016). Simon Wedlund et al. (2019) calculated the in situ ionization frequency due to charge exchange and impact ionization by solar wind H^+ , He^+ and He^{2+} ions at 67P/C-G for an H₂O coma. They compared these with the photoionization and electron impact ionization frequencies reported by Heritier et al. (2018). They calculated the electron impact ionization rates from the electron flux densities retrieved by the Ion and Electron Sensor of the Rosetta Plasma Consortium; these electrons include photoelectrons and solar wind electrons (Madanian et al., 2016). Simon Wedlund et al. (2019) find that on an average, for 67P/C-G, the rate of solar wind charge exchange is a factor of 5 lower than the photoionization rate during the early and late mission period, for cometocentric distances < 50km and heliocentric distances > 2.8 AU. At higher outgassing rates, when the heliocentric distance is < 2.4 AU, the efficiency of solar wind charge exchange becomes lower than photoionization by 2 orders of magnitude.

4.4.6 Dissociative Recombination Rates

The dissociative recombination rates that are used for the water group ions H_2O^+ and H_3O^+ in the present chemical network are given by the KIDA database, where the rates vary as $T_e^{-0.5}$, T_e being the electron temperature. Rubin et al. (2014) use dissociative recombination rates given by Schunk & Nagy (2009), for which the temperature dependence is $T_e^{-0.74}$ when T_e is in the range of 800-4000



Figure 4.10: Variation of the dissociative recombination rate in 2I/Borisov with cometocentric distance for the temperature relations given by KIDA and Schunk & Nagy (2009).

K and $T_e^{-1.111}$ for $T_e > 4000$ K. The total dissociative recombination rate for H_3O^+ ions (including all branches) is the same as that of H_2O^+ . The variation of the total recombination rate with cometocentric distance for the modeled coma temperature of 2I/Borisov is given in Figure 4.10.

It is seen that in the high temperature region of electrons (cometocentric distance > 50 km), the rates given by the different relations deviate, and the recombination rate given by Schunk & Nagy (2009) is lower than that given by KIDA by about a factor of 5. In 2I/Borisov, the relative reaction rate for the loss of H_2O^+ by dissociative recombination is $\leq 1\%$ at distances less than 5000 km and about 3% at 10⁴ km, and hence use of the rate prescribed by Schunk & Nagy (2009) is not likely to affect the H_2O^+ abundance within this distance. On the other hand, the relative rate of the loss of H_3O^+ by dissociative recombination is about 10% at 1000 km, and it increases on moving further outwards. However, the ion pileup region that was observed in 1P/Halley (due to the increase in electron temperature that shuts off recombination) is not likely to be present in the coma of 2I/Borisov. This is because the electron temperature attains a high value at a low cometocentric distance, where loss of H_3O^+ by proton transfer is

more dominant.

4.5 Summary

A multifluid combined chemical-hydrodynamical model is used to study the coma of the interstellar comet 2I/Borisov. This comet shows a CO/H_2O ratio that is higher than that observed in Solar System comets within 2.5 AU, which alters the chemistry and dynamics of the gas-phase coma. The following is the summary of the model results for 2I/Borisov:

- The coupling between the electron and neutral fluid temperatures in the coma exists only up to a short distance ~ 20 km from the nucleus. In the higher temperature region of the electron fluid, an important mechanism by which cooling of electrons occurs is due to inelastic collisions resulting in the vibrational excitation of CO.
- Protonated ions formed by H⁺ ion transfer to parent species show a high abundance up to ~ 100 km. Beyond this distance, the fluxes of these ions tend to flatten, and ions formed by the photolysis of parent species become more abundant.
- CO⁺ and HCO⁺ abundances are high due to the presence of a large amount of CO. Both these ions have a considerable effect on the formation/destruction rates of other ions such as H₂O⁺, H₃O⁺, N-bearing ions and large organic ions. HCO⁺ plays a significant role in causing the protonation of neutral species.
- One of the loss processes for ions in the coma is dissociative recombination. The relative rates of these reactions are considerably influenced by the electron temperature.
- High abundance of CO results in higher abundance of many large organic ion and neutral species. CH_3OH_2^+ is formed due to the protonation of CH_3OH by H_3O^+ and HCO^+ ions. Due to the higher abundance of HCO^+

ions, more amount of $CH_3OH_2^+$ is formed, which is a precursor of other organic ions and neutrals.

• The addition of charge exchange and impact ionization reactions with the solar wind in the coma model of 2I/Borisov can increase the number densities of $\rm CO^+$ and $\rm H_2O^+$ ions by $\sim 30 - 40\%$, which in turn increases the abundance of other protonated species and major ions.

Chapter 5

Study of the Formation of Organics in the Coma

The modeling studies on the formation of organic species in the gas phase cometary atmosphere, done as part of this thesis work, is discussed in this chapter.

A sample of four Oort cloud comets is selected, in order to study the formation of organics in their gas-phase comae. These comets are, in chronological order of their discovery, C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy) and C/2014 Q2 (Lovejoy). All of these are bright comets, with high production rates near perihelion (Combi et al., 2014, 2018, 2019), which facilitated the remote detection of a large number of organic molecules, while sensitive upper limits were obtained for others. The relative abundances of complex organic molecules in most comets vary within one order of magnitude (Biver & Bockelée-Morvan, 2019). The organic abundances in Jupiter family comets do not differ significantly from Oort cloud comets (Biver & Bockelée-Morvan, 2019); however there are lesser measurements of organics available for JFCs, because they generally exhibit comparatively lower activity. The organic molecules are generally assumed to originate from the icy nucleus, though this is still unproven. Most of the ground-based observations lack the spatial information which can constrain the nucleus versus coma origins of these organics. It is pertinent to study the gas-phase formation pathways of organics and how successful these proposed formation pathways are in producing organics in a cometary coma. Particularly, comets showing moderate to high activity can reach sufficient coma densities for molecules to form by active gas-phase coma chemistry (Cordiner & Charnley, 2021).

5.1 Importance of Cometary Organics

Some of the molecular species that have been detected in comets, and form in the gas-phase in the coma, are of biological importance. HCN, one of the main reservoirs of cometary volatile nitrogen, is a key precursor in the synthesis of amino acids and is likely to play an integral role in the creation of biomolecules (Oro et al., 1991). H_2CO is a chemical precursor to sugars, and CH_3OH is the simplest alcohol that is the starting point from which more complex organics form in the interstellar medium (Garrod et al., 2008; Herbst & van Dishoeck, 2009; Oberg et al., 2009). Glycolaldehyde is a two-carbon sugar precursor, and is an important biomarker molecule since it is postulated to be a building block for ribose, the backbone of RNA (Jalbout et al., 2007). Ethylene glycol is a chemically reduced variant of glycoladehyde and is found in many of the same locations as glycolaldehyde (Hollis et al., 2002; Li et al., 2017; Pagani et al., 2017). Methyl formate is the structural isomer of glycolaldehyde and acetic acid, and is an important complex organic molecules that leads to the synthesis of bio-polymers. Formamide is a particularly promising organic molecule since it has an amide functional group which is essential in forming amino acid chains. It has been identified as a key precursor of prebiotic molecules, carboxylic acids and sugars (Saladino et al., 2012; Saitta & Saija, 2014; Botta et al., 2018). Glycine is the simplest amino acid and is a key building block for proteins and peptides (Wincel et al., 2000).

5.2 Comets Studied in this Work

5.2.1 C/1996 B2 (Hyakutake)

C/1996 B2 (Hyakutake) is a long period comet which was discovered on 30 January 1996, when its total visual magnitude was 11. This comet made a close approach to Earth, reaching a geocentric distance of 0.102 AU on 25 March 1996, and crossed perihelion on 1 May 1996 at a heliocentric distance of 0.25 AU. The close-Earth approach and favourable viewing geometry of C/1996 B2 led to a significant improvement in our knowledge of cometary compositions. A large observational campaign was organized for this cometary passage, which mobilized most of the telescopes available at the time. Some of these observational campaigns include those conducted by the James Clerk Maxwell Telescope (JCMT; Irvine et al., 1996; Biver et al., 1999), the Hubble Space Telescope (HST; McPhate et al., 1996), the NASA Infrared Telescope Facility (IRTF; Brooke et al., 1996; Mumma et al., 1996; DiSanti et al., 2003), the Caltech Submillimeter Observatory (CSO; Lis et al., 1997), and the Institut de Radioastronomie Millimétrique (IRAM; Biver et al., 1999). These observations resulted in the first cometary identifications of hydrogen isocyanide (HNC), isocyanic acid (HNCO) and acetonitrile (CH₃CN) at millimeter wavelengths (Dutrey et al., 1996; Irvine et al., 1996; Lis et al., 1997), and the first IR detection of the hydrocarbons CH_4 , C_2H_6 and C_2H_2 (Brooke et al., 1996; Mumma et al., 1996).

5.2.2 C/2012 F6 (Lemmon)

C/2012 F6 (Lemmon) is a long-period comet that originated from the Oort cloud, and was discovered on 23 March 2012, when it was at 5 AU from the sun. This comet reached perihelion at a heliocentric distance of 0.73 AU on 24 March 2013. C/2012 F6 was a bright, naked-eye comet, reaching a visual magnitude of 4.5, exhibiting a high production rate ($\sim 10^{30} \text{ mol s}^{-1}$) near perihelion (Combi et al., 2014). Paganini et al. (2014a) report on the observations of this comet, from February to June 2013, using different facilities including the CRIRES spectrograph of the Very Large Telescope (VLT), the Near Infrared Spectrometer (NIRSPEC) on the Keck-2 Telescope, and the CSHELL spectrograph on NASA IRTF. Observations of C/2012 F6 during March-April 2013, made using the IRAM 30 m telescope, are reported by Biver et al. (2014). Water production rates along its entire apparition is reported by Combi et al. (2014), from observations made using the Solar Wind Anisotropies (SWAN) camera on board the Solar and Heliosphere Observatory (SOHO). Other reported observations of C/2012 F6 include its long-term monitoring by the TRAPPIST telescope at the La Silla Observatory (Opitom et al., 2015a) and the spatially resolved distributions of several volatiles from measurements made using ALMA (Cordiner et al., 2014).

5.2.3 C/2013 R1 (Lovejoy)

C/2013 R1 (Lovejoy) is a high-inclination dynamically old Oort cloud comet that was discovered in September 2013, at a heliocentric distance of 1.94 AU. It crossed perihelion on 22 December 2013 at 0.81 AU from the sun, reaching a visual magnitude of 4.8 and a water production rate $\sim 10^{29}$ mol s⁻¹. Observations of C/2013 R1 made during November-December 2013 at IRAM are reported by Agúndez et al. (2014) and Biver et al. (2014). Photometry and imaging results obtained by the TRAPPIST monitoring of this comet is reported by Opitom et al. (2015b). Since the discovery of many new organics in comet C/1995 O1 (Hale-Bopp), the large organics namely formamide, ethylene glycol, and acetaldehyde were re-detected for the first time in the comets C/2012 F6 and C/2013 R1 (Biver et al., 2014). Sensitive upper limits for some other molecules such as methyl formate and glycolaldehyde are reported for these two comets (Biver et al., 2014).

5.2.4 C/2014 Q2 (Lovejoy)

C/2014 Q2 (Lovejoy) is a young long-period Oort cloud comet that reached a perihelion distance of 1.29 AU on 30 January 2015. Biver et al. (2015) report on the spectral survey of this comet, conducted between 13 - 16 and 23 - 26 January 2015. A total of 21 molecules were detected in this spectral survey, and this included the first confirmed identification of C₂H₅OH and CH₂OHCHO in

a comet. The other organic molecules observed in C/2014 Q2, such as formic acid (HCOOH), formamide (NH₂CHO), acetaldehyde (CH₃CHO), methyl formate (HCOOCH₃) and ethylene glycol [(CH₂OH)₂] were first detected in Hale-Bopp. The molecular abundances calculated by Biver et al. (2015) show that the production rates with respect to water for CH₃OH and HCOOCH₃ are similar to that observed in comet Hale-Bopp. The production rates for most of the other volatiles are lower by a factor of 2 - 3, with the exception of cyanoacetylene (HC₃N) and CO that show a depletion by a factor of 10 or more.

Dello Russo et al. (2022) obtained the IR spectroscopic observations of C/2014 Q2 a few days after perihelion, on 2 and 3 February 2015. They report on the abundances of a number of volatiles, including the aliphatic hydrocarbons CH₄, C₂H₆, C₂H₄ and C₂H₂. C₂H₄ was detected in the coma of comet 67P/Churyumov-Gerasimenko by the ROSINA instrument of the *Rosetta* mission (Luspay-Kuti et al., 2015; Rubin et al., 2015; Altwegg et al., 2017), though the production rate is not well-constrained. Dello Russo et al. (2022) present evidence of the detection of C₂H₄ in a comet from a ground-based facility for the first time, by the spectral analysis of the emission lines of C/2014 Q2.

5.3 Model Inputs

Coma model runs are obtained for the four comets, namely C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2. The water production rate and size of the

Comet	$Q_{\rm H_2O}~(\rm mol~s^{-1})$	r_h (AU)	Radius (km)
C/1996 B2 (Hyakutake)	1.7×10^{29}	1.06	2.1
C/2012 F6 (Lemmon)	6.7×10^{29}	0.78	5
C/2013 R1 (Lovejoy)	9.13×10^{28}	0.92	1.3
C/2014 Q2 (Lovejoy)	4.07×10^{29}	1.3	4.3

Table 5.1: Parameters used as model inputs for the different comets. References for $Q_{\rm H_2O}$ are Mumma et al. 1996 (C/1996 B2), Combi et al. 2014 (C/2012 F6), Combi et al. 2018 (C/2013 R1 and C/2014 Q2). References for the radius are https://ssd.jpl.nasa.gov/ (C/1996 B2), Paradowski 2020 (C/2013 R1, C/2014 Q2).

Molecule	C/1996 B2	$C/2012 \ F6$	C/2013 R1	C/2014 Q2
	(Hyakutake)	(Lemmon)	(Lovejoy)	(Lovejoy)
СО	19	4.0	7.2	1.8
CO_2	4			
CH_4	0.8	0.67	0.91	0.75
C_2H_6	0.6	0.31	0.69	0.68
C_2H_2	0.5	0.08^{a}	0.07^{a}	0.11
C_2H_4				0.22
H ₂ CO	1	0.7	0.7	0.3
CH ₃ OH	2	1.6	2.6	2.4
НСООН		0.07^{a}	0.12	0.028
$(CH_2OH)_2$		0.24	0.35	0.07
HCOOCH ₃		0.16^{a}	0.20^{a}	0.08
CH ₃ CHO	0.12^{a}	0.07^{a}	0.10	0.047
CH ₂ OHCHO		0.08^{a}	0.07^{a}	0.016
C_2H_5OH	0.21^{a}			0.12
H_2O_2	0.055^{a}			
HCN	0.2	0.14	0.26	0.09
HNC	0.01			0.004
NH ₃	0.5	0.58	0.1	0.64
HNCO	0.07	0.025	0.021	0.009
CH ₃ CN	0.01			0.015
NH ₂ CHO	0.1^{a}	0.016	0.021	0.008
HC ₃ N	0.08^{a}			0.002

Table 5.2: Volatile species abundance percentages with respect to H_2O , used as model inputs. The superscript *a* against some of the volatiles abundances indicates the reported upper limit for this species. The references for the abundances are C/1996 B2: McPhate et al. (1996); Lis et al. (1997); Bockelée-Morvan et al. (2004), C/2012 F6: Biver et al. (2014, 2016); Paganini et al. (2014b); Lippi et al. (2020), C/2013 R1: Biver et al. (2014); Paganini et al. (2014a), C/2014 Q2: Biver et al. (2015); Dello Russo et al. (2022).

cometary nucleus that are used as inputs for each of these comets are shown in Table 5.1. The radius of the nucleus of C/2012 F6 is unavailable in literature, and a value of 5 km is assumed for radius of the nucleus of this comet, which is about the average cometary size for long period comets. The heliocentric distances at
which the photolytic reaction rates are calculated for the different comets are also given in Table 5.1.

The abundance percentages with respect to H_2O for the parent volatiles outgassing from the nucleus, as reported by different authors, are given in Table 5.2. The production rate for each species for a particular comet can be found by multiplying these relative abundances with the respective water production rate given in Table 5.1. These species production rates are then used as the initial input composition for the model runs. In order to study the gas phase formation of an organic species in the coma, production of that species from the nucleus is taken to be zero, while the other species abundances are used as calculated from Tables 5.1 and 5.2. This ensures that the modeled abundance of that species is due to coma chemistry alone. Some of the species abundances are reported as upper limits in literature, though this will not have any effect if that species is being studied, since its initial abundance is taken to be zero.

5.4 Results

5.4.1 Temperature Profiles

The temperature profiles for the neutral, electron and ion fluids, for the comets C/2012 F6 and C/2013 R1 (representing the highest and lowest values, respectively of the water production rates) are shown in Figure 5.1. The profiles for the other two comets are in the same range, and are therefore not shown. The profiles are qualitatively similar to such profiles obtained previously by gas-phase coma modeling. As shown by earlier models, there is a coupling between the electron and neutral temperatures up to some distance from the nucleus. The energetic electrons that are created due to photochemical reactions lose their energy to the neutral fluid (specifically H_2O and CO; see Chapter 3) due to inelastic collisions, resulting in the rotational and vibrational excitation of the neutral molecules. On moving outwards in the coma, the coupling is lost and the electron temperature decouples from the neutral temperature at a larger distance because of higher



Figure 5.1: Temperature profile of the coma, showing the variation of the fluid temperatures with cometocentric distance. T_n , T_e , and T_i denote the temperatures of the neutral, electron, and ion fluids, respectively. The line styles indicate different cometary compositions (solid: C/2012 F6, dotted: C/2013 R1).

coma density, and the rise in the electron temperature is also comparatively less steep.

5.4.2 Species Formation in the Coma

The most abundant molecular species in the coma are the parent molecules that sublimate directly from the nucleus. These molecules undergo photolytic processes to create ions, electrons and neutral radicals in the coma, which drive the coma chemistry. Figures 5.2-5.8, 5.10-5.12, 5.14, and 5.15 are the formation rate plots of assorted radicals, ions and neutral organic species for different cometary compositions, while Figures 5.9, 5.13 and 5.16 show the resulting variation of the flux of these species. In the formation rate plots, the black lines (scale: left y-axis) show the variation of the net coma formation rate P_i with cometocentric distance, for the species. The colored lines (scale: right y-axis) show the variation of the relative reaction rates (%) of the major coma formation pathways. The labels on the colored lines indicate the reactants that produce the species for which the plot is shown. Other product(s) that form are not mentioned, though a full list of these reactions can be found in the Appendix. The line styles (black or colored) used in the formation rate plots indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2). Changes in the temperature and species number densities in different regions of the coma result in changes in the relative reaction rate. Thus, the dominant processes leading to the creation of a species get altered in the different regions of the coma.

5.4.2.1 CHO-bearing organics

The organic molecules $HCOOCH_3$, HCOOH, CH_3CHO , C_2H_5OH , $(CH_2OH)_2$ and CH_2OHCHO originate as parent molecules but can also be synthesized in the coma by gas-phase reactions. Figures 5.2-5.8 show the formation rate plots of these CHO-bearing organic neutrals and their corresponding protonated species, and radicals of organic origin created in the coma.

Figure 5.2 shows the variation of the production rates per unit volume and the formation pathways of $HCOOCH_3$ and $HCOOCH_4^+$ with cometocentric distance. The dominant formation mechanism of $HCOOCH_3$ in the coma is by the dissociative recombination of $HCOOCH_4^+$. The neutral-neutral reaction of CH₃OCH₂ with atomic O does not contribute much to HCOOCH₃ formation. This is because the Arrhenius coefficient α of this neutral-neutral bimolecular reaction is nearly three orders of magnitude smaller than that of the recombination reaction, and the abundance of CH_3OCH_2 is also low. Most of the $HCOOCH_4^+$ in the coma forms by the ion-neutral reaction of $CH_3OH_2^+$ with H_2CO . The relative rate of the ion-neutral reaction of $CH_3OH_2^+$ with HCOOH is $\leq 0.1\%$ up to a distance ~ 1000 km, and reduces further as the distance increases. This is because the rate coefficient of the reaction of $CH_3OH_2^+$ with H_2CO is nearly two orders of magnitude higher than that of $CH_3OH_2^+$ with HCOOH. In addition, the outgassing rate of H_2CO is a factor of 5-10 times more that of HCOOH (see Table 5.2), resulting in higher H_2CO abundance in the coma. Beyond ~ 100 km, protonated methyl formate also forms when HCOOCH₃ gets cycled back into $HCOOCH_4^+$ by accepting H^+ cations from H_3O^+ ions. $HCOOCH_3$ also gets



Figure 5.2: Coma formation rates for the species (a) HCOOCH_3 and (b) HCOOCH_4^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

cycled back into HCOOCH_4^+ by undergoing proton transfer with HCO^+ , though the relative rate of this reaction is $\lesssim 1\%$ beyond 10^4 km. H_3^+ abundance is low in the coma, and hence it does not contribute much to the cyclic conversion of

 $HCOOCH_3$ into $HCOOCH_4^+$ by proton transfer.

Ethanol undergoes H-abstraction with the atomic and molecular radicals O, H and OH, resulting in the formation of the radicals CH₂CH₂OH and CH₃CHOH. These two radicals further react with atomic oxygen to generate other organic species such as formic acid, acetaldehyde and glycolaldehyde. Figure 5.3 shows the variation of the formation rates per unit volume of CH_2CH_2OH and CH_3CHOH , and also the relative strengths of the different H-abstraction reactions. The net rates of formation per unit volume, and the number densities of CH₂CH₂OH and CH₃CHOH depend upon the availability of ethanol in the coma. In the coma models of C/1996 B2 and C/2014 Q2, the net formation rates are high as indicated by the black lines in Figure 5.3, because C_2H_5OH is present as a parent molecule. C_2H_5OH is also produced in small quantities by gas-phase reactions in the coma (discussed later in this section), from which CH_2CH_2OH and CH_3CHOH form in the comae of C/2012 F6 and C/2013 R1, although the formation rate is many orders smaller than in the case where ethanol is a parent species. In the region of the coma within ~ 2000 km, H-abstraction occurs mainly by the reaction of OH with ethanol. Beyond this region, atomic O and H become more dominant as radicals with which C_2H_5OH undergoes the H-abstraction reaction. The rates of the reaction of C₂H₅OH with the atomic radicals O and H depend on the temperature of the neutral species, which keeps increasing on moving outwards in the coma (Section 5.4.1), thereby increasing the reaction rates. Ethanol also undergoes H-abstraction with the CH₃ radical, though the contribution of this process is < 0.1% in the region of the coma beyond 10^4 km, because of lower CH₃ abundance as compared to O and H in the outer regions. In addition, the H-abstraction reaction of ethanol with CH_3 is again strongly dependent on temperature, similar to the reaction with O and H. Thus it does not contribute much to the formation of CH₂CH₂OH and CH₃CHOH in the inner regions where the temperature is lower.

Figure 5.4 shows the variation of the production rates per unit volume and



Figure 5.3: Coma formation rates for the species (a) CH_2CH_2OH and (b) CH_3CHOH . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).



Figure 5.4: Coma formation rates for the species (a) HCOOH and (b) HCOOH_2^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

the formation pathways of HCOOH and $HCOOH_2^+$ in the coma. The formation rates of HCOOH in C/1996 B2 and C/2014 Q2 are several orders of magnitude higher than in C/2012 F6 and C/2013 R1. The neutral-neutral bimolecular reaction of the CH₃CHOH radical with atomic oxygen is an efficient way of forming HCOOH in the coma. Nearly all of the coma-produced HCOOH forms by this process in the comae of C/1996 B2 and C/2014 Q2, because of the higher formation rate leading to a higher abundance of CH₃CHOH in these two comets (Figure 5.3). When CH_3CHOH abundance is low, HCOOH forms by the dissociative recombination of $HCOOH_2^+$, and proton transfer reactions of $\mathrm{HCOOH_2}^+$ with methanol, ammonia, acetaldehyde and water. This is true for the case of C/2012 F6 and C/2013 R1, where the proton transfer reactions dominate within a few hundred km from the nucleus, but on moving further outward in the coma, the dissociative recombination reaction gains importance. Of the proton transfer reactions forming HCOOH, the reaction of $HCOOH_2^+$ with methanol has the highest relative rate. NH_3 has a higher proton affinity than methanol, but the relative rate of the $HCOOH_2^+$ proton transfer reaction with NH_3 is lesser because of lower abundance of ammonia as compared to methanol. In addition, the relative abundance of NH_3 in C/2013 R1 is nearly 6 times lower than the NH_3 abundance in C/2012 F6, resulting in the relative reaction rate of $\mathrm{HCOOH_2^+}$ with $\rm NH_3$ being lower in C/2013 R1 by almost an order of magnitude. In C/1996 B2 and C/2014 Q2, the proton transfer and dissociative recombination reactions of HCOOH_2^+ have a net contribution $\lesssim 0.5\%$ towards the HCOOH formation rate, in different regions of the coma. CH_3CN also reacts with $HCOOH_2^+$ but the relative strength of this reaction is quite low. This is because of low abundance of CH₃CN as compared to the other neutral species participating in proton transfer reactions in C/2012 F6 and C/2013 R1, and because the bimolecular reaction of O with CH_3CHOH completely dominates over proton transfer reactions in C/1996 B2 and C/2014 Q2. The coma-produced $HCOOH_2^+$ originates mainly by the radiative association of water with HCO⁺ ions. Since HCOOH production in the comae of C/1996 B2 and C/2014 Q2 is high, it participates in proton transfer reactions with the ions HCO^+ , $CH_3OH_2^+$ and H_2COH^+ to get converted into $HCOOH_2^+$. The sum of the relative rates of these reactions is shown by the lines

labeled 'HCOOH+ion' in Figure 5.4(b). The proton transfer reaction rates vary inversely with the square-root of the temperature and their relative contribution falls off beyond ~ 1000 km. The relative production of HCOOH_2^+ by the ion-neutral reaction of CH_4 and O_2^+ also shows variation with temperature and its contribution can go up to ~ 1-2% in some regions of the coma.

Figure 5.5 shows the variation of the production rates per unit volume and the formation pathways of CH_3CHO and CH_3CHOH^+ in the coma. Most of the CH₃CHO molecules are created in the coma by the neutral-neutral reactions of CH with CH₃OH, and of O with C₂H₅. While the reaction of CH with CH₃OH is dominant at distances ≤ 1000 km, the reaction of O with C_2H_5 becomes dominant beyond that. At distances < 100 km, the relative rate of the reaction of CH with CH₃OH reduces, and the proton transfer reaction of CH₃CHOH⁺ with NH₃ has a significant contribution to the CH₃CHO formation rate. In the innermost regions, the relative rate of the proton transfer reaction can even exceed that of the neutral-neutral reaction, as in the case of C/2012 F6. The relative rate of the neutral-neutral reaction of O with CH_3CHOH varies between 1 - 10% in C/1996 B2 and C/2014 Q2, and is negligible in C/2012 F6 and C/2013 R1 due to low CH₃CHOH density. Dissociative recombination of CH₃CHOH⁺, C₂H₅OH⁺ and $C_2H_5OH_2^+$ also produces CH_3CHO in the coma. The sum of the relative reaction rates of all three of these dissociative recombination reactions, denoted by the lines labeled 'diss. recom.' in Figure 5.5(a), is $\sim 1-2\%$ in C/2012 F6 and C/2013 R1 and up to ~ 40% in C/1996 B2 and C/2014 Q2. Since C_2H_5OH is not present as a parent species in C/2012 F6 and C/2013 R1, the abundance of the photo-produced ion $C_2H_5OH^+$ and the protonated molecule $C_2H_5OH_2^+$ is lesser in the comae of these two comets, resulting in lesser relative rate of the sum total of the dissociative recombination reactions. Other neutral-neutral reactions, such as the reaction of CH₃CO with parent molecules like CH₄, C₂H₆, CH₃OH and H₂CO do not contribute much towards the gas-phase formation of CH₃CHO, because of low abundance of the CH₃CO radical. The relative rates of the formation reactions of CH₃CHO show significant variation in the different regions of the coma. Nearly all of these formation reactions have non-zero values of the Arrhenius coefficients β and γ , which determine the temperature dependence, and



Figure 5.5: Coma formation rates for the species (a) CH_3CHO and (b) CH_3CHOH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

the values of these parameters are also quite dissimilar for the different reactions. Thus, while the rates of the dissociative recombination reactions vary inversely as the square-root of the temperature, the bimolecular reaction rate of CH with CH₃OH varies roughly as the inverse square of the temperature. Protonated acetaldehyde or CH₃CHOH⁺ forms mainly by the methyl cation transfer reaction of H₂CO and CH₃OH₂⁺ in the region of the coma $\lesssim 500$ km from the nucleus. On moving further outward, proton transfer reactions of CH_3CHO with H_3O^+ , HCO^+ and $HCOOH_2^+$ ions gain prominence, and the sum of the relative rates of these reactions is shown by the lines labeled ' CH_3CHO +ion' in Figure 5.5(b). The relative contribution of the ion-neutral reaction of CH_4 and H_2CO^+ to the formation of CH₃CHOH⁺ varies for the different cometary compositions due to varying abundances of the reacting species. Ion-neutral reactions of the neutral species C_2H_5OH , CH_2CH_2OH and CH_3CHOH with C^+ or H^+ ions contribute significantly towards forming CH_3CHOH^+ in the outer regions of the comae of C/1996 B2 and C/2014 Q2. However, the contribution of these reactions is very little in C/2012 F6 and C/2013 R1, due to reduced abundances of the reacting neutrals. The total contribution of these ion-neutral reactions is shown by the lines labeled 'neutral+ion' in Figure 5.5(b).

Figure 5.6 shows the variation of the production rates per unit volume and the formation pathways of C₂H₅OH and C₂H₅OH₂⁺ in the coma. NH₃ has a higher proton affinity than C₂H₅OH, and H⁺ cation transfer takes place from protonated ethanol to ammonia, resulting in the formation of C₂H₅OH. This reaction is the dominant mechanism for ethanol formation close to the nucleus, at distances ≤ 100 km, while its contribution begins to decrease on moving further outward, and the relative rate of the dissociative recombination reaction undergone by C₂H₅OH₂⁺ increases. Beyond ~ 2000 km, nearly all of the coma-produced ethanol is created by the dissociative recombination reaction. C₂H₅OH₂⁺ forms mainly by two radiative association reactions, namely C₂H₄ with H₃O⁺, and C₂H₅⁺ with water. Out of these two reactions, the association of C₂H₄ and H₃O⁺ is faster, and its Arrhenius coefficient α is two orders of magnitude higher than that of the reaction of C₂H₅⁺ with H₂O. In addition, C₂H₄ is present as a parent molecule in C/2014 Q2 and thus it has a high coma abundance. This results in a high



Figure 5.6: Coma formation rates for the species (a) C_2H_5OH and (b) $C_2H_5OH_2^+$. The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

rate of formation of $C_2H_5OH_2^+$ in C/2014 Q2, as compared to the other comets, and almost all of the coma produced $C_2H_5OH_2^+$ in this comet forms by the radiative association of C_2H_4 and H_3O^+ . In the other comets, the radiative association of H_2O and $C_2H_5^+$ is the dominant formation mechanism close to the nucleus, and its contribution begins to fall off beyond 100 km, when the radiative association of C_2H_4 and H_3O^+ takes over. Similar to the cyclic conversion of methyl formate into protonated methyl formate, a small quantity of C_2H_5OH (formed from protonated ethanol) gets cycled back into $C_2H_5OH_2^+$ by undergoing proton transfer reactions with H_3^+ , H_3O^+ and HCO^+ ions, beyond ~ 100 km. The net contribution of the proton transfer reactions (shown in Figure 5.6(b) as the lines labeled ' C_2H_5OH +ions') to the overall $C_2H_5OH_2^+$ production is 1-3% in the outer regions of the coma of C/2014 Q2, and even lesser in the other comets. Thus, the relative rate of the cyclic formation of the protonoted species from the neutral species in ethanol is less as compared to the same process undergone by methyl formate, by one order of magnitude or more.

Figure 5.7 shows the variation of the production rates per unit volume and the formation pathways of $(CH_2OH)_2$ and $(CH_2OH)_2H^+$ in the coma. At distances < 5000 km, (CH₂OH)₂ forms primarily by the combination of two CH_2OH radicals. In the outer region of the coma, the relative rate of this reaction falls off sharply, leading to a sharp reduction in the $(CH_2OH)_2$ formation rate. The steep reduction can be explained by a sudden decrease in the abundance of CH₂OH, which is destroyed rapidly by water in the outer region of the coma. The rate of this destruction reaction is highly dependent on the neutral fluid temperature, and when the temperature increases in the outer coma region, there is an exponential increase in the destruction rate of CH_2OH . In C/2012 F6, the temperature of the neutral fluid at any distance is relatively higher (Figure 5.1), and the reduction in the CH_2OH abundance and the $(CH_2OH)_2$ formation rate occurs at a lower cometocentric distance as compared to the other comets. In the outer coma region, the dissociative recombination of $(CH_2OH)_2H^+$ takes over as the major formation pathway of ethylene glycol. $(CH_2OH)_2H^+$ forms in the come by the proton transfer reaction of $(CH_2OH)_2$ with H_3O^+ and HCO^+ ions. The relative rate of the reaction with HCO⁺ is low, but rises gradually and can



Figure 5.7: Coma formation rates for the species (a) $(CH_2OH)_2$ and (b) $(CH_2OH)_2H^+$. The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

contribute $\sim 1-10\%$ towards the formation of $(CH_2OH)_2H^+$ in the outer regions, depending upon the cometary composition. The relative reaction rate of ethylene glycol with H_3^+ ions is negligible due to low H_3^+ abundance.

Figure 5.8 shows the variation of the production rates per unit volume and the formation pathways of CH_2OHCHO and $CH_2OHCHOH^+$ in the coma. Glycolaldehyde forms by the neutral-neutral reaction of atomic oxygen with the CH_2CH_2OH radical. The high abundance of CH_2CH_2OH in the comae of C/1996 B2 and C/2014 Q2 results in higher rates of glycolaldehyde formation by many orders of magnitude as compared to C/2012 F6 and C/2013 R1. The dissociative recombination of protonated glycolaldehyde or CH₂OHCHOH⁺ does not contribute much to the formation of glycolaldehyde. This is because the net coma formation rate of CH₂OHCHOH⁺ is comparatively lower than the formation rate of CH_2CH_2OH , as seen in Figures 5.3(a) and 5.8(b), leading to lower abundance of the protonated molecule. CH₂OHCHOH⁺ forms when glvcolaldehyde undergoes proton transfer reactions with H_3O^+ and HCO^+ ions. Similar to the formation of (CH₂OH)₂H⁺, the contribution of the proton transfer reaction of CH₂OHCHO with HCO⁺ is less but increases on moving outward in the coma. In addition, the proton transfer reaction of CH_2OHCHO with H_3^+ hardly contributes to the formation of $CH_2OHCHOH^+$, as in the case of $(CH_2OH)_2H^+$.

Figure 5.9 shows the variation of the flux of the CHO-bearing neutral and protonated organic species, in the comets C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2. The solid lines indicate the flux of the neutral species, while the dashed lines show the flux of the corresponding protonated species. As already described in Chapter 4, the flux is calculated by multiplying the species number density with the factor $4\pi r^2 v$, where r is the cometocentric distance and v is the gas velocity. This removes the r^{-2} dependence of the number density, and the stretching or compression effects due to acceleration or deceleration of the coma gas.

As seen from the coma formation rate plots, some of the species have low rates of formation by gas-phase coma chemistry, and do not form as efficiently as compared to others. This results in lower flux of some of the molecules, as compared to others. HCOOCH₃ and C_2H_5OH are both created from their corre-



Figure 5.8: Coma formation rates for the species (a) CH₂OHCHO and (b) CH₂OHCHOH⁺. The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).



Figure 5.9: Variation of the flux of the CHO-bearing neutral organic species and their corresponding protonated forms (a) HCOOCH_3 and HCOOCH_4^+ , (b) HCOOH and HCOOH_2^+ , (c) CH_3CHO and CH_3CHOH^+ , (d) $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OH}_2^+$, (e) $(\text{CH}_2\text{OH})_2$ and $(\text{CH}_2\text{OH})_2\text{H}^+$, and (f) CH_2OHCHO and $\text{CH}_2\text{OHCHOH}^+$, for different cometary compositions. The solid lines indicate the neutral species abundances and the dashed lines indicate the protonated species abundances.

sponding protonated molecules. However, the formation rate per unit volume of protonated methyl formate is higher than that of protonated ethanol, by several orders of magnitude, resulting in higher molecular fluxes of methyl formate, as compared to ethanol. The gas-phase formation of CH₂OHCHO requires the presence of ethanol in the coma. In C/2012 F6 and C/2013 R1, where C₂H₅OH is not outgassing from the nucleus but produced in the coma, the flux of CH₂OHCHO produced in the coma is low, of the order $\leq 10^{12}$ molecules s⁻¹ (not shown in the figure). Similarly, the flux of HCOOH in C/1996 B2 and C/2014 Q2 is higher than in C/2012 F6 and C/2013 R1 due to the presence of C₂H₅OH as a parent species. Thus, more amount of HCOOH and CH₂OHCHO form by gas-phase chemistry if there is ethanol outgassing from the nucleus.

The flux of the protonated species are generally correlated to their corresponding neutral forms, meaning that if a neutral species has high flux, then its protonated version will also show higher abundance. This is because the neutral and protonated species are interlinked via proton transfer and dissociative recombination reactions. The ions $HCOOH_2^+$ and CH_3CHOH^+ are exceptions to this general trend. $HCOOH_2^+$ mainly forms by the radiative association of H_2O and HCO⁺. Neutral-neutral reactions are dominant mechanisms for the formation of HCOOH, for some cometary compositions. In these cases, the abundances of HCOOH and $HCOOH_2^+$ become independent of each other. The same is true for the case of CH_3CHOH^+ , which forms mainly by the methyl cation transfer reaction of $CH_3OH_2^+$ with H_2CO , and other ion-neutral reactions involving ethanol and H-abstracted ethanol. On the other hand, CH₃CHO forms by a set of neutral-neutral reactions. However, proton-transfer and dissociative recombination reactions do play a limited role in interconnecting the abundances of CH₃CHOH⁺ and CH₃CHO, and correlations are seen in some parts of the coma. Some of the protonated species such as $(CH_2OH)_2H^+$ and CH_2OHCHO are only created in the coma by the protonation of their respective neutrals, and do not have alternate routes of formation in the coma by ion-neutral or radiativeassociation reactions. In these cases, the protonated species abundance is always less than that of the neutral molecules.

5.4.2.2 N-bearing organics

The gas-phase coma formation mechanisms of the N-bearing organic molecules CH_3CN , NH_2CHO and HC_3N are discussed in this section. Figures 5.10-5.12 show the formation rate plots of these organic neutrals and their corresponding protonated molecules.

Figure 5.10 shows the variation of the production rates per unit volume and the formation pathways of CH₃CN and CH₃CNH⁺ in the coma. CH₃CN is produced in the coma primarily by the dissociative recombination of the protonated species CH_3CNH^+ . Other bimolecular reactions that form CH_3CN have significant contributions at distances ≤ 50 km and $\geq 10^4$ km. The relative rate of the ion-neutral reaction of CNC⁺ with C_2H_6 can go up to ~ 30% at about ~ 10 km, though it reduces with increasing distance and reaches a value $\lesssim 0.1\%$ in the outer regions. The relative rate of the reaction of C_2H_4 with metastable nitrogen, $N(^{2}D)$ can go up to ~ 10%, and this rate is comparatively higher in C/2014 Q2 because C_2H_4 has a higher abundance in this comet. In the other comets, this neutral-neutral reaction contributes up to $\sim 5\%$ to the CH₃CN formation rate, beyond 1000 km. The neutral-neutral reactions of CN with the hydrocarbons CH_4 and C_3H_6 also contribute to the formation of CH_3CN . In the coma region \lesssim 50 km and beyond \sim 1000 km, the relative rate of the reaction of CN with CH_4 contributes up to ~ 50% towards the CH_3CN formation rate. However, the contribution from the reaction of CN with C_3H_6 is $\lesssim 0.5\%$, and this reaction forms CH_3CN only in the region of the coma between $\sim 100 - 1000$ km. The protonated species CH₃CNH⁺ mainly forms by the methyl cation transfer reaction between CH_4^+ ions and neutral HCN molecules, and this is the dominant formation mechanism at distances $\gtrsim 100$ km. The contribution of the radiative association of CH_3^+ ions with HNC or HCN molecules towards CH_3CNH^+ formation is high only in the innermost regions (≤ 100 km), and falls off on moving outward. This fall is sharper in the case of the reaction with HCN because the temperature dependence is stronger ($\beta = -3.0$), as compared to the reaction with HNC ($\beta = -0.5$). Protonation of CH₃CN by ions such as H₃O⁺, HCO⁺, HC_3NH^+ , etc. contributes only a very small fraction (< 1%) to the formation



Figure 5.10: Coma formation rates for the species (a) CH_3CN and (b) CH_3CNH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

of CH_3CN at distances > 100 km. The sum total of the relative reaction rates of the proton transfer reaction is plotted with the label ' CH_3CN +ion' in Figure 5.10(b).

Figure 5.11 shows the variation of the production rates per unit volume and the formation pathways of NH₂CHO and NH₂CHOH⁺ in the coma. NH₂CHO is mainly created by the neutral-neutral reaction of the NH₂ radical with H₂CO. The photodissociation scale length of H₂CO is ~ 10⁴ km, and the H₂CO flux begins to reduce beyond this cometocentric distance. This causes a reduction in the neutral-neutral relative reaction rate, and the relative rate of the dissociative recombination of NH₂CHOH⁺ increases. This decrease is stronger in C/2012 F6, since the coma of this comet is modeled at the least heliocentric distance of the four comets, resulting in a higher photodissociation rate due to increased solar UV radiation flux. This reduces the scale length and the abundance of H₂CO in the outer region of the coma the most in this comet. Similar to the formation of protonated ethylene glycol and protonated glycolaldehyde, NH₂CHOH⁺ forms by the protonation of NH₂CHO by H₃O⁺ and HCO⁺ ions, with the contribution of the HCO⁺ ion towards NH₂CHOH⁺ formation increasing on moving outwards in the coma.

Figure 5.12 shows the variation of the production rates per unit volume and the formation pathways of HC₃N and HC₃NH⁺ in the coma. HC₃N mainly forms by the neutral-neutral reaction of CN with C₂H₂, and the relative rate of this reaction remains constant in most regions of the coma. In the innermost and outermost regions of the coma, i.e. ≤ 30 km and $\geq 10^4$ km, the relative contribution of this reaction reduces. The neutral-neutral bimolecular reactions of C₂H with HCN and HNC contribute to the formation of HC₃N in the outer coma region beyond ~ 1000 km. In the coma models of C/1996 B2 and C/2014 Q2, the reaction of C₂H with HNC forms HC₃N even in the inner regions, since HNC is a parent and has high abundance in these two comets. The neutralneutral reactions of C₃N with the hydrocarbons C₂H₂ and C₂H₆ form HC₃N in the inner regions of the coma, though the sum total of the contribution of these reactions falls off beyond ~ 100 km, as shown by the lines labeled 'C₃N+neutral' in Figure 5.12(a). The relative reaction rate of the dissociative recombination of



Figure 5.11: Coma formation rates for the species (a) NH_2CHO and (b) NH_2CHOH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).



Figure 5.12: Coma formation rates for the species (a) HC_3N and (b) HC_3NH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

 $\rm HC_3NH^+$, forming $\rm HC_3N$, increases beyond ~ 100 km, and can reach up to ~ 25% in the outer coma regions. $\rm HC_3NH^+$ forms by a number of ion-neutral reactions, including proton transfer reactions, and the relative rates of these reactions vary in different regions of the coma. The relative rate of the ion-neutral reaction of $\rm C_2H_2$ with $\rm HCN^+$ is a few percent, though it rises up to ~ 40% in the coma region beyond 10⁴ km. The relative rate of the ion-neutral reaction of $\rm HCN$ with $\rm C_2H_2^+$ is ~ 60 - 80% up to ~ 50 km, but reduces beyond this distance. $\rm HC_3N$ undergoes proton transfer reactions with a large number of ions, some of which are $\rm H_3O^+$, $\rm HCO^+$ and $\rm HCNH^+$. The sum total of the relative rates of these reactions is indicated by the lines labeled ' $\rm HC_3N+ion'$ in Figure 5.12(b). Their net contribution remains constant in the region of the coma between ~ 100 - 10⁴ km, but falls off outside this region. $\rm HC_3N^+$ undergoes ion-neutral reactions with the parent species $\rm H_2O$, $\rm CH_4$ and $\rm C_2H_4$ to form $\rm HC_3NH^+$, and the net contribution of these reactions is ~ 10 - 20%, as indicated by the lines labeled ' $\rm HC_3N^+$ +neutral' in Figure 5.12(b).

Figures 5.13 shows the variation of the flux of the N-bearing neutral and protonated organic species, in the comets C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2. The solid lines indicate the flux of the neutral species, while the dashed lines show the flux of the corresponding protonated species. The flux of NH₂CHO molecules is quite high, since they are created from the abundant neutrals H₂CO (present as a parent species) and NH₂ (created rapidly by the photodissociation of NH₃). Since NH₂CHOH⁺ is only created by the protonation of NH₂CHO, and does not have other formation routes, its abundance is less than that of NH₂CHO. Similarly, the dominant mechanism for the formation of HC₃NH⁺ in most regions of the coma is the protonation of HC₃N, and thus HC₃NH⁺ shows lower abundance than HC₃N. On the other hand, CH₃CN is created almost entirely by the dissociative recombination of CH₃CNH⁺, and therefore the abundance of the protonated species is slightly higher than the neutral molecule.



Figure 5.13: Variation of the flux of the N-bearing neutral organic species and their corresponding protonated forms (a) CH_3CN and CH_3CNH^+ , (b) NH_2CHO and NH_2CHOH^+ , and (c) HC_3N and HC_3NH^+ , for different cometary compositions. The solid lines indicate the neutral species abundances and the dashed lines indicate the protonated species abundances.

5.4.2.3 Other Organics: CH₃OCH₃, CH₃COOH and HC₅N

Organic molecules can be present in the coma in the form of isomers, for example, ethanol (C_2H_5OH) and dimethyl ether (CH_3OCH_3) are the isomeric forms of C_2H_6O , while $C_2H_4O_2$ has methyl formate (HCOOCH₃), glycolaldehyde (CH_2OHCHO) and acetic acid (CH_3COOH) as its isomers. In addition, carbon chain species having more than three carbon atoms may also be present.

Figure 5.14(a) is the coma formation rate plot of CH_3OCH_3 and the pro-



Figure 5.14: Coma formation rates for the species (a) $CH_3OCH_4^+$ and CH_3OCH_3 (b) CH_3COOH . In (a), the black and red lines (scale: left y-axis) show the net coma formation rate P_i of $CH_3OCH_4^+$ and CH_3OCH_3 respectively, and the other colored lines (scale: right y-axis) show the relative rates of the major formation reactions for $CH_3OCH_4^+$. In (b), the black and colored lines show the net coma formation rate P_i , and the relative reaction rate respectively, for CH_3COOH . The line styles in (a) and (b) indicate different cometary compositions (dotteddashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

tonated species $CH_3OCH_4^+$. CH_3OCH_3 forms by the dissociative recombination of $CH_3OCH_4^+$, and the rate of formation (P_i) for the four different cometary compositions is shown by the red lines in the figure. $CH_3OCH_4^+$ primarily forms by the methyl cation transfer reaction between CH_3OH and $CH_3OH_2^+$, while a small contribution comes from the radiative association of CH_3OH and CH_3^+ . The cycling of CH_3OCH_3 back into $CH_3OCH_4^+$, due to proton transfer reactions of CH_3OCH_3 with H_3O^+ and HCO^+ ions (with relative rates denoted in Figure 5.14(a) by the lines labeled ' CH_3OCH_3 +ion'), takes place in the regions of the coma at distances > 1000 km. This is similar to the cyclic conversion of $HCOOCH_3$ and C_2H_5OH to their protonated forms.

Figure 5.14(b) shows the variation of the production rates per unit volume for the formation of CH₃COOH in the coma. CH₃CHOH radicals (created by H-abstraction of C₂H₅OH) react with neutral O atoms, via three channels, and one of these channels produces CH₃COOH. As already discussed, the abundance of CH₃CHOH radicals is high in the coma of C/1996 B2 and C/2014 Q2, since ethanol is present as a parent species in these two comets. Thus, the formation rate of CH₃COOH in these two comets is also high. In C/2012 F6 and C/2013 R1, the formation rate of CH₃COOH is lower by many orders of magnitude due to insufficient amount of ethanol forming in the coma. This is similar to the case of the coma formation of glycolaldehyde, where low ethanol abundance results in a lower glycolaldehyde formation rate in C/2012 F6 and C/2013 R1.

Figure 5.15 shows the variation of the production rates per unit volume and the formation pathways of HC₅N and HC₅NH⁺ in the coma. The dominant HC₅N formation mechanism in C/1996 B2 and C/2014 Q2 is the neutral-neutral reaction of C₂H with HC₃N, while in C/2012 F6 and C/2013 R1, HC₅N mainly forms by the reaction of C₂H₂ with the neutral radicals C₃N and C₅N (indicated in Figure 5.15(a), by the lines labeled 'C₂H₂+neutral'). The reaction of CN with C₄H₂ varies inversely with temperature, and contributes up to ~ 10% towards the formation of HC₅N in certain regions of the coma. The combined relative reaction rate of the dissociative recombination of C₅H₄N⁺ and HC₅NH⁺ is shown by the lines labeled 'diss. recom.' in Figure 5.15(a). In C/1996 B2 and C/2014 Q2, this varies between ~ 20 – 30% in the region of the coma from 50 km to 10⁴



Figure 5.15: Coma formation rates for the species (a) HC_5N and (b) HC_5NH^+ . The black lines (scale: left y-axis) show the net coma formation rate P_i of the species, and the colored lines (scale: right y-axis) show the relative rates of the major formation reactions. The line styles (black or colored) indicate different cometary compositions (dotted-dashed: C/1996 B2, solid: C/2012 F6, dotted: C/2013 R1 and dashed: C/2014 Q2).

km. In C/2012 F6 and C/2013 R1, the relative dissociative recombination rates are low, though they increase and contribute up to ~ 10% towards the formation of HC₅N at 10⁴ km. Beyond 10⁴ km, the relative contribution of the neutralneutral reactions decrease, while the dissociative recombination reaction rates show an increase. HC₅NH⁺ forms in the coma by the ion-neutral reactions of CH₄ with C₄N⁺, and C₂H₄ with HC₅N⁺, and the proton transfer reaction of HC₅N with HCO⁺. In the modelled coma of C/2014 Q2, C₂H₄ has a high abundance due to its presence as a parent molecule, and the reaction of C₂H₄ with HC₅N⁺ is the dominant formation mechanism at cometocentric distances < 100 km, while the proton transfer reaction becomes increasingly dominant on moving further outward. In C/1996 B2, C/2012 F6 and C/2013 R1, C₂H₄ has a low abundance, resulting in proton transfer being the predominant formation mechanism, while the contribution of the reaction of C₂H₄ with HC₅N⁺ is ≤ 0.1 %. The relative rate of the reaction of CH₄ with C₄N⁺ is $\leq 1 - 2$ % at distances > 1000 km, though it can have a high contribution close to the nucleus in C/1996 B2.

Figures 5.13 shows the variation of the flux of CH₃OCH₃, CH₃COOH and HC₅N, and their corresponding protonated forms, in the comets C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2. Gas-phase formation mechanisms produce higher quantities of CH₃OCH₃ than its isomer C₂H₅OH, even though both are created by chemical reactions undergone by their protonated forms. This is because protonated dimethyl ether has a higher formation rate than protonated ethanol. This is similar to the case of higher abundance of methyl formate as compared to ethanol. Similar to higher abundances of glycoladehyde in C/1996 B2 and C/2014 Q2, its isomer CH₃COOH has a higher abundance in these two comets, due to the presence of ethanol as a parent, while the flux of CH₃COOH in C/2012 F6 and C/2013 R1 is < 10¹³ molecules s⁻¹. It is to be noted that the coma produced abundance of CH₃COOH is higher than that of CH₂OHCHO. This is because acetic acid forms when oxygen atoms react with CH₃CHOH, which has a higher coma formation rate than the other H-abstracted ethanol radical namely CH₂CH₂OH (from which CH₂OHCHO forms).



Figure 5.16: Variation of the flux of neutral organic species and their corresponding protonated forms: (a) CH_3OCH_3 and $CH_3OCH_4^+$, (b) CH_3COOH and $CH_3COOH_2^+$, and (c) HC_5N and HC_5NH^+ , for different cometary compositions. The solid lines indicate the neutral species abundances and the dashed lines indicate the protonated species abundances.

5.4.3 Upper Limits on Formation Rates

In Table 5.2, the abundance of some of the molecules are given as upper limits. Two classes of models have been run. In one, the species whose gas phase formation is under study has its initial abundance set to zero, and upper limits are not a cause for concern in that situation. However, in the second class of model runs in which the upper limits are considered, the formation rate of a species may be affected by other molecules whose abundances are given as upper

limits. Thus, if these molecules contribute to the formation of another organic species, then the corresponding formation rates are to be taken as upper limits, while the actual formation rate is likely to be lower. The coma formation rate plots can be used to constrain the formation rate in such cases.

As an example, consider the formation of organic molecules from ethanol. Figure 5.6 shows the coma formation rate of ethanol, while Figure 5.9(d) shows the resulting abundance of ethanol when it is not outgassing from the nucleus and is formed by gas phase chemistry only. Taking these two plots in conjunction, it can be said that gas phase formation of ethanol is slow, leading to a low abundance of ethanol in the coma. Now consider the formation of other molecules from ethanol, when its outgassing from the nucleus is considered. In C/1996 B2, an upper limit on ethanol detection is reported. Thus, in Figure 5.3, the formation rates of CH_2CH_2OH and CH_3CHOH from ethanol in C/1996 B2 will be lower when its outgassing is not considered. The same can be said for the formation of HCOOH, CH_2OHCHO and CH_3COOH in C/1996 B2, as described in Section 5.4.2.

5.4.4 Formation of Glycine

Glycine (NH₂CH₂COOH) is among the most abundant amino acids that is found in CI and CM type carbonaceous chondrites. Crovisier et al. (2004) calculated an upper limit of 0.15% relative to water for glycine in the comet C/1995 O1 (Hale-Bopp). Elsila et al. (2009) report on the detection of glycine, along with its possible precursor molecules methylamine (CH₃NH₂) and ethylamine (C₂H₅NH₂), in the dust samples of comet 81P/Wild 2 brought back by the *Stardust* mission, although there was suspected terrestrial contamination. Altwegg et al. (2016) report the confirmed presence of glycine, along with CH₃NH₂ and C₂H₅NH₂, in the coma of 67P/C-G, measured by the ROSINA spectrometer aboard the *Rosetta* spacecraft. The relative abundance of glycine with respect to water was found to lie in the range 0 – 0.0025, while those of methylamine and ethylamine with respect to glycine are 1.0 ± 0.5 and 0.3 ± 0.2 , respectively. The presence of glycine in comets can be explained by its formation due to chemistry occurring in interstellar icy dust mantles or by the irradiation of ice by UV, and the subsequent preservation in cometary ices (Meierhenrich et al., 2005; Bossa et al., 2010; Garrod, 2013). A possible gas-phase formation route of glycine is acetic acid (CH₃COOH) and protonated hydroxylamine (NH₃OH⁺) reacting to form protonated glycine, which in turn undergoes recombination with electrons to form glycine, as proposed by Garrod (2013). However, the present model found this to be an insignificant mechanism of producing glycine in the coma, due to the presence of insufficient amounts of NH₃OH⁺. Garrod (2013) find that glycine can form within and upon dust-grain ice mantles by radical-radical addition mechanisms at temperatures ~ 40 - 120 K.

5.5 Summary

In this work, the chemical-hydrodynamical simulations of the coma of four Oort cloud comets is obtained, that were bright with high water production rates, so that a number of organics were detected in their comae. The coma formation pathways and rates of the CHO-bearing molecules HCOOCH₃, HCOOH, CH₃CHO, C₂H₅OH, (CH₂OH)₂ and CH₂OHCHO, and the N-bearing molecules CH₃CN, NH₂CHO and HC₃N are studied. The formation of CH₃OCH₃ and CH₃COOH, which are the isomeric forms of parent species, and the carbon chain species HC₅N is also studied. The highlights of the results are as follows:

- CH₃OH₂⁺ undergoes ion-neutral reaction with H₂CO to create HCOOCH₄⁺, which in turn undergoes dissociative recombination to form HCOOCH₃. Protonation of HCOOCH₃ by H₃O⁺ and HCO⁺ ions results in its cyclic conversion to HCOOCH₄⁺ in the outer regions of the coma.
- 2. HCOOH forms in the coma when its protonated form HCOOH₂⁺ undergoes proton transfer reactions with neutral molecules such as CH₃OH, NH₃ and H₂O, and dissociative recombination with electrons. HCOOH₂⁺ itself forms by the radiative association of H₂O and HCO⁺. In comets where C₂H₅OH is present as a parent, most of the HCOOH forms in the coma by the reaction of CH₃CHOH with atomic oxygen.

- 3. CH₃CHO mainly forms by neutral-neutral reactions, while dissociative recombination of the ions CH₃CHOH⁺, C₂H₅OH⁺ and C₂H₅OH₂⁺ contribute up to 40% to the CH₃CHO formation rate in some regions of the coma. CH₃CHOH⁺ forms by a set of ion-neutral reactions, including methyl cation and proton transfer reactions.
- 4. C_2H_5OH forms in the coma when its protonated form $C_2H_5OH_2^+$ undergoes proton transfer with NH₃ in the inner coma regions, and dissociative recombination with electrons in the outer region. $C_2H_5OH_2^+$ forms by the radiative association of C_2H_4 with H_3O^+ , and H_2O with $C_2H_5^+$. Similar to methyl formate, C_2H_5OH also undergoes protonation reactions to get cycled and create $C_2H_5OH_2^+$, though the relative rate of this process towards the formation of $C_2H_5OH_2^+$ is low.
- 5. $(CH_2OH)_2$ forms by the combination of two CH_2OH radicals at distances < 5000 km, and by dissociative recombination of $(CH_2OH)_2H^+$ in the outer coma regions. There is a sharp reduction in the $(CH_2OH)_2$ formation rate in the outer high temperature region of the coma, where CH_2OH radicals are rapidly destroyed by water. $(CH_2OH)_2H^+$ is created when $(CH_2OH)_2$ undergoes protonation reactions with H_3O^+ and HCO^+ ions.
- 6. CH₂OHCHO forms in the coma by the reaction of CH₂CH₂OH radicals with oxygen atoms. The coma-formation rate of CH₂OHCHO is high in comets where ethanol is present as a parent. Similar to the creation of protonated ethylene glycol, CH₂OHCHOH⁺ is created when CH₂OHCHO undergoes protonation reactions with H_3O^+ and HCO⁺ ions.
- 7. $\rm CH_3CN$ is primarily produced in the coma by the dissociative recombination of $\rm CH_3CNH^+$. Other neutral-neutral and ion-neutral reactions contribute to the formation of $\rm CH_3CN$ at distances > 10⁴ km and < 50 km. $\rm CH_3CNH^+$ forms in the coma by the methyl cation transfer reaction of $\rm CH_4^+$ with HCN, with some contribution coming from the radiative association reactions of HCN and HNC with $\rm CH_3^+$ ions.
- 8. NH₂CHO forms mainly by the neutral-neutral reaction of NH₂ with H₂CO.

In the outer region of the coma, the abundance of H_2CO reduces due to its destruction by photodissociation. In this region, there is an increase in the relative contribution of the dissociative recombination of NH_2CHOH^+ towards the NH_2CHO formation rate. The protonation of NH_2CHO by H_3O^+ and HCO^+ forms NH_2CHOH^+ in the coma.

- 9. HC₃N forms in the coma by the bimolecular reactions of carbon chain molecules C₂H and C₂H₂ with the N-bearing neutrals CN, HCN and HNC. The reactions of the carbon chain radical C₃N with the hydrocarbons C₂H₂ and C₂H₆, and the dissociative recombination of HC₃NH⁺ also create HC₃N in some regions of the coma. HC₃NH⁺ is created in the coma by a number of ion-neutral reactions, including protonation reactions undergone by HC₃N.
- 10. Methyl cation transfer reaction from CH₃OH₂⁺ to CH₃OH creates CH₃OCH₄⁺, which undergoes dissociative recombination to form CH₃OCH₃. The reaction of atomic oxygen with CH₃CHOH radicals produces CH₃COOH, and the coma formation rate is high when ethanol is present as a parent.
- 11. HC₅N forms by a number of neutral-neutral reactions involving carbon chain species, with dissociative recombination reactions contributing up to $\sim 30\%$. HC₅NH⁺ mainly forms by the protonation of HC₅N, while other ion-neutral reactions contribute at lower cometocentric distances.

Chapter 6

Cometary Organics: Efficiency of Coma Chemistry

The origin of organics in comets can be traced to the interstellar medium (ISM) at least partially, if not completely. Over 250 molecular species have been observed in the ISM, and many of these species are complex organic molecules or COMs (Herbst & Garrod, 2022). As discussed in Chapter 1, the number of volatile parent species (namely those present in the ices in the interior of the cometary nucleus), that are currently known, is 72, out of which 37 are complex organic molecules. This includes those species that have been only tentatively detected. It is pertinent to ask if all the known cometary volatiles form exclusively via ice chemistry, or if a fraction of them is formed via gas-phase coma chemistry. The four comets C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy) and C/2014 Q2 (Lovejoy), whose gas-phase organic formation mechanisms are discussed in Chapter 5, are revisited in this chapter. The contribution of coma chemistry, and the importance of the various type of gas-phase reactions towards the formation of cometary organics in these comets, is explored.

6.1 Clues from the Interstellar Medium

The origin of the material incorporated in comets is still a subject of debate. Abundance measurements and isotopic composition of the molecules detected in 67P/C-G indicate that a part of the cometary ices have prestellar origins (Hoppe et al., 2018). It is suggested that micron sized grains in prestellar cores transform into millimeter sized dust particles seen in protoplanetary disks (Pagani et al., 2010; Miotello et al., 2014), which subsequently assemble into meter sized planetesimals that form comets. Drozdovskaya et al. (2016) find that dynamic infall and the chemistry en route to the midplanes of protoplanetray disks may alter some of the prestellar abundances. This includes an increase in the CO₂ abundance by grain-surface reactions and the conversion of CH₃OH into complex organic ices. Once the planetesimals assemble to form kilometer sized cometary bodies, they are unlikely to undergo significant thermal processing. Thus, bulk cometary ices are likely to resemble the molecules found in disks and prestellar cores (Pontoppidan et al., 2014).

It is well-known that in the interstellar medium, organic molecules can form efficiently on the surface of dust grains. These surface reactions proceed via the addition of species such as hydrogen at low temperatures (~ 10 K), and the subsequent addition of other atoms and radicals as the grain temperature rises (Herbst & van Dishoeck, 2009; Oberg et al., 2009; Oberg, 2016; Herbst & Garrod, 2022). A similar prescription can be used to explain the formation cometary organics in low temperature ices. For example, organic molecules such as CH_3OH , C₂H₅OH, CH₃CHO, HCOOH and NH₂CHO that are found in comets, share a common pathway of formation, starting from CO ice. The addition of hydrogen atoms to CO molecules frozen on cold dust grains results in the production of the formyl radical (HCO). Subsequently, the addition of heavy atoms and/or further addition of hydrogen atoms results in the synthesis of heavier organics (Charnley & Rodgers, 2008; Herbst & van Dishoeck, 2009). Thus, the formation of CH₃OH, HCOOH, NH₂CHO, CH₃CHO and C₂H₅OH can proceed as CO $\xrightarrow{\text{H}}$ $\mathrm{HCO} \xrightarrow{\mathrm{H}} \mathrm{H_2CO} \xrightarrow{\mathrm{H}} \mathrm{CH_2OH} \xrightarrow{\mathrm{H}} \mathrm{CH_3OH}, \ \mathrm{HCO} \xrightarrow{\mathrm{O}} \mathrm{HCOO} \xrightarrow{\mathrm{H}} \mathrm{HCOOH}, \ \mathrm{HCO} \xrightarrow{\mathrm{N}}$ HNCO $\xrightarrow{2H}$ NH₂CHO, and HCO \xrightarrow{C} HCCO \xrightarrow{H} CH₂CO $\xrightarrow{2H}$ CH₃CHO $\xrightarrow{2H}$ C_2H_5OH . An intermediate that is created in the hydrogenation of H_2CO to CH_3OH is the hydroxymethyl radical (CH_2OH). Radical-radical recombination reactions undergone by HCO and CH₂OH results in the formation ethylene glycol and glycolaldehyde at low temperatures (Butscher et al., 2015). Many of these
formation reactions have been experimentally verified (for example, Linnartz et al., 2015).

In addition to the formation of organics from CO ice, surface chemistry can also lead to the formation of hydrocarbons. CH_4 is most likely to form by hydrogen addition reactions with atomic carbon on the surface of dust grains (Qasim et al., 2020), while C_2H_2 can form when atomic carbon reacts with molecular hydrogen (Martínez et al., 2020). The addition of hydrogen atoms to simple hydrocarbons such as C_2H_2 by grain-surface reactions (Tielens, 1992; Mumma et al., 1996; Kobayashi et al., 2017) or the irradiation of CH_4 ices (Gerakines et al., 1996; Mumma et al., 1996; Bennett et al., 2006) can form C_2H_6 in comets. More complex hydrocarbons can in turn form by the irradiation of C_2H_6 (de Barros et al., 2016) and C_2H_2 (Frenklach & Feigelson, 1989; Cernicharo, 2004).

The relative abundance with respect to water of cometary CO varies over a wide range. de Val-Borro et al. (2018) compared the mixing ratios of organic species in comets with their CO abundance for several comets, to investigate the likelihood that they may have originated in cold interstellar dust grains (for example, Disanti & Mumma, 2008). The mixing ratio of CH₃OH is independent of the CO abundance, and de Val-Borro et al. (2018) suggest that this is because the efficiency of the formation of CH₃OH is high, and its probability of formation is limited only by the surface availability of hydrogen atoms. Laboratory studies too have confirmed high efficiencies of the conversion of CO to CH₃OH. de Val-Borro et al. (2018) do not observe any definite relation in the abundances of CH₃CHO and C₂H₅OH with the CO abundance, and propose that there may be alternative formation pathways for them, other than the hydrogenation of CO ice. One of these alternative mechanisms might be a sequence of hydrogenation and oxidation reactions starting from C₂H₂ (for example, Charnley, 2004), though this is unsupported by the trend of mixing ratios compared to C₂H₂.

The importance of gas-phase reactions in the production of organics in the interstellar medium cannot be discounted. The detection of acetaldehyde (CH₃CHO), dimethyl ether (CH₃OCH₃), methyl formate (HCOOCH₃), and ketene (CH₂CO) in the cold prestellar core L1689B at temperatures of around 10 K (Bacmann et al., 2012) suggests that gas-phase formation may be important, since grain-surface chemistry requires temperatures of around 30 K. Similarly, the discovery of complex organic molecules in the cold and dense core B1-b (Cernicharo et al., 2012), the solar-type protostar IRAS 16293-2422 (Jaber et al., 2014) and the prestellar core L1544 (Jiménez-Serra et al., 2016) are difficult to explain if the hypothesis that the COMs are exclusively formed on the dust-grain surface is correct. All of these sources require some involvement of gas-phase mechanisms for the creation of COMs.

A similar scenario can exist for cometary organics as well. Cordiner & Charnley (2021) found that HC_3N and NH_2CHO can be efficiently produced via two-body neutral-neutral gas-phase reactions, involving abundant coma species. These reactions have been discussed in Chapter 5. Cordiner & Charnley (2021) propose that the presence of extended sources in the coma can synthesize sufficient quantities of HC_3N and NH_2CHO , that can match previously reported abundances of these species. Thus it is evident that cometary organics formed by gas-phase coma chemistry may have some contribution to the observed organic abundances.

6.2 Coma Abundances due to Gas-Phase Chemistry

Figures 6.1 and 6.2 show the variation of the flux of assorted neutral organic molecules, in the comets C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2. The formation rates and mechanisms of these organics in the gas-phase coma are discussed in Chapter 5. Two sets of species abundances are shown in Figures 6.1 and 6.2. The first are the species abundances shown by the solid lines, that are the result of gas-phase chemistry creating the respective organic species in the coma. The second set of abundances are the ones shown by the dashed lines, which indicate the species flux due outgassing from the nucleus, i.e. the parent species abundance. Not all the species shown in Figures 6.1 and 6.2 are present as parent species in each of the four comets, as can be seen from Table 5.2.

The dashed lines show that in most cases, parent species have nearly con-



Figure 6.1: Variation of the flux of the CHO-bearing organic species (a) $HCOOCH_3$, (b) HCOOH, (c) CH_3CHO , (d) C_2H_5OH , (e) $(CH_2OH)_2$, and (f) CH_2OHCHO , for different cometary compositions. The solid lines indicate the species abundances due to their formation in the coma by gas-phase chemistry. The dashed lines indicate the species abundances in the coma due to outgassing from the nucleus.



Figure 6.2: Variation of the flux of the N-bearing organic species (a) CH_3CN , (b) NH_2CHO , and (c) HC_3N , for different cometary compositions. The solid lines indicate the species abundances due to their formation in the coma by gas-phase chemistry. The dashed lines indicate the species abundances in the coma due to outgassing from the nucleus.

stant flux throughout the modeled region of the coma and survive up to 10^5 km. This is consistent with photochemical reactions proceeding at a dissociation/ionization rate $\leq 10^{-5}$ s⁻¹, and a gas outflow velocity of the order of ~ 1 km s⁻¹. The species CH₃CHO, CH₃CN and HC₃N begin to show a decay in their 'parent-molecule flux' beyond 10^4 km, due to higher photolytic decomposition rates. HCOOH is also an exception, since it photodissociates at a particularly high rate, of the order ~ 10^{-3} s⁻¹, resulting in a scale-length of a few thousand kilometers.

The solid lines, which represent the flux profiles of the molecules forming in the coma, show an initial rise. At low cometocentric distances, the density of the coma is high, and molecules quickly form due to active gas-phase coma chemistry. Thereafter, on moving further outward, the timescales for these species to form by gas-phase reactions become more than the dynamic timescale, and the flux profiles tend to flatten. At distances greater than 10^4 km, the flux profiles of CH₃CHO, CH₃CN and HC₃N show a dip, due to photolytic effects. This is similar to the case when they are present as parent molecules, and this effect is again stronger in HCOOH. Ignoring photolytic effects, the flux of the parent species are within 1-2 orders of magnitude of each other. This is consistent with a variation of 1-2 orders of magnitude in the mixing ratios of these organics, as seen in Table 5.2. On the other hand, the flux of the coma produced molecules show a wide variation over many orders of magnitude. Gas-phase chemical reactions do not form all the molecules with the same degree of efficiency, and some molecules have higher formation rates as compared to others. A comparative description of the species abundances resulting from gas phase chemistry as opposed to the abundances of the selfsame species outgassing from the nucleus as parent molecules is as follows.

- 1. The parent molecular flux of HCOOCH₃ lies in the range $1.8 \times 10^{26} 1.1 \times 10^{27}$ molecules s⁻¹ for the different comets. The coma produced flux of HCOOCH₃ acquires a constant value beyond ~ 1000 km, ranging from $8.6 \times 10^{23} 1.2 \times 10^{25}$ molecules s⁻¹. For the comets C/2012 F6 and C/2013 R1, the flux of HCOOCH₃ as shown by the dashed lines are upper limits given by observation, and the actual outgassing rate from the nucleus may be lower. The fluxes due to coma chemistry, as shown by the solid lines, constrain the lower abundance limit of HCOOCH₃ in the coma.
- 2. The production rate of HCOOH from the nucleus varies between $(1.1 4.7) \times 10^{26}$ molecules s⁻¹ for the different cometary compositions. Beyond ~ 3000 km, this flux drops sharply due to rapid photodissociation. The flux of HCOOH molecules created in the coma peaks around 1000 3000 km, acquiring a value ranging from $10^{20} 10^{23}$ molecules s⁻¹. Most of the

HCOOH molecules originating from the nucleus are destroyed in the outer region of the coma, yet they continue to form due to gas phase chemistry. Thus, in a spatially resolved coma, the HCOOH molecules in the outer coma are primarily those originating from gas-phase chemistry.

- 3. The flux of CH_3CHO due to outgassing from the nucleus lies in the range of $9.2 \times 10^{25} - 4.7 \times 10^{26}$ molecules s⁻¹ for the different comets. The coma production rate of CH_3CHO acquires a maximum value in the region of the coma from $10^3 - 10^4$ km, and the values lie between $3.6 \times 10^{23} - 4.1 \times 10^{24}$ molecules s⁻¹. Here again, the CH_3CHO abundances in C/1996 B2 and C/2012 F6 are observational upper limits, which can be constrained by the coma-produced fluxes shown by the solid lines.
- 4. C_2H_5OH is present as a parent molecule only in two comets, namely C/1996 B2 and C/2014 Q2, with production rates of 3.5×10^{26} and 5.0×10^{26} molecules s⁻¹ respectively. The production rate of C_2H_5OH due to coma chemistry acquires a constant value in the outer region of the coma, lying in the range $7.1 \times 10^{15} - 5.0 \times 10^{18}$ molecules s⁻¹. This is lower than the nucleus outgassing rate, by many orders of magnitude. Thus, gas-phase chemistry is not efficient in producing C_2H_5OH in the coma.
- 5. The parent molecular flux of $(CH_2OH)_2$ lies in the range of $2.0 \times 10^{26} 1.6 \times 10^{27}$ molecules s⁻¹ for the different comets. The production rate of $(CH_2OH)_2$ due to chemical reactions in the coma acquires a peak value lying in the range of $3.6 \times 10^{17} 4.7 \times 10^{19}$ molecules s⁻¹. In this case too, gas-phase chemistry does not seem to be efficient.
- 6. The parent molecular flux of CH₂OHCHO lies in the range 6.5 × 10²⁵ − 6.5 × 10²⁶ molecules s⁻¹ for the different comets. The peak value of the production rate of CH₂OHCHO forming in the gas-phase coma of C/1996 B2 and C/2014 Q2 is ~ 10²² molecules s⁻¹. In C/2012 F6 and C/2013 R1, the flux of CH₂OHCHO due to coma chemistry is even lower, of the order ≤ 10¹² molecules s⁻¹ (not shown in Figure 6.1). Though gas-phase chemistry may produce some quantities of CH₂OHCHO in C/1996 B2 and

C/2014 Q2, it is ineffective in producing observable levels of CH_2OHCHO in C/2012 F6 and C/2013 R1.

- 7. CH₃CN is present as a parent molecule in C/1996 B2 and C/2014 Q2, with production rates of 1.7×10^{25} and 6.1×10^{25} molecules s⁻¹ respectively. The production rate of CH₃CN due to chemical reactions in the coma lies in the range from $9.2 \times 10^{20} - 1.2 \times 10^{22}$ molecules s⁻¹.
- 8. The parent molecular flux of NH₂CHO lies in the range 1.9×10²⁵-2.0×10²⁶ molecules s⁻¹ for the different comets. The flux of NH₂CHO forming in the coma acquires a constant value beyond ~ 1000 km, lying in the range ~ 5.0×10²³-9.7×10²⁵ molecules s⁻¹. NH₂CHO has a high coma formation rate, and the abundance of the coma-produced NH₂CHO in C/2012 F6 is only slightly less than its production from the nucleus. Besides, the amount of NH₂CHO produced in the coma of comets C/2012 F6 and C/2014 Q2, that exhibit higher activity, is nearly equal to or even exceeds the amount of NH₂CHO outgassing from the nucleus of the lower activity comet, namely C/2013 R1.
- 9. The flux of HC₃N outgassing from the nucleus of C/1996 B2 is 1.4 × 10²⁶ molecules s⁻¹, while it is 8.1 × 10²⁴ molecules s⁻¹ in the case of C/2014 Q2. The production rate of HC₃N acquires a peak value around ~ 3000 5000 km, lying in the range ~ 3.5 × 10²² 5.2 × 10²³ molecules s⁻¹ for different cometary compositions. The outgassing rate of HC₃N from the nucleus of C/1996 B2 is an upper limit, which can be constrained by the comaproduced value, as in the case of other molecules discussed previously.

6.3 Role of Gas Phase Chemistry

6.3.1 Chemical Reactions Forming Organic Species

The gas-phase reactions that lead to the formation of organic molecules and their protonated forms can be broadly divided into four categories: (1) neutral-neutral bimolecular reactions, (2) ion-neutral bimolecular reactions, (3) dissociative re-

combination reactions, and (4) radiative association reactions. As seen in Section 5.4.2, the relative contribution of each of these chemical processes towards the species formation rates generally varies with distance from the nucleus. This is because the reaction rates are dependent on the abundances of the reacting species, and their temperature, which vary in different regions of the coma.

6.3.1.1 Neutral-Neutral Bimolecular Reactions

A new reaction scheme for the formation of organics by the chemical activation of ethanol was added to our gas-phase network (Skouteris et al., 2018), as discussed in Chapter 2. The H-abstraction of ethanol can occur at three different sites, leading to the formation of the radicals CH₂CH₂OH, CH₃CHOH and CH₃CH₂O, though CH_3CH_2O has not been experimentally detected (Caravan et al., 2015). The branching ratio for the formation of CH₂CH₂OH and CH₃CHOH due to the H-abstraction reaction with OH shows some variation with temperature, and a value of 0.1:0.9 is chosen. Subsequently, an O atom can get added to these radicals, resulting in the formation of an intermediate, which can finally result in the cleavage of the C-C bond, or the elimination of an H atom or OH radical. Glycolaldehyde forms as a result of the H-atom elimination of the intermediate formed from CH₂CH₂OH, while acetic acid forms from a similar process undergone by the intermediate resulting from CH_3CHOH . The C-C bond cleavage of the CH₃CHOH and O intermediate results in the creation of formic acid, while OH-radical elimination forms acetaldehyde. Our model results show that if ethanol is sublimating from the nucleus, i.e. it is a parent molecule, then this reaction scheme is an efficient way of forming organic molecules in the coma. However, it is to be noted that the input abundance of ethanol in C/1996 B2 is the observational upper limit derived for this comet, and the actual production rate of ethanol from the nucleus can be lower than the limit given in Table 5.2. Hence the abundances obtained for the organics forming directly (CH₂CH₂OH and CH₃CHOH) or indirectly (e.g. HCOOH, CH₂OHCHO) from ethanol in C/1996 B2 are also upper limits. A similar H-abstraction reaction undergone by methanol results in the creation of CH_2OH radicals, which form ethylene glycol in the coma. Figure 6.3 shows the number densities of the radicals



Figure 6.3: Cometocentric distance variation of the number densities of the H-abstracted radicals CH_2CH_2OH , CH_3CHOH and CH_2OH , and the species from which they form namely C_2H_5OH and CH_3OH , for the comets (a) C/1996 B2, (b) C/2012 F6, (c) C/2013 R1, and (d) C/2014 Q2.

created due to H-abstraction reactions, and the species from which they form, namely ethanol and methanol. The relative abundance of ethanol with respect to water in C/1996 B2 is nearly double that of C/2014 Q2, yet the water production rate in C/2014 Q2 is more than double of that in C/1996 B2. This implies that the outgassing rate of ethanol from the nucleus is higher in the case of C/2014 Q2, resulting in the coma formation rate of CH₂CH₂OH and CH₃CHOH being slightly more. Similarly, the relative abundance of methanol with respect to water in C/2012 F6 is the lowest, yet it has higher activity, and thus the abundance of CH₂OH is also higher in this comet.



Figure 6.4: Cometocentric distance variation of the number densities of neutral radicals bearing carbon atoms, for the comets (a) C/1996 B2, (b) C/2012 F6, (c) C/2013 R1, and (d) C/2014 Q2.

Neutral-neutral reactions also play an important role in the creation of carbon-chain bearing organic molecules such as CH_3CHO , HC_3N and HC_5N . The

saturated and unsaturated hydrocarbons namely CH_4 , C_2H_6 , C_2H_2 and C_2H_4 are present as parent molecules at abundances varying roughly between 0.1 - 1%of H₂O. They photodissociate to create carbon-bearing radicals such as CH, C₂, C_2H and C_2H_5 . These radicals react with one another and with other neutral species to create carbon-chain radicals such as C_4H_2 (formed from C_2H reacting with C_2H_2) and C_3N (formed from C_2 reacting with HCN and HNC), to name a few. All of these radicals contribute to the formation of carbon-chain organics, and the number densities of these carbon-bearing radicals are shown in Figure 6.4. The number densities of the radicals bearing two or more carbon atoms are higher in C/1996 B2, since the relative abundance of C_2H_2 (from which they are created) is higher in C/1996 B2 than that in the other comets, by atleast a factor of five.

6.3.1.2 Ion-Neutral, Proton Transfer and Radiative Association Reactions

Ion-neutral reactions lead to the formation of both neutral organic molecules and their protonated forms. Proton transfer reactions are a special class of ion-neutral reactions, between an H⁺-bearing cation (protonated species) and a neutral molecule. The protonated organic species themselves form by (1) radiative association reactions of ion and neutral species, (2) proton transfer reactions between H⁺-bearing cations and neutral molecules having higher proton affinity, and (3) methyl cation transfer reactions.

In general, the ion that participates in a radiative association reaction is itself formed by the protonation of a neutral molecule, and thus carries an extra H⁺ cation. For example, in the case of the formation of HCOOH_2^+ by the association of H₂O and HCO^+ , the HCO^+ ions are formed by the protonation of CO. Thus, an H⁺-bearing species or protonated species combines radiatively with a neutral molecule, and the result is the formation of a heavier H⁺-bearing ion. In the formation of HCOOH_2^+ and $\text{C}_2\text{H}_5\text{OH}_2^+$ ions, radiative association is the predominant formation pathway, with minor contributions from proton transfer reactions. The Arrhenius coefficients α for the proton transfer reactions are generally higher than those of radiative association reaction. However, the neutral molecules that participate in radiative association are generally parent species, namely H_2O and C_2H_4 , and thus they have high abundance.

If a protonated species forms by a methyl cation transfer reaction, then this mechanism will have a larger contribution than radiative association, in most regions of the coma. This can be seen in the formation of CH_3CNH^+ and $CH_3OCH_4^+$. Similar to the case of the proton transfer reactions, the Arrhenius coefficients α are also higher for methyl cation transfer as compared to radiative association. In addition, the neutral molecules that participate in the methyl cation transfer reactions, namely HCN and CH_3OH are also parent species. This establishes that not only the rate coefficients, but also the availability of reacting species play a key role in determining the relative contribution of a reaction towards species formation.

6.3.1.3 Dissociative Recombination Reactions

The dissociative recombination of protonated organic species result in the formation of the corresponding neutral molecules. These reactions are generally dependent on temperature and may proceed via multiple branches, such as $C_2H_5OH_2^+$ dissociating to form both C_2H_5OH and CH_3CHO . A neutral organic molecule can form due to dissociative recombination of other ions as well, apart from its protonated form. For example, CH_3CHO forms by the dissociative recombination of its protonated form CH_3CHOH^+ , as well as by similar reactions undergone by $C_2H_5OH^+$ and $C_2H_5OH_2^+$ ions. In some cases, dissociative recombination is the only mechanism by which organic molecules are created in the coma. This may be either due to low abundance of other reacting species, as in the case of the formation of HCOOCH₃, or the absence of other formation pathways, similar to the case of CH_3OCH_3 formation. The contribution of dissociative recombination reactions towards organic formation is less in the inner regions of the coma, but increases on moving outwards, due to increasing flux of photoelectrons.

6.3.2 Effect of Temperature on Reaction Rates

The parameters α , β and γ are required to calculate the rate coefficients of the temperature-dependent reactions. In the Arrhenius formula for calculating rate coefficients, the values of α for the dissociative recombination reactions are generally larger than those for the proton transfer reactions by 2 to 4 orders of magnitude, while $\beta \sim -0.5$ and $\gamma = 0$ in general. As previously discussed, the different fluids considered in the coma model have separate temperatures, and in any region of the coma, the temperature-dependent collisional reactions occur at an effective temperature $T_{\rm eff}$ (Flower et al., 1985), such that

$$T_{\rm eff} = \frac{m_k T_l + m_l T_k}{m_l + m_k}.$$
 (6.1)

In the above equation, T_l and T_k are the respective fluid temperatures to which the reacting species having masses m_l and m_k belong. The reactions having electrons as one of the reactants have $T_{\text{eff}} \approx T_e$, since the mass of the electron is much less than the mass of the other reacting species. The temperature dependence of the reactions can cause a change in the reaction rate coefficients by 1 to 2 orders of magnitude in the different regions of the coma.

In general, the dissociative recombination reactions would proceed at a faster rate as compared to the proton transfer reactions, under the temperature conditions of the coma. However, it is seen that if both these types of reactions contribute to the formation of a neutral species, then the higher contribution in the inner regions of the coma is from the proton transfer reactions, while the recombination reactions become relatively more dominant on moving outwards. This is because the percentage contribution of each reaction towards the formation of a molecule depends on the rate constants and temperature, and also on the availability of the reacting species. The flux of photoelectrons required for ions to undergo recombination is low in the inner regions of the coma, within a few hundred kilometers from the nucleus, and this results in lower relative rates of these reactions. As the distance from the nucleus increases, the increasing electron flux results in an increase in the relative reaction rate of the dissociative recombination reactions.

6.4 Summary

A comparison is made of the abundances of organic species forming in the coma of the comets C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy) and C/2014 Q2 (Lovejoy). The highlights are as follows:

- 1. It is found that HCOOH, HCOOCH₃, CH₃CHO, CH₃CN, HC₃N, and NH₂CHO can have increased production rates due to incorporation of new pathways which can account atleast partially towards their total production rate. However, C₂H₅OH, (CH₂OH)₂, CH₂OHCHO and glycine formation is inefficient, and may be exclusively dependent on the surface chemistry.
- 2. Neutral-neutral synthesis of organic molecules from the radicals CH₂CH₂OH and CH₃CHOH, created due to H-abstraction of ethanol, is an efficient gas-phase formation mechanism of organic molecules, if ethanol is present as a parent molecule.
- 3. Proton transfer and dissociative recombination reactions undergone by the protonated organics are important mechanisms for the formation of neutral organic molecules. Some neutral-neutral reactions involving radicals created due to photodissociation of parent species also have a significant contribution, particularly in the formation of carbon-chain organics.
- 4. The protonated species themselves form by radiative association of an ion and a neutral species, methyl cation transfer reaction of $CH_3OH_2^+$ with a neutral molecule, or by other ion-neutral bimolecular reactions. In some cases, an organic molecule forming from its protonated version, undergoes proton transfer with ions such as H_3O^+ and HCO^+ to get cycled back into its protonated form.
- 5. The net rates of formation of organic molecules, and their abundances are dependent on a host of factors. This includes the temperature of the reacting species, the relative abundances of the reactants, and also the initial cometary composition.

Chapter 7

Conclusions, Implications and Future Work

7.1 Conclusions

One of the fundamental questions of planetary sciences is to understand the primordial composition and the evolution of planetary systems like ours. In various phases of the evolution of planetary systems, starting from the gravitational collapse of interstellar material, simple through complex molecules are created in abundance. Thus, an increase in molecular complexity is a part of this grand journey that results in an evolved system like our Solar System. Comets are made up of the leftover volatile material that are the relics of the protoplanetary disk that formed the Solar System. The frozen volatile ices in the cometary interiors can represent the oldest and largely unprocessed material in the Solar System. This make comets the best candidates to study the early formation history of the Solar System. Although measurements of the D/H ratio indicate that comets contributed to a relatively small fraction of the terrestrial water, yet they probably delivered organics and prebiotic material to the planet by impact processes (Chyba et al., 1990; Ehrenfreund et al., 2002; Rubin et al., 2019). Organics are the seeds for creating molecules of biological interest, and investigations of their formation in comets provide clues in understanding the prebiotic chemistry.

Most of our knowledge about comets comes indirectly by studying the

cometary atmosphere, the coma. An understanding of the physical and chemical properties of the coma can be achieved with the help of modeling studies. In this thesis, a combined chemical and hydrodynamical model for the gas phase cometary atmosphere has been built, which is employed for modeling studies of the comae of the interstellar comet 2I/Borisov, a Halley-type comet, C/1996 B2 (Hyakutake), C/2012 F6 (Lemmon), C/2013 R1 (Lovejoy) and C/2014 Q2 (Lovejoy).

The modeling results of Chapter 4 show that in the coma of 2I/Borisov, the electron temperature decouples from the neutral fluid temperature at a smaller cometocentric distance as compared to a typical Solar System comet of the Halley-type composition. The presence of a large amount of CO reduces the overall efficiency of inelastic collisions of electrons with the neutral fluid, which is what causes the decoupling of the electron temperature sooner in 2I/Borisov. At large cometocentric distances, the rate of cooling of the electron fluid due to electron-CO inelastic collisions is equal to, or even higher than the electron-H₂O inelastic collisions. The high CO abundance results in larger abundances of CO⁺ and HCO^+ ions in the coma. The presence of these two ions in large quantities affect the formation and destruction rates of H_2O^+ , H_3O^+ , N-bearing ions and organic ions. It is predicted that many of the organic species abundances is higher in a 2I-type comet as opposed to a Halley-type comet. This is because a high abundance of HCO^+ ions (due to high CO abundance) results in the creation of larger quantities of $CH_3OH_2^+$, which is the starting point for creating other organic ions and neutral species. Thus it can be concluded that the high CO abundance in 2I/Borisov has significant bearing in affecting both the physical and the chemical properties of the coma.

From the modeling results on the gas phase formation of organics in the comets C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2, as discussed in Chapter 5, it is predicted that proton transfer reactions lead to the formation of neutral organic species such as HCOOH, CH₃CHO and C₂H₅OH. Neutral organics are also created by the dissociative recombination of their protonated forms, though these reactions are generally important at large cometocentric distances, where the electron temperatures and flux of photoelectrons is higher.

CH₂CH₂OH and CH₃CHOH radicals created by the H-abstraction of ethanol have high abundance when ethanol is present as a parent molecule, and reactions of these two radicals with atomic oxygen are efficient mechanisms for the formation of neutral organics. Neutral-neutral reactions involving carbon chain radicals also form organics in the coma.

The comparative study of the organic abundances due to gas-phase chemistry, as opposed to their abundances due to outgassing from the nucleus is done in Chapter 6. It is seen from the neutral organic abundances in the coma of the comets C/1996 B2, C/2012 F6, C/2013 R1 and C/2014 Q2 that some of the organic molecules that originate from the nucleus, can also form efficiently in the coma. These molecules are HCOOH, HCOOCH₃, CH₃CHO, CH₃CN, HC₃N and NH₂CHO, and their formation in the gas phase can partially account for the total cometary production rate. Other molecules such as C₂H₅OH, (CH₂OH)₂, CH₂OHCHO and glycine do not form efficiently, due to lack of sufficient gas phase formation pathways. The observational upper limits on the abundances of some of the organic species can be constrained by the gas phase chemistry.

7.2 Implications

Numerical simulations by Levison et al. (2010) imply that a considerable fraction of Oort cloud comets are from the protoplanetary disks of other stars. The properties of such objects that would set them apart from Solar System comets are unclear. The orbit of comet 2I/Borisov causes it to be conclusively identified as originating from outside the Solar System. 2I/Borisov exhibits properties that are similar to Solar System comets such as similar abundances of HCN and the depletion of carbon-chain radicals, though the two major characteristics that set it apart are the high CO/H_2O ratio and the high elemental abundance of carbon with respect to oxygen (Bodewits et al., 2020). The study of this comet paves the way for the identification and investigation of Oort cloud comets that may have had origins outside the Solar System.

The volatile composition of 2I/Borisov also provides some insight into the prevailing conditions of its host system. The host system may have been chemi-

cally different from the Solar System in order for the comet to have such a large CO abundance relative to H_2O . Besides, the comet must have formed outside the CO snowline in order to preserve the large CO/H₂O ratio. The detection of HCN and CO indicates that simple C, N, and O bearing molecular ices were in abundance in the formation environment of comet 2I/Borisov. Studies are already underway to correlate the compositions of Solar System comets to protoplanetary disks (Drozdovskaya et al., 2019; Eistrup et al., 2019), which will aid in discerning the primordial disk composition. The volatile composition of comet 2I/Borisov and its high CO/H₂O ratio as compared to Solar System comets provides insights into the prevailing conditions of its host system. 2I/Borisov was faint and not many volatiles could be detected, though a comparative study of the interstellar comet with Solar System comets will aid in making a chemical inventory of 2I/Borisov's natal disk, including possible organics that could be present.

The elemental budget of organic molecules consists mostly of carbon, hydrogen, oxygen and nitrogen, with small quantities of heavy elements like phosphorus and sulfur. These elements are found in abundance in astrochemical regions in general, and cometary environments in particular. This raises the question of how organic chemistry works in these environments and what are the molecular abundances we can expect to find. Answering these questions will prove vital in understanding the evolutionary history of the Solar System, and the exogenous delivery of organics to terrestrial planets.

Many of the organic molecules that have been detected in comets have also been found in the interstellar medium, particularly in hot cores close to massive young stars. A comparison of the range of abundances of organic molecules in comets, with the abundances in low and high mass protostars, reveals similarities (Biver et al., 2015; Biver & Bockelée-Morvan, 2019). Various reaction pathways have been suggested to explain organic formation in the interstellar medium (Herbst & Garrod, 2022). Most of these studies propose the formation of organics on cold grain surfaces by the addition of hydrogen, and subsequent addition of other atoms and radicals. However, there are an increasing number of studies that demonstrate the importance of gas-phase chemical reactions towards the formation of organic molecules (Vasyunin & Herbst, 2013; Balucani et al., 2015; Vasyunin et al., 2017; Skouteris et al., 2018). New experimental results show that many reactions that were previously considered to be unimportant because of the presence of energy barriers, are actually quite promising. The requirement of the rate coefficients for more number of chemical reactions to explain the formation of organics in cometary environments provides an incentive to undertake theoretical and experimental studies to expand the gas-phase networks. Laboratory studies and rate measurements of additional organic forming reactions will aid in further understanding the chemistry of organic species, including molecules of increasing complexity. Modeling studies of cometary organics can also be used to prepare a template for future in situ measurements.

7.3 Future Work

The chemical-hydrodynamical model that has been built as part of this thesis work can potentially be used to undertake further studies of the cometary atmosphere. Below are listed some of the projects that will be undertaken in the imminent future.

1. A particularly unique comet is the Solar System comet C/2016 R2 (PanSTARRS) that is highly CO dominant, with a CO abundance that is nearly four orders of magnitude higher than H₂O (Wierzchos & Womack, 2018; McKay et al., 2019). The N₂/CO ratio in this comet is also one of the highest reported amongst cometary values (Cochran & McKay, 2018). These compositional peculiarities can have considerable bearing on the physico-chemical properties of the coma, including organic abundances. In the modeling studies for 2I/Borisov undertaken in this thesis, a higher abundance of several organic ions and neutrals has been predicted when the CO/H₂O ratio is ~ 1, as opposed to a water-dominated coma. The effect on organic abundances when the CO enrichment is four orders of magnitude higher than H₂O will be investigated for C/2016 R2, alongwith other coma properties such as energy exchange rates between fluids.

- 2. The comet C/1995 O1 (Hale-Bopp) was an extremely bright comet, that showed unprecedented levels of activity. A host of organic molecules were detected in this comet, and upper limits were obtained on several others (Bockelée-Morvan et al., 2000; Crovisier et al., 2004). The high activity of this comet can enhance the coma formation rates of organic molecules, which will be investigated through modeling studies. One of the limitations of the model that has been constructed is that it does not consider the spatial distribution of extended sources in the coma, which may lead to an underestimation of species fluxes. However, this can be overcome by modeling the extended sources, following Cordiner & Charnley (2021). Another limitation is that extremely high production rates result in high densities, which may pose computational challenges when using an extensive chemical network like the one that is employed in this thesis.
- 3. It is seen that carbon chain radicals such as C₂, C₂H, C₂H₅, C₄H₂ and C₃N have the capability to increase the molecular complexity of the coma by forming organic molecules such as CH₃CN, HC₃N and HC₅N. C_xH_x species and other carbon chain radicals have been detected by the mass spectrometers onboard *Rosetta* (Altwegg et al., 2017; Schuhmann et al., 2019). The coma model will be used to make an in-depth study of the formation and destruction mechanisms of these radicals.
- 4. Multiwavelength observations allow us to constrain the column densities of molecules and lead to better constraints on the coma processes. In the coma models, these coma processes are modeled numerically and species column densities can be calculated, which can then be used to generate synthetic spectra. A comparison of the synthetic spectra with observed spectra will allow us to find the major processes present in the coma and constrain the composition of the coma.

Appendix A

Major Organic Formation Reactions

The major gas-phase chemical reactions for the formation of organic molecules, that are used in the chemical network, are listed here. Formula 1 indicates that the reaction rates need to be calculated using Equation 2.27. Formula 2 indicates that Equations 2.32 or 2.33 need to be used, depending on the temperature.

Reaction	α	β	K	Reference	Formula
$\rm OH+C_2H_5OH\rightarrow H_2O+CH_2CH_2OH$	2.70(-12)	0.00	0.00	Skouteris et al. (2018)	1
$\mathrm{O} + \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH} ightarrow \mathrm{OH} + \mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{OH}$	1.58(-13)	3.23(0)	2.34(3)	Wu et al. (2007)	1
$\rm H + C_2 H_5 OH \rightarrow H_2 + CH_2 CH_2 OH$	7.91(-13)	2.81(0)	3.77(3)	Sivaramakrishnan et al. (2010)	Т
$\mathrm{CH}_3 + \mathrm{C}_2\mathrm{H}_5\mathrm{OH} ightarrow \mathrm{CH}_4 + \mathrm{CH}_2\mathrm{CH}_2\mathrm{OH}$	1.06(-13)	3.45(0)	5.54(3)	Olm et al. (2016)	1
$\rm OH+C_2H_5OH\rightarrow H_2O+CH_3CHOH$	2.40(-11)	0.00	0.00	Skouteris et al. (2018)	
$0 + C_2 H_5 OH \rightarrow OH + CH_3 CHOH$	3.11(-13)	2.47(0)	4.41(2)	Wu et al. (2007)	Ţ
$\rm H+C_2H_5OH\rightarrow H_2+CH_3CHOH$	6.24(-13)	2.68(0)	1.46(3)	Sivaramakrishnan et al. (2010)	1
$\rm CH_3 + \rm C_2H_5OH \rightarrow \rm CH_4 + \rm CH_3CHOH$	8.87(-15)	3.37(0)	3.95(3)	Olm et al. (2016)	Т
$\mathrm{H_2O} + \mathrm{HCO^+} \rightarrow \mathrm{HCOOH_2^+} + h\nu$	4.00(-13)	-1.30(0)	0.00	Herbst (1985)	Т
$\mathrm{CH}_4 + \mathrm{O}_2^+ \to \mathrm{H} + \mathrm{HCOOH}_2^+$	3.80(-12)	-1.80(0)	0.00	Wakelam et al. (2015)	
$\rm HCOOH + \rm HCO^{+} \rightarrow \rm CO + \rm HCOOH_{2}^{+}$	1.00(0)	1.01(-9)	2.77(0)	Woon & Herbst (2009)	2
$\rm HCOOH + CH_{3}OH_{2}^{+} \rightarrow CH_{3}OH + \rm HCOOH_{2}^{+}$	3.70(-10)	-5.00(-1)	0.00	Freeman et al. (1978)	1
$\rm HCOOH + H_2COH^+ \rightarrow H_2CO + \rm HCOOH_2^+$	2.00(-9)	-5.00(-1)	0.00	Freeman et al. (1978)	Ţ
$CH_3CHO + HCOOH_2^+ \rightarrow HCOOH + CH_3CHOH^+$	2.90(-9)	-5.00(-1)	0.00	Feng & Lifshitz (1994)	
$CH_3CN + HCOOH_2^+ \rightarrow HCOOH + CH_3CNH^+$	4.07(-9)	-5.00(-1)	0.00	Feng & Lifshitz (1994)	Ц
$CH_3OH + HCOOH_2^+ \rightarrow HCOOH + CH_3OH_2^+$	2.29(-9)	-5.00(-1)	0.00	Feng & Lifshitz (1994)	1

		ı)		
Reaction	α	β	7	Reference	Formula
$\mathrm{NH}_3 + \mathrm{HCOOH}_2^+ \rightarrow \mathrm{HCOOH} + \mathrm{NH}_4^+$	1.38(-9)	-5.00(-1)	0.00	Feng & Lifshitz (1994)	1
$\rm H_{2}O + \rm HCOOH_{2}^{+} \rightarrow \rm HCOOH + \rm H_{3}O^{+}$	2.10(-11)	-5.00(-1)	0.00	Van Doren et al. (1986)	1
$\mathrm{HCOOH}_{2}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{H} + \mathrm{HCOOH}$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$0 + CH_3CHOH \rightarrow CH_3 + HCOOH$	3.90(-10)	1.80(-1)	4.90(-1)	Skouteris et al. (2018)	1
$\rm H_2CO+CH_3OH_2^+ \rightarrow H_2 + HCOOCH_4^+$	1.00(0)	9.53(-10)	5.15(0)	Woon & Herbst (2009)	2
$\rm HCOOH + CH_{3}OH_{2}^{+} \rightarrow \rm H_{2}O + \rm HCOOCH_{4}^{+}$	1.70(-11)	0.00	0.00	Cole et al. (2012)	1
$\rm HCOOCH_3 + H_3^+ \rightarrow H_2 + \rm HCOOCH_4^+$	4.05(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm HCOOCH_3 + \rm HCO^+ \rightarrow \rm CO + \rm HCOOCH_4^+$	1.55(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm HCOOCH_3 + H_3O^+ \rightarrow H_2O + \rm HCOOCH_4^+$	1.81(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm HCOOCH_4^+ + e^- \rightarrow H + \rm HCOOCH_3$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm O+CH_3OCH_2 \rightarrow H+HCOOCH_3$	2.56(-10)	1.50(-1)	0.00	Ruaud et al. (2015)	1
$\rm CH_4 + H_2 \rm CO^+ \rightarrow \rm H + \rm CH_3 \rm CHOH^+$	1.65(-11)	0.00	0.00	Wakelam et al. (2015)	1
$C_2H_5OH + C^+ \rightarrow CH + CH_3CHOH^+$	7.07(-10)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_5OH} + \mathrm{H^+} \rightarrow \mathrm{H_2} + \mathrm{CH_3CHOH^+}$	3.30(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_5OH} + \mathrm{H_3}^+ \rightarrow \mathrm{H_2} + \mathrm{H_2} + \mathrm{CH_3CHOH}^+$	5.00(-10)	-5.00(-1)	0.00	Sung Lee et al. (1992)	1
$\rm CH_3CHOH + H^+ \rightarrow H + CH_3CHOH^+$	3.00(-9)	-5.00(-1)	0.00	Skouteris et al. (2018)	1
$CH_2CH_2OH + H^+ \rightarrow H + CH_3CHOH^+$	3.00(-9)	-5.00(-1)	0.00	Skouteris et al. (2018)	1

	- continued fro	m previous	s page		
Reaction	σ	β	λ	Reference	Formula
$\mathrm{H_2CO} + \mathrm{CH_3OH_2^+} \rightarrow \mathrm{H_2O} + \mathrm{CH_3CHOH^+}$	2.10(-11)	-5.00(-1)	0.00	Karpas & Mautner (1989)	1
$\rm CH_3OCH_3 + H^+ \rightarrow H_2 + \rm CH_3CHOH^+$	2.50(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$CH_3OCH_3 + CH_3^+ \rightarrow CH_4 + CH_3CHOH^+$	3.50(-10)	-5.00(-1)	0.00	Wilson et al. (1994)	1
$CH_3OCH_3 + O_2^+ \rightarrow O_2H + CH_3CHOH^+$	1.35(-9)	-5.00(-1)	0.00	McElroy et al. (2013)	1
$C_3H_6 + O_2^+ \rightarrow H + CO + CH_3CHOH^+$	3.00(-11)	0.00	0.00	McElroy et al. (2013)	1
$\rm CH_3CHO + H_3^+ \rightarrow H_2 + \rm CH_3CHOH^+$	6.20(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$CH_3CHO + HCO^+ \rightarrow CO + CH_3CHOH^+$	2.50(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm CH_3CHO + H_3O^+ \rightarrow H_2O + CH_3CHOH^+$	2.86(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm NH_3 + CH_3CHOH^+ \rightarrow CH_3CHO + NH_4^+$	1.80(-9)	-5.00(-1)	0.00	Wilson et al. (1994)	1
$\rm CH_3CHOH^+ + e^- \rightarrow \rm H + \rm CH_3CHO$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_5OH_2^+} + \mathrm{e^-} \rightarrow \mathrm{H} + \mathrm{H_2} + \mathrm{CH_3CHO}$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_5OH^+} + \mathrm{e^-} \rightarrow \mathrm{H_2} + \mathrm{CH_3CHO}$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm CH + CH_3OH \rightarrow CH_3CHO + H$	2.49(-10)	-1.93(0)	0.00	McElroy et al. (2013)	1
$0 + CH_3CHOH \rightarrow OH + CH_3CHO$	4.80(-11)	1.90(-1)	3.90(-1)	Skouteris et al. (2018)	1
$\rm O+C_2H_5 \rightarrow H+CH_3CHO$	1.33(-10)	0.00	0.00	Wakelam et al. (2015)	1
$\rm HCO + CH_3CO \rightarrow CO + CH_3CHO$	1.50(-11)	0.00	0.00	Hebrard et al. (2009)	1
$H_2CO + CH_3CO \rightarrow HCO + CH_3CHO$	3.01(-13)	0.00	6.51(3)	Hebrard et al. (2009)	1

		I			
Reaction	σ	β	Z	Reference	Formula
$CH_3OH + CH_3CO \rightarrow CH_3CHO + CH_2OH$	2.17(-13)	3.00(0)	6.21(3)	Hebrard et al. (2009)	1
${ m H}_2 + { m CH}_3 { m CO} ightarrow { m H} + { m CH}_3 { m CHO}$	2.21(-13)	1.82(0)	8.87(3)	Hebrard et al. (2009)	1
$CH_4 + CH_3CO \rightarrow CH_3 + CH_3CHO$	4.92(-14)	2.88(0)	1.08(4)	Hebrard et al. (2009)	1
$\mathrm{C_2H_6} + \mathrm{CH_3CO} \rightarrow \mathrm{CH_3CHO} + \mathrm{C_2H_5}$	1.95(-13)	2.75(0)	8.83(3)	Hebrard et al. (2009)	1
$CH_3CO + CH_3CO \rightarrow CH_2CO + CH_3CHO$	1.49(-11)	0.00	0.00	Hebrard et al. (2009)	1
$O_2 + CH_3OCH_2 \rightarrow O_2H + CH_3CHO$	6.30(-14)	0.00	5.50(2)	Sander et al. (2011)	1
$OH + C_3H_6 \rightarrow CH_3CHO + CH_3$	2.08(-11)	-2.03(0)	1.70(2)	McElroy et al. (2013)	1
$\mathrm{C_2H_4} + \mathrm{H_3O^+} \rightarrow \mathrm{C_2H_5OH_2^+} + h\nu$	2.40(-14)	-2.80(0)	0.00	Herbst (1987)	1
$\mathrm{H_2O} + \mathrm{C_2H_5^+} \rightarrow \mathrm{C_2H_5OH_2^+} + h\nu$	4.10(-16)	-2.40(0)	0.00	Herbst (1987)	1
$\mathrm{C_2H_5OH} + \mathrm{H_3}^+ \rightarrow \mathrm{H_2} + \mathrm{C_2H_5OH_2}^+$	1.30(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_5OH} + \mathrm{HCO^+} \rightarrow \mathrm{CO} + \mathrm{C_2H_5OH_2^+}$	8.50(-10)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_5OH} + \mathrm{H_3O^+} \rightarrow \mathrm{H_2O} + \mathrm{C_2H_5OH_2^+}$	1.79(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm NH_3 + C_2H_5OH_2^+ \rightarrow C_2H_5OH + \rm NH_4^+$	1.97(-9)	-5.00(-1)	0.00	Feng & Lifshitz (1995)	1
$\mathrm{C_2H_5OH_2^+ + e^- \rightarrow H + C_2H_5OH}$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$(\mathrm{CH}_2\mathrm{OH})_2 + \mathrm{H}_3^+ \to \mathrm{H}_2 + (\mathrm{CH}_2\mathrm{OH})_2\mathrm{H}^+$	1.48(-9)	0.00	0.00	Garrod et al. (2007)	1
$(CH_2OH)_2 + H_3O^+ \to H_2O + (CH_2OH)_2H^+$	6.13(-10)	0.00	0.00	Garrod et al. (2007)	Ţ
$(CH_2OH)_2 + HCO^+ \rightarrow CO + (CH_2OH)_2H^+$	5.07(-10)	0.00	0.00	Garrod et al. (2007)	1

- CC	ontinued fror	n previous	s page		
Reaction	σ	β	K	Reference	Formula
$(CH_2OH)_2H^+ + e^- \rightarrow (CH_2OH)_2 + H$	1.50(-8)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$\rm CH_2OH + \rm CH_2OH \rightarrow (\rm CH_2OH)_2$	1.60(-11)	0.00	0.00	Tsang (1987)	1
$\rm CH_2OHCHO + H_3^+ \rightarrow H_2 + CH_2OHCHOH^+$	5.22(-9)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$\rm CH_2OHCHO + H_3O^+ \rightarrow H_2O + CH_2OHCHOH^+$	2.19(-9)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$CH_2OHCHO + HCO^+ \rightarrow CO + CH_2OHCHOH^+$	1.82(-9)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$\rm CH_2OHCHOH^+ + e^- \rightarrow CH_2OHCHO + H$	1.50(-8)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$O + CH_2CH_2OH \rightarrow H + CH_2OHCHO$	1.10(-10)	1.60(-1)	5.50(-1)	Skouteris et al. (2018)	1
$\mathrm{HNC} + \mathrm{CH}_3^+ \to \mathrm{CH}_3\mathrm{CNH}^+ + h\nu$	9.00(-9)	-5.00(-1)	0.00	Loison et al. (2014)	1
$\mathrm{HCN} + \mathrm{CH}_3^+ \to \mathrm{CH}_3\mathrm{CNH}^+ + h\nu$	2.00(-10)	-3.00(0)	0.00	Herbst (1985)	1
$\mathrm{HCN} + \mathrm{CH}_4^+ \rightarrow \mathrm{H} + \mathrm{CH}_3\mathrm{CNH}^+$	3.30(-9)	0.00	0.00	Plessis et al. (2010)	1
$CH_3CN + H_3^+ \rightarrow H_2 + CH_3CNH^+$	1.00(0)	2.91(-9)	6.58(0)	Woon & Herbst (2009)	2
$CH_3CN + HCO^+ \rightarrow CO + CH_3CNH^+$	1.00(0)	1.18(-9)	6.58(0)	Woon & Herbst (2009)	2
$\rm CH_3CN + H_3O^+ \rightarrow H_2O + CH_3CNH^+$	1.00(0)	1.35(-9)	6.58(0)	Woon & Herbst (2009)	2
$CH_3CN + HCO_2^+ \rightarrow CO_2 + CH_3CNH^+$	1.00(0)	1.05(-9)	6.58(0)	Woon & Herbst (2009)	2
$\rm CH_3CN + C_2H_2^+ \rightarrow C_2H + CH_3CNH^+$	8.36(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{CH}_3\mathrm{CN} + \mathrm{C}_2\mathrm{H}_5^+ ightarrow \mathrm{C}_2\mathrm{H}_4 + \mathrm{CH}_3\mathrm{CNH}^+$	3.80(-9)	0.00	0.00	Anicich (2003)	1
$CH_3CN + HCNH^+ \rightarrow HCN + CH_3CNH^+$	3.80(-9)	0.00	0.00	Anicich (2003)	1

		-)		
Reaction	α	β	X	Reference	Formula
$CH_3CN + C_3H^+ \rightarrow C_3 + CH_3CNH^+$	4.50(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{CH}_3\mathrm{CN} + \mathrm{C}_4\mathrm{H}_7^+ \to \mathrm{C}_4\mathrm{H}_6 + \mathrm{CH}_3\mathrm{CNH}^+$	5.00(-10)	0.00	0.00	McElroy et al. (2013)	1
$\rm CH_3CN + HC_3NH^+ \rightarrow HC_3N + CH_3CNH^+$	3.60(-9)	-5.00(-1)	0.00	Raksit & Bohme (1984)	1
$\rm CH_3CN + N_2H^+ \rightarrow N_2 + CH_3CNH^+$	4.10(-9)	-5.00(-1)	0.00	Mackay et al. (1976)	1
$\mathrm{CNC}^+ + \mathrm{C}_2\mathrm{H}_6 \rightarrow \mathrm{CH}_3\mathrm{CN} + \mathrm{C}_2\mathrm{H}_3^+$	1.20(-10)	0.00	0.00	Anicich (2003)	1
$\rm CH_3CNH^+ + e^- \rightarrow \rm H + \rm CH_3CN$	1.30(-7)	-5.00(-1)	0.00	Loison et al. (2014)	1
$\mathrm{CN}+\mathrm{CH}_4 \rightarrow \mathrm{H}+\mathrm{CH}_3\mathrm{CN}$	7.21(-15)	2.64(0)	7.80(1)	Hebrard et al. (2009)	1
$\mathrm{C_2H_4} + \mathrm{N(^2D)} ightarrow \mathrm{H} + \mathrm{CH_3CN}$	2.52(-10)	0.00	0.00	Hebrard et al. (2009)	1
$\mathrm{CN} + \mathrm{C}_3\mathrm{H}_6 \rightarrow \mathrm{C}_2\mathrm{H}_3 + \mathrm{CH}_3\mathrm{CN}$	1.73(-10)	0.00	-1.02(2)	Hebrard et al. (2009)	1
$\rm NH_2CHO + H_3^+ \rightarrow H_2 + \rm NH_2CHOH^+$	1.00(0)	2.84(-9)	6.62(0)	Woon & Herbst (2009)	2
$\rm NH_2CHO + HCO^+ \rightarrow CO + \rm NH_2CHOH^+$	1.00(0)	1.14(-9)	6.62(0)	Woon & Herbst (2009)	2
$\rm NH_2CHO + H_3O^+ \rightarrow H_2O + NH_2CHOH^+$	1.00(0)	1.30(-9)	6.62(0)	Woon & Herbst (2009)	2
$\rm NH_2CHO + N_2H^+ \rightarrow N_2 + NH_2CHOH^+$	1.00(0)	1.14(-9)	6.62(0)	Woon & Herbst (2009)	2
$\rm NH_2CHOH^+ + e^- \rightarrow H + NH_2CHO$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	
$\rm NH_2 + H_2CO \rightarrow H + NH_2CHO$	1.00(-10)	0.00	0.00	Wakelam et al. (2015)	Ц
$\mathrm{CH}_4 + \mathrm{C}_2\mathrm{N}^+ ightarrow \mathrm{H}_2 + \mathrm{HC}_3\mathrm{NH}^+$	2.10(-10)	0.00	0.00	Wakelam et al. (2015)	
$C_2H_2 + HCN^+ \rightarrow H + HC_3NH^+$	1.35(-10)	0.00	0.00	Anicich (2003)	1

	- continued fro	m previous	s page		
Reaction	α	β	λ	Reference	Formula
$C_2H_4 + CN^+ \rightarrow H_2 + HC_3NH^+$	6.50(-11)	0.00	0.00	Anicich (2003)	1
$\rm HCN + C_2H_2^+ \rightarrow \rm H + \rm HC_3NH^+$	1.33(-10)	0.00	0.00	Wakelam et al. (2015)	
$\rm HNC + C_2H_2^+ \rightarrow \rm H + \rm HC_3\rm NH^+$	1.30(-10)	0.00	0.00	Wakelam et al. (2015)	1
$\mathrm{CH}_3\mathrm{CN} + \mathrm{C}_3\mathrm{H}^+ \rightarrow \mathrm{C}_2\mathrm{H}_2 + \mathrm{HC}_3\mathrm{NH}^+$	1.05(-9)	0.00	0.00	Anicich (2003)	1
$\rm H_2 + HC_3N^+ \rightarrow \rm H + HC_3NH^+$	5.00(-12)	0.00	0.00	Wakelam et al. (2015)	1
$\mathrm{CH}_4 + \mathrm{HC}_3\mathrm{N}^+ ightarrow \mathrm{CH}_3 + \mathrm{HC}_3\mathrm{NH}^+$	1.77(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{C_2H_4} + \mathrm{HC_3N^+} \rightarrow \mathrm{C_2H_3} + \mathrm{HC_3NH^+}$	1.34(-10)	0.00	0.00	Anicich (2003)	
${ m H_2O} + { m HC_3N^+} ightarrow { m OH} + { m HC_3NH^+}$	6.70(-10)	0.00	0.00	Anicich (2003)	1
$\rm H_2O + C_4N^+ \rightarrow CO + HC_3NH^+$	5.00(-1)	7.45(-10)	5.41(0)	Woon & Herbst (2009)	2
$\mathrm{CH}_2\mathrm{CHCN} + \mathrm{H}^+ ightarrow \mathrm{H}_2 + \mathrm{HC}_3\mathrm{NH}^+$	7.50(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{C}_{2}\mathrm{H}_{3}^{+} \rightarrow \mathrm{C}_{2}\mathrm{H}_{2} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(0)	1.35(-9)	5.44(0)	Woon & Herbst (2009)	2
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{H}_{3}^{+} \rightarrow \mathrm{H}_{2} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(0)	3.37(-9)	5.44(0)	Woon & Herbst (2009)	2
$\rm HC_{3}N + CH_{5}^{+} \rightarrow CH_{4} + HC_{3}NH^{+}$	1.00(0)	1.58(-9)	5.44(0)	Woon & Herbst (2009)	2
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{C}_{2}\mathrm{H}_{4}^{+} \rightarrow \mathrm{C}_{2}\mathrm{H}_{3} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(0)	1.33(-9)	5.44(0)	Woon & Herbst (2009)	2
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{HCO}^{+} \rightarrow \mathrm{CO} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(0)	1.32(-9)	5.44(0)	Woon & Herbst (2009)	2
$\mathrm{HC}_{3}\mathrm{N}+\mathrm{N}_{2}\mathrm{H}^{+} ightarrow \mathrm{N}_{2}+\mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(0)	1.32(-9)	5.44(0)	Woon & Herbst (2009)	2
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{H}_{3}\mathrm{O}^{+} \rightarrow \mathrm{H}_{2}\mathrm{O} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(0)	1.52(-9)	5.44(0)	Woon & Herbst (2009)	2

Reaction	a	β	7	Reference	Formula
$\mathrm{HC}_{3}\mathrm{N}+\mathrm{CH}_{2}^{+}\rightarrow\mathrm{CH}+\mathrm{HC}_{3}\mathrm{NH}^{+}$	4.10(-9)	0.00	0.00	Anicich (2003)	1
$\mathrm{HC}_{3}\mathrm{N}+\mathrm{CH}_{4}^{+} ightarrow \mathrm{CH}_{3}+\mathrm{HC}_{3}\mathrm{NH}^{+}$	2.50(-9)	0.00	0.00	Anicich (2003)	1
$\mathrm{HC}_{3}\mathrm{N}+\mathrm{C}_{2}\mathrm{H}^{+} ightarrow\mathrm{C}_{2}+\mathrm{HC}_{3}\mathrm{NH}^{+}$	1.41(-9)	0.00	0.00	Anicich (2003)	1
$\mathrm{HC}_{3}\mathrm{N}+\mathrm{C}_{2}\mathrm{H}_{5}^{+} ightarrow \mathrm{C}_{2}\mathrm{H}_{4}+\mathrm{HC}_{3}\mathrm{NH}^{+}$	3.55(-9)	0.00	0.00	Anicich (2003)	1
$\mathrm{HC}_{3}\mathrm{N}+\mathrm{C}_{3}\mathrm{H}_{5}^{+} ightarrow \mathrm{C}_{3}\mathrm{H}_{4}+\mathrm{HC}_{3}\mathrm{NH}^{+}$	1.00(-10)	0.00	0.00	Plessis et al. (2010)	1
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{HCN}^{+} ightarrow \mathrm{CN} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	2.21(-9)	0.00	0.00	Anicich (2003)	1
$\mathrm{HC}_{3}\mathrm{N} + \mathrm{HC}\mathrm{NH}^{+} \rightarrow \mathrm{HCN} + \mathrm{HC}_{3}\mathrm{NH}^{+}$	3.40(-9)	0.00	0.00	Anicich (2003)	1
$\mathrm{C_2H_2} + \mathrm{HC_3N^+} \rightarrow \mathrm{HC_3N} + \mathrm{C_2H_2^+}$	1.28(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{C_2H_4} + \mathrm{HC_3N^+} \rightarrow \mathrm{HC_3N} + \mathrm{C_2H_4^+}$	5.36(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{C_4H_2} + \mathrm{HC_3N^+} \rightarrow \mathrm{HC_3N} + \mathrm{C_4H_2^+}$	8.90(-10)	0.00	0.00	Anicich (2003)	1
$\rm NH_3 + HC_3N^+ \rightarrow HC_3N + NH_3^+$	1.70(-9)	0.00	0.00	Anicich (2003)	1
$\rm H_2O + C_4N^+ \rightarrow \rm HC_3N + \rm HCO^+$	5.00(-1)	7.45(-10)	5.41(0)	Woon & Herbst (2009)	2
$\rm CH_3CN + C_3H^+ \rightarrow \rm HC_3N + \rm C_2H_3^+$	6.00(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{NH}_3 + \mathrm{HC}_3\mathrm{NH}^+ ightarrow \mathrm{HC}_3\mathrm{N} + \mathrm{NH}_4^+$	2.00(-9)	0.00	0.00	Anicich (2003)	1
${ m HC_3NH^+ + e^- \rightarrow H + HC_3N}$	6.00(-7)	-5.80(-1)	0.00	Loison et al. (2017)	1
$\mathrm{HC_5NH^+} + \mathrm{e^-} \rightarrow \mathrm{C_2H} + \mathrm{HC_3N}$	$1.20 imes 10^{-7}$	-0.70	0.00	Wakelam et al. (2015)	1
$C_2H + HCN \rightarrow H + HC_3N$	5.30(-12)	0.00	7.70(2)	Hebrard et al. (2009)	1

Reaction	σ	β	х	Reference	Formula
$C_2H + HNC \rightarrow H + HC_3N$	2.00(-10)	0.00	0.00	Loison et al. (2014)	1
$\mathrm{CN} + \mathrm{C_2H_2} \to \mathrm{H} + \mathrm{HC_3N}$	2.72(-10)	-5.20(-1)	1.90(1)	Wakelam et al. (2015)	1
$\rm H_2 + C_3N \rightarrow \rm H + \rm HC_3N$	1.20(-11)	0.00	9.98(2)	Hebrard et al. (2009)	1
$\mathrm{CH}_2 + \mathrm{C}_3\mathrm{N} \to \mathrm{CH} + \mathrm{HC}_3\mathrm{N}$	3.00(-11)	0.00	0.00	Hebrard et al. (2009)	1
$C_3N + CH_4 \rightarrow CH_3 + HC_3N$	5.73(-12)	0.00	6.75(2)	Hebrard et al. (2009)	1
$\rm C_2H_2 + C_3N \rightarrow C_2H + HC_3N$	2.19(-10)	0.00	0.00	Harada et al. (2010)	1
$\mathrm{C}_3\mathrm{N} + \mathrm{C}_2\mathrm{H}_3 \to \mathrm{C}_2\mathrm{H}_2 + \mathrm{H}\mathrm{C}_3\mathrm{N}$	1.60(-12)	0.00	0.00	Hebrard et al. (2009)	1
$\mathrm{C}_3\mathrm{N} + \mathrm{C}_2\mathrm{H}_5 \to \mathrm{H}\mathrm{C}_3\mathrm{N} + \mathrm{C}_2\mathrm{H}_4$	3.00(-12)	0.00	0.00	Hebrard et al. (2009)	1
$\mathrm{C}_3\mathrm{N} + \mathrm{C}_2\mathrm{H}_6 \to \mathrm{H}\mathrm{C}_3\mathrm{N} + \mathrm{C}_2\mathrm{H}_5$	2.08(-11)	2.20(-1)	-5.80(1)	Hebrard et al. (2009)	1
$\mathrm{CH}_4 + \mathrm{C}_4 \mathrm{N}^+ ightarrow \mathrm{H}_2 + \mathrm{HC}_5 \mathrm{NH}^+$	1.00(-10)	0.00	0.00	Wakelam et al. (2015)	1
$\mathrm{HC}_5\mathrm{N} + \mathrm{HCO}^+ ightarrow \mathrm{CO} + \mathrm{HC}_5\mathrm{NH}^+$	8.70(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_4} + \mathrm{HC_5N^+} \rightarrow \mathrm{C_2H_3} + \mathrm{HC_5NH^+}$	9.00(-10)	0.00	0.00	Anicich (2003)	1
$\mathrm{HC_5NH^+} + \mathrm{e^-} ightarrow \mathrm{H} + \mathrm{HC_5N}$	9.20(-7)	-7.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_5H_4N^+} + \mathrm{e^-} ightarrow \mathrm{H} + \mathrm{H_2} + \mathrm{HC_5N}$	1.50(-7)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{CN} + \mathrm{C}_4\mathrm{H}_2 \to \mathrm{H} + \mathrm{HC}_5\mathrm{N}$	2.72(-10)	-5.20(-1)	1.90(1)	Wakelam et al. (2015)	1
$\mathrm{C_2H} + \mathrm{HC_3N} \to \mathrm{H} + \mathrm{HC_5N}$	1.06(-10)	-2.50(-1)	0.00	Wakelam et al. (2015)	1
$\mathrm{C_2H_2} + \mathrm{C_3N} ightarrow \mathrm{H} + \mathrm{HC_5N}$	1.30(-10)	0.00	0.00	Hebrard et al. (2009)	1

		•			
Reaction	α	β	X	Reference	Formula
$C_2H_2 + C_5N \rightarrow C_2H + HC_5N$	2.19(-10)	0.00	0.00	Harada et al. (2010)	
$CH_3OH + CH_3^+ \rightarrow CH_3OCH_4^+ + h\nu$	7.80(-12)	-1.10(0)	0.00	Herbst (1987)	1
$\rm CH_3OH + CH_3OH_2^+ \rightarrow \rm H_2O + CH_3OCH_4^+$	1.00(-10)	-1.00(0)	0.00	Wakelam et al. (2015)	1
$\mathrm{CH}_3\mathrm{OCH}_3 + \mathrm{H}_3^+ \to \mathrm{H}_2 + \mathrm{CH}_3\mathrm{OCH}_4^+$	3.00(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$CH_3OCH_3 + HCO^+ \rightarrow CO + CH_3OCH_4^+$	1.20(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm CH_3OCH_3 + H_3O^+ \rightarrow H_2O + CH_3OCH_4^+$	1.37(-9)	-5.00(-1)	0.00	Wakelam et al. (2015)	1
$\rm CH_3OCH_4^+ + e^- \rightarrow H + CH_3OCH_3$	1.19(-7)	-7.00(-1)	0.00	Hamberg et al. (2010)	1
$\rm CH_3COOH + H_3^+ \rightarrow H_2 + \rm CH_3COOH_2^+$	3.33(-9)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$\rm CH_3COOH + H_3O^+ \rightarrow H_2O + CH_3COOH_2^+$	7.41(-9)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$CH_3COOH + HCO^+ \rightarrow CO + CH_3COOH_2^+$	1.16(-9)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$CH_3COOH_2^+ + e^- \rightarrow CH_3COOH + H$	1.50(-8)	-5.00(-1)	0.00	Garrod et al. (2007)	1
$0 + CH_3CHOH \rightarrow H + CH_3COOH$	2.20(-10)	1.60(-1)	5.90(-1)	Skouteris et al. (2018)	1
$\rm CH_3COOH + \rm NH_3OH^+ \rightarrow \rm H_2O + \rm NH_2CH_2COOH_2^+$	1.00(-9)	0.00	0.00	Garrod (2013)	1
$\rm NH_2CH_2COOH_2^+ + e^- \rightarrow NH_2CH_2COOH + H$	1.50(-8)	-5.00(-1)	0.00	Garrod (2013)	1

Bibliography

- Agúndez, M., Biver, N., Santos-Sanz, P., Bockelée-Morvan, D., & Moreno, R. 2014, Astronomy & Astrophysics, 564, L2 [Cited on page 114.]
- A'Hearn, M. F. 2006, *Science*, 314, 1708 [Cited on page 24.]
- A'Hearn, M. F., Millis, R. C., Schleicher, D. O., Osip, D. J., & Birch, P. V. 1995, *Icarus*, 118, 223 [Cited on pages 25, 26, and 82.]
- A'Hearn, M. F., Belton, M. J. S., Delamere, W. A., et al. 2005, *Science*, 310, 258 [Cited on page 17.]
- A'Hearn, M. F., Belton, M. J. S., Delamere, W. A., et al. 2011, Science, 332, 1396 [Cited on page 17.]
- Altwegg, K. 2008, Space Science Reviews, 138, 291 [Cited on page 31.]
- Altwegg, K. 2017, Proceedings of the International Astronomical Union, 13, 153 [Cited on page 54.]
- Altwegg, K., Balsiger, H., & Fuselier, S. A. 2019, Annual Review of Astronomy and Astrophysics, 57, 113 [Cited on pages 4 and 17.]
- Altwegg, K., Balsiger, H., Bar-Nun, A., et al. 2015, *Science*, 347, 1261952 [Cited on page 7.]
- —. 2016, *Science Advances*, 2, e1600285 [Cited on pages 4, 21, and 147.]
- Altwegg, K., Balsiger, H., Berthelier, J. J., et al. 2017, Monthly Notices of the Royal Astronomical Society, 469, S130 [Cited on pages 21, 115, and 172.]

- Altwegg, K., Balsiger, H., Hänni, N., et al. 2020, *Nature Astronomy*, 4, 533 [Cited on pages 61 and 84.]
- Anicich, V. G. 2003, JPL Publication 03-19 (Pasadena: California Institute of Technology) [Cited on pages 52, 178, 179, 180, 181, and 182.]
- Aravind, K., Ganesh, S., Venkataramani, K., et al. 2021, Monthly Notices of the Royal Astronomical Society, 502, 3491 [Cited on pages vi, 80, and 82.]
- Bacmann, A., Taquet, V., Faure, A., Kahane, C., & Ceccarelli, C. 2012, Astronomy & Astrophysics, 541, L12 [Cited on page 153.]
- Balsiger, H., Altwegg, K., Buhler, F., et al. 1986, *Nature*, 321, 330 [Cited on page 16.]
- Balucani, N., Ceccarelli, C., & Taquet, V. 2015, Monthly Notices of the Royal Astronomical Society, 449, L16 [Cited on page 171.]
- Bannister, M. T., Opitom, C., Fitzsimmons, A., et al. 2020, arXiv:2001.11605 [Cited on pages vi, 80, 82, and 84.]
- Bauer, J. M., Grav, T., Fernández, Y. R., et al. 2017, The Astronomical Journal, 154, 53 [Cited on page 8.]
- Behar, E., Nilsson, H., Alho, M., Goetz, C., & Tsurutani, B. 2017, Monthly Notices of the Royal Astronomical Society, 469, S396 [Cited on page 15.]
- Benna, M., & Mahaffy, P. 2007, Planetary and Space Science, 55, 1031 [Cited on page 74.]
- Benna, M., & Mahaffy, P. R. 2006, Geophysical Research Letters, 33, L10103 [Cited on pages 16 and 62.]
- Bennett, C. J., Jamieson, C. S., Osamura, Y., & Kaiser, R. I. 2006, The Astrophysical Journal, 653, 792 [Cited on page 153.]
- Biele, J., Ulamec, S., Maibaum, M., et al. 2015, Science, 349, aaa9816 [Cited on page 17.]

- Biermann, L. 1951, Zeitschrift für Astrophysik, 29, 274 [Cited on pages 6 and 13.]
- —. 1968, Joint Institute for Laboratory Astrophysics Report No. 93 (Boulder: University of Colorado) [Cited on page 11.]
- Biermann, L., Brosowski, B., & Schmidt, H. U. 1967, Solar Physics, 1, 254 [Cited on page 14.]
- Biermann, L., Giguere, P. T., & Huebner, W. F. 1982, Astronomy & Astrophysics, 108, 221 [Cited on page 30.]
- Biver, N., & Bockelée-Morvan, D. 2019, ACS Earth and Space Chemistry, 3, 1550 [Cited on pages 111 and 170.]
- Biver, N., Bockelée-Morvan, D., Crovisier, J., et al. 1999, The Astronomical Journal, 118, 1850 [Cited on page 113.]
- Biver, N., Bockelée-Morvan, D., Debout, V., et al. 2014, Astronomy & Astrophysics, 566, L5 [Cited on pages xiv, 21, 114, and 116.]
- Biver, N., Bockelée-Morvan, D., Moreno, R., et al. 2015, Science Advances, 1, 1500863 [Cited on pages xiv, 17, 21, 114, 115, 116, and 170.]
- Biver, N., Moreno, R., Bockelée-Morvan, D., et al. 2016, Astronomy & Astrophysics, 589, A78 [Cited on pages xiv and 116.]
- Biver, N., Bockelée-Morvan, D., Paubert, G., et al. 2018, Astronomy & Astrophysics, 619, A127 [Cited on page 97.]
- Bobrovnikoff, N. T. 1942, Reviews of Modern Physics, 14, 164 [Cited on page 13.]
- Bockelée-Morvan, D. 2011, in *The Molecular Universe: Proceedings of the International Astronomical Union Symposium No. 280*, ed. J. Cernicharo & R. Bachiller (Cambridge: Cambridge University Press), 261 [Cited on page 18.]
- Bockelée-Morvan, D., & Biver, N. 2017, Philosophical Transactions of the Royal Society A, 375, 20160252 [Cited on pages xiii, 4, 19, 20, 82, and 83.]

- Bockelée-Morvan, D., Colom, P., Crovisier, J., Despois, D., & Paubert, G. 1991, Nature, 350, 318 [Cited on page 21.]
- Bockelée-Morvan, D., Crovisier, J., Colom, P., & Despois, D. 1994, Astronomy & Astrophysics, 287, 647 [Cited on page 20.]
- Bockelée-Morvan, D., Crovisier, J., Mumma, M. J., & Weaver, H. A. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 391 [Cited on pages xiv, 11, 17, 31, 84, 85, and 116.]
- Bockelée-Morvan, D., Lis, D. C., Wink, J. E., et al. 2000, Astronomy & Astrophysics, 353, 1101 [Cited on pages 21 and 172.]
- Bockelée-Morvan, D., Crovisier, J., Erard, S., et al. 2016, *Monthly Notices of the Royal Astronomical Society*, 462, S170 [Cited on page 20.]
- Bodewits, D., Bonev, B. P., Cordiner, M. A., & Villanueva, G. L. 2022, arXiv:2209.02616 [Cited on pages 11 and 17.]
- Bodewits, D., Noonan, J. W., Feldman, P. D., et al. 2020, *Nature Astronomy*, 4, 867 [Cited on pages vi, 22, 23, 80, 81, 82, 83, and 169.]
- Boice, D. C., Huebner, W. F., Sablik, M. J., & Konno, I. 1990, Geophysical Research Letters, 17, 1813 [Cited on page 31.]
- Bossa, J.-B., Borget, F., Duvernay, F., Theulé, P., & Chiavassa, T. 2010, Journal of Physical Organic Chemistry, 23, 333 [Cited on page 148.]
- Botta, L., Saladino, R., Bizzarri, B. M., et al. 2018, Advances in Space Research,
 62, 2372 [Cited on page 112.]
- Bottke, W. F., Durda, D. D., Nesvorný, D., et al. 2005, *Icarus*, 179, 63 [Cited on page 22.]
- Brandt, J. C., & Chapman, R. D. 2004, Introduction to Comets, 2nd edn. (Cambridge: Cambridge University Press) [Cited on pages 11, 12, 13, 24, and 25.]
- Brooke, T. Y., Tokunaga, A. T., Weaver, H. A., et al. 1996, *Nature*, 383, 606 [Cited on page 113.]
- Brownlee, D., Tsou, P., Aléon, J., et al. 2006, *Science*, 314, 1711 [Cited on pages 3, 7, and 17.]
- Brownlee, D. E., Horz, F., Newburn, R. L., et al. 2004, *Science*, 304, 1764 [Cited on page 10.]
- Buratti, B. J., Hicks, M. D., Soderblom, L. A., et al. 2004, *Icarus*, 167, 16 [Cited on page 10.]
- Butscher, T., Duvernay, F., Theule, P., et al. 2015, Monthly Notices of the Royal Astronomical Society, 453, 1587 [Cited on page 152.]
- Capaccioni, F., Coradini, A., Filacchione, G., et al. 2015, *Science*, 347, aaa0628 [Cited on pages 4 and 21.]
- Caravan, R. L., Shannon, R. J., Lewis, T., Blitz, M. A., & Heard, D. E. 2015, The Journal of Physical Chemistry A, 119, 7130 [Cited on page 160.]
- Carusi, A., & Valsecchi, G. B. 1987, *Publications of the Astronomical Institute* of the Czechoslovak Academy of Sciences, 2, 21 [Cited on page 25.]
- Cernicharo, J. 2004, *The Astrophysical Journal Letters*, 608, L41 [Cited on page 153.]
- Cernicharo, J., Marcelino, N., Roueff, E., et al. 2012, The Astrophysical Journal Letters, 759, L43 [Cited on page 154.]
- Chamberlin, P. C., Woods, T. N., & Eparvier, F. G. 2007, Space Weather, 5, S07005 [Cited on page 74.]
- —. 2008, Space Weather, 6, S05001 [Cited on page 74.]
- Chamberlin, P. C., Eparvier, F. G., Knoer, V., et al. 2020, *Space Weather*, 18, e02588 [Cited on page 74.]

- Chambers, J. 2007, in *Treatise on Geochemistry*, ed. H. D. Holland & K. K. Turekian (Oxford: Pergamon), 1–17 [Cited on page 3.]
- Charnley, S. B. 2004, Advances in Space Research, 33, 23 [Cited on page 153.]
- Charnley, S. B., & Rodgers, S. D. 2008, Space Science Reviews, 138, 59 [Cited on page 152.]
- Charnoz, S., & Morbidelli, A. 2003, *Icarus*, 166, 141 [Cited on page 22.]
- Choukroun, M., Altwegg, K., Kührt, E., et al. 2020, Space Science Reviews, 216,
 44 [Cited on pages 9 and 62.]
- Chyba, C. F., & Sagan, C. 1997, in *Comets and the Origin and Evolution of Life*, ed. P. J. Thomas, C. F. Chyba, & C. P. McKay (New York: Springer), 147 [Cited on page 4.]
- Chyba, C. F., Thomas, P. J., Brookshaw, L., & Sagan, C. 1990, Science, 249, 366 [Cited on pages 32 and 167.]
- Coates, A. J. 1997, Advances in Space Research, 20, 255 [Cited on page 15.]
- Coates, A. J., Mazelle, C., & Neubauer, F. M. 1997, Journal of Geophysical Research, 102, 7105 [Cited on page 17.]
- Cochran, A. L., Barker, E. S., & Gray, C. L. 2012, *Icarus*, 218, 144 [Cited on page 26.]
- Cochran, A. L., & McKay, A. J. 2018, The Astrophysical Journal Letters, 854, L10 [Cited on page 171.]
- Coddington, O., Lean, J. L., Pilewskie, P., Snow, M., & Lindholm, D. 2016, Bulletin of the American Meteorological Society, 97, 1265 [Cited on page 74.]
- Cole, C. A., Wehres, N., Yang, Z., & Thomsen, D. L. 2012, The Astrophysical Journal Letters, 754, L5 [Cited on pages 48 and 175.]
- Colom, P., Crovisier, J., Bockelée-Morvan, D., Despois, D., & Paubert, G. 1992, Astronomy & Astrophysics, 264, 270 [Cited on page 21.]

- Combi, M. R., Bertaux, J. L., Quémerais, E., et al. 2014, The Astronomical Journal, 147, 126 [Cited on pages xiv, 111, 113, 114, and 115.]
- Combi, M. R., Harris, W. M., & Smyth, W. H. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 523 [Cited on pages 11, 12, 18, 31, 38, and 61.]
- Combi, M. R., Mäkinen, T. T., Bertaux, J. L., Quémerais, E., & Ferron, S. 2019, *Icarus*, 317, 610 [Cited on pages 12 and 111.]
- Combi, M. R., Mäkinen, T. T., Bertaux, J. L., et al. 2018, *Icarus*, 300, 33 [Cited on pages xiv, 12, 81, 111, and 115.]
- Combi, M. R., Reinard, A. A., Bertaux, J. L., Quemerais, E., & Mäkinen, T. 2000, *Icarus*, 144, 191 [Cited on page 12.]
- Combi, M. R., Shou, Y., Mäkinen, T., et al. 2021, *Icarus*, 365, 114509 [Cited on page 12.]
- Combi, M. R., & Smyth, W. H. 1988, *The Astrophysical Journal*, 327, 1026 [Cited on pages 30 and 31.]
- Cordiner, M. A., & Charnley, S. B. 2021, Monthly Notices of the Royal Astronomical Society, 504, 5401 [Cited on pages 112, 154, and 172.]
- Cordiner, M. A., Remijan, A. J., Boissier, J., et al. 2014, The Astrophysical Journal Letters, 792, L2 [Cited on page 114.]
- Cordiner, M. A., Milam, S. N., Biver, N., et al. 2020, Nature Astronomy, 4, 861 [Cited on pages vi, 22, 23, 80, 81, 82, 83, and 100.]
- Cottin, H., & Fray, N. 2008, Space Science Reviews, 138, 179 [Cited on page 21.]
- Cottin, H., Gazeau, M. C., Benilan, Y., & Raulin, F. 2001, The Astrophysical Journal, 556, 417 [Cited on page 31.]
- Cravens, T. E. 1989, in Solar System Plasma Physics, ed. J. Waite, J. H., J. L. Burch, & R. L. Moore, Vol. 54 (Washington DC: American Geophysical Union), 353 [Cited on page 15.]

- Cravens, T. E., & Korosmezey, A. 1986, *Planetary and Space Science*, 34, 961 [Cited on page 69.]
- Cravens, T. E., Kozyra, J. U., Nagy, A. F., Gombosi, T. I., & Kurtz, M. 1987, Journal of Geophysical Research, 92, 7341 [Cited on pages 74, 76, 104, and 106.]
- Crifo, J. F. 1991, in International Astronomical Union Colloquium 116: Comets in the post-Halley era, ed. J. Newburn, R. L., M. Neugebauer, & J. Rahe (Cambridge: Cambridge University Press), 937 [Cited on pages 29 and 55.]
- Crifo, J. F., Rodionov, A. V., & Bockelée-Morvan, D. 1999, *Icarus*, 138, 85 [Cited on page 97.]
- Crovisier, J., Bockelée-Morvan, D., Colom, P., et al. 2004, Astronomy & Astrophysics, 418, 1141 [Cited on pages 21, 147, and 172.]
- Dalai, P., Kaddour, H., & Sahai, N. 2016, *Elements*, 12, 401 [Cited on page 4.]
- de Barros, A. L. F., da Silveira, E. F., Fulvio, D., Rothard, H., & Boduch, P. 2016, *The Astrophysical Journal*, 824, 81 [Cited on page 153.]
- de la Fuente Marcos, C., & de la Fuente Marcos, R. 2019, Monthly Notices of the Royal Astronomical Society, 489, 951 [Cited on page 79.]
- de León, J., Licandro, J., Serra-Ricart, M., et al. 2019, Research Notes of the American Astronomical Society, 3, 131 [Cited on page 79.]
- de León, J., Licandro, J., de la Fuente Marcos, C., et al. 2020, *Monthly Notices* of the Royal Astronomical Society, 495, 2053 [Cited on pages vi, 80, and 82.]
- De Sanctis, M. C., Capaccioni, F., Ciarniello, M., et al. 2015, *Nature*, 525, 500 [Cited on page 7.]
- de Val-Borro, M., Milam, S. N., Cordiner, M. A., et al. 2018, Monthly Notices of the Royal Astronomical Society, 474, 1099 [Cited on page 153.]
- Dello Russo, N., Kawakita, H., Vervack, R. J., & Weaver, H. A. 2016a, *Icarus*, 278, 301 [Cited on pages 17, 18, 19, 20, 27, 82, 84, and 100.]

- Dello Russo, N., Vervack, R. J., J., Lisse, C. M., et al. 2011, The Astrophysical Journal Letters, 734, L8 [Cited on page 20.]
- Dello Russo, N., Vervack, R. J., Kawakita, H., et al. 2016b, *Icarus*, 266, 152 [Cited on page 20.]
- 2022, The Planetary Science Journal, 3, 6 [Cited on pages xiv, 115, and 116.]
- Disanti, M. A., & Mumma, M. J. 2008, Space Science Reviews, 138, 127 [Cited on page 153.]
- DiSanti, M. A., Mumma, M. J., Dello Russo, N., Magee-Sauer, K., & Griep, D. M. 2003, *Journal of Geophysical Research: Planets*, 108, 5061 [Cited on pages 61 and 113.]
- DiSanti, M. A., Mumma, M. J., Russo, N. D., & Magee-Sauer, K. 2001, *Icarus*, 153, 361 [Cited on page 61.]
- Draine, B. T. 1980, *The Astrophysical Journal*, 241, 1021 [Cited on page 68.]
- —. 1986, Monthly Notices of the Royal Astronomical Society, 220, 133 [Cited on pages xiii, 65, 66, and 67.]
- Drozdovskaya, M. N., van Dishoeck, E. F., Rubin, M., Jørgensen, J. K., & Altwegg, K. 2019, Monthly Notices of the Royal Astronomical Society, 490, 50 [Cited on page 170.]
- Drozdovskaya, M. N., Walsh, C., van Dishoeck, E. F., et al. 2016, *Monthly Notices* of the Royal Astronomical Society, 462, 977 [Cited on pages 32 and 152.]
- Dutrey, A., Despois, D., Bockelee-Morvan, D., et al. 1996, International Astronomical Union Circulars, 6364, 1 [Cited on page 113.]
- Edgeworth, K. E. 1949, Monthly Notices of the Royal Astronomical Society, 109,600 [Cited on page 24.]
- Ehrenfreund, P., & Charnley, S. B. 2000, Annual Review of Astronomy and Astrophysics, 38, 427 [Cited on page 3.]

- Ehrenfreund, P., Irvine, W., Becker, L., et al. 2002, *Reports on Progress in Physics*, 65, 1427 [Cited on pages 32 and 167.]
- Eistrup, C., Walsh, C., & van Dishoeck, E. F. 2019, Astronomy & Astrophysics, 629, A84 [Cited on page 170.]
- Elsila, J. E., Glavin, D. P., & Dworkin, J. P. 2009, Meteoritics & Planetary Science, 44, 1323 [Cited on pages 7, 21, and 147.]
- Feldman, P. D., Cochran, A. L., & Combi, M. R. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 425 [Cited on pages 11 and 84.]
- Feng, W. Y., & Lifshitz, C. 1994, The Journal of Physical Chemistry, 98, 3658 [Cited on pages 174 and 175.]
- —. 1995, International Journal of Mass Spectrometry and Ion Processes, 149-150,
 13 [Cited on pages 50 and 177.]
- Fernández, Y. R., Kelley, M. S., Lamy, P. L., et al. 2013, *Icarus*, 226, 1138 [Cited on page 8.]
- Festou, M. C. 1981, Astronomy & Astrophysics, 95, 69 [Cited on page 30.]
- Festou, M. C., Rickman, H., & West, R. M. 1993, The Astronomy and Astrophysics Review, 4, 363 [Cited on page 18.]
- Fink, U. 2009, *Icarus*, 201, 311 [Cited on page 26.]
- Fink, U., & Disanti, M. A. 1990, The Astrophysical Journal, 364, 687 [Cited on page 84.]
- Finson, M. J., & Probstein, R. F. 1968, The Astrophysical Journal, 154, 327 [Cited on page 13.]
- Fitzsimmons, A., Hainaut, O., Meech, K. J., et al. 2019, The Astrophysical Journal Letters, 885, L9 [Cited on pages vi, 80, and 82.]

- Flower, D. R., Pineau des Forets, G., & Hartquist, T. W. 1985, *Monthly Notices* of the Royal Astronomical Society, 216, 775 [Cited on pages 64 and 165.]
- Fornasier, S., Hasselmann, P. H., Barucci, M. A., et al. 2015, Astronomy & Astrophysics, 583, A30 [Cited on page 10.]
- Fornasier, S., Mottola, S., Keller, H. U., et al. 2016, *Science*, 354, 1566 [Cited on page 7.]
- Freeman, C. G., Harland, P. W., & McEwan, M. 1978, Australian Journal of Chemistry, 31, 2157 [Cited on page 174.]
- Frenklach, M., & Feigelson, E. D. 1989, The Astrophysical Journal, 341, 372 [Cited on page 153.]
- Fuchs, G. W., Cuppen, H. M., Ioppolo, S., et al. 2009, Astronomy & Astrophysics, 505, 629 [Cited on page 100.]
- Fuselier, S. A., Shelley, E. G., Balsiger, H., et al. 1988, Geophysical Research Letters, 15, 549 [Cited on page 15.]
- Fuselier, S. A., Altwegg, K., Balsiger, H., et al. 2015, Astronomy & Astrophysics, 583, A2 [Cited on page 106.]
- Galand, M., Héritier, K. L., Odelstad, E., et al. 2016, Monthly Notices of the Royal Astronomical Society, 462, S331 [Cited on page 106.]
- Galeev, A. A., Gribov, B. E., Gombosi, T., et al. 1986, Geophysical Research Letters, 13, 841 [Cited on page 15.]
- Garrod, R. T. 2013, *The Astrophysical Journal*, 765, 60 [Cited on pages 148 and 183.]
- Garrod, R. T., Wakelam, V., & Herbst, E. 2007, Astronomy & Astrophysics, 467, 1103 [Cited on pages 50, 53, 177, 178, and 183.]
- Garrod, R. T., Widicus Weaver, S. L., & Herbst, E. 2008, The Astrophysical Journal, 682, 283 [Cited on page 112.]

- Gary, G. A., & Odell, C. R. 1974, *Icarus*, 23, 519 [Cited on page 14.]
- Geiss, J., Altwegg, K., Anders, E., et al. 1991, Astronomy & Astrophysics, 247, 226 [Cited on page 29.]
- Gerakines, P. A., Schutte, W. A., & Ehrenfreund, P. 1996, Astronomy & Astrophysics, 312, 289 [Cited on page 153.]
- Giguere, P. T., & Huebner, W. F. 1978, *The Astrophysical Journal*, 223, 638 [Cited on page 30.]
- Glassmeier, K.-H., Boehnhardt, H., Koschny, D., Kührt, E., & Richter, I. 2007, Space Science Reviews, 128, 1 [Cited on page 17.]
- Glavin, D. P., Dworkin, J. P., & Sandford, S. A. 2008, Meteoritics & Planetary Science, 43, 399 [Cited on page 7.]
- Goesmann, F., Rosenbauer, H., Bredehöft, J. H., et al. 2015, *Science*, 349, aab0689 [Cited on pages 4 and 21.]
- Goetz, C., Gunell, H., Johansson, F., et al. 2021, Annales Geophysicae, 39, 379 [Cited on pages 15 and 105.]
- Goetz, C., Koenders, C., Richter, I., et al. 2016, Astronomy & Astrophysics, 588, A24 [Cited on page 16.]
- Goetz, C., Behar, E., Beth, A., et al. 2022, Space Science Reviews, 218, 65 [Cited on page 14.]
- Gombosi, T. I., Cravens, T. E., & Nagy, A. F. 1985, The Astrophysical Journal, 293, 328 [Cited on page 30.]
- Gombosi, T. I., & Körösmezey, A. 1989, in Solar System Plasma Physics, ed. J. Waite, J. H., J. L. Burch, & R. L. Moore (Washington DC: American Geophysical Union), 433 [Cited on page 31.]
- Gombosi, T. I., Nagy, A. F., & Cravens, T. E. 1986, Reviews of Geophysics, 24, 667 [Cited on pages 30 and 55.]

- Gomes, R., Levison, H. F., Tsiganis, K., & Morbidelli, A. 2005, *Nature*, 435, 466 [Cited on page 4.]
- Gringauz, K. I., & Verigin, M. I. 1991, in *Cometary Plasma Processes*, ed. A. Johnstone, Vol. 61 (Washington DC: American Geophysical Union), 107 [Cited on pages 15 and 16.]
- Gringauz, K. I., Verigin, M. I., Richter, A. K., et al. 1986a, in ESA Special Publication, Vol. 250, 20th ESLAB Symposium on the Exploration of Halley's Comet, ed. B. Battrick, E. J. Rolfe, & R. Reinhard (Paris, France: European Space Agency), 93 [Cited on page 16.]
- Gringauz, K. I., Gombosi, T. I., Tátrallyay, M., et al. 1986b, Geophysical Research Letters, 13, 613 [Cited on page 15.]
- Gringauz, K. I., Gombosi, T. I., Remizov, A. P., et al. 1986c, *Nature*, 321, 282 [Cited on page 15.]
- Grün, E., & Jessberger, E. K. 1990, in *Physics and Chemistry of Comets*, ed.W. F. Huebner (Heidelberg: Springer Berlin), 113 [Cited on page 13.]
- Gulkis, S., Allen, M., von Allmen, P., et al. 2015, *Science*, 347, aaa0709 [Cited on page 17.]
- Gunell, H., Goetz, C., Simon Wedlund, C., et al. 2018, Astronomy & Astrophysics, 619, L2 [Cited on pages 15 and 105.]
- Guzik, P., Drahus, M., Rusek, K., et al. 2020, Nature Astronomy, 4, 53 [Cited on pages 79 and 85.]
- Häberli, R. M., Altwegg, K., Balsiger, H., & Geiss, J. 1995, Astronomy & Astrophysics, 297, 881 [Cited on page 16.]
- Hamberg, M., Österdahl, F., Thomas, R. D., et al. 2010, Astronomy & Astrophysics, 514, A83 [Cited on pages 49 and 183.]
- Hänni, N., Altwegg, K., Combi, M., et al. 2022, Nature Communications, 13, 3639 [Cited on page 61.]

- Hansen, K. C., Bagdonat, T., Motschmann, U., et al. 2007, Space Science Reviews, 128, 133 [Cited on pages xiv and 104.]
- Hansen, K. C., Altwegg, K., Berthelier, J. J., et al. 2016, Monthly Notices of the Royal Astronomical Society, 462, S491 [Cited on page 16.]
- Harada, N., Herbst, E., & Wakelam, V. 2010, The Astrophysical Journal, 721, 1570 [Cited on pages 53, 182, and 183.]
- Haser, L. 1957, Bulletin de la Societe Royale des Sciences de Liege, 43, 740 [Cited on page 29.]
- Hebrard, E., Dobrijevic, M., Pernot, P., et al. 2009, The Journal of Physical Chemistry A, 113, 11227 [Cited on pages 49, 52, 53, 176, 177, 179, 181, and 182.]
- Henri, P., Vallières, X., Hajra, R., et al. 2017, Monthly Notices of the Royal Astronomical Society, 469, S372 [Cited on page 15.]
- Herbst, E. 1985, *The Astrophysical Journal*, 291, 226 [Cited on pages 51, 52, 174, and 178.]
- —. 1987, The Astrophysical Journal, 313, 867 [Cited on pages 50, 177, and 183.]
- Herbst, E., & Garrod, R. T. 2022, Frontiers in Astronomy and Space Sciences,8, 209 [Cited on pages 151, 152, and 170.]
- Herbst, E., & van Dishoeck, E. F. 2009, Annual Review of Astronomy and Astrophysics, 47, 427 [Cited on pages 18, 22, 112, and 152.]
- Heritier, K. L., Galand, M., Henri, P., et al. 2018, Astronomy & Astrophysics, 618, A77 [Cited on page 106.]
- Hirao, K. 1986, *Nature*, 321, 294 [Cited on page 11.]
- Hiraoka, K., Ohashi, N., Kihara, Y., et al. 1994, Chemical Physics Letters, 229, 408 [Cited on page 100.]
- Hodges, R. R. 1990, *Icarus*, 83, 410 [Cited on page 31.]

- Hollis, J. M., Lovas, F. J., Jewell, P. R., & Coudert, L. H. 2002, The Astrophysical Journal Letters, 571, L59 [Cited on page 112.]
- Hoppe, P., Rubin, M., & Altwegg, K. 2018, Space Science Reviews, 214, 106 [Cited on pages 7 and 152.]
- Horner, J., Evans, N. W., Bailey, M. E., & Asher, D. J. 2003, Monthly Notices of the Royal Astronomical Society, 343, 1057 [Cited on page 25.]
- Huebner, W. F. 1985, in NATO Science Series C, Vol. 157, Molecular Astrophysics: State of the Art and Future Directions, ed. G. H. F. Diercksen, W. F. Huebner, & P. W. Langhoff (Dordrecht: Springer), 311 [Cited on page 31.]
- Huebner, W. F. 1990, in *Physics and Chemistry of Comets*, ed. W. F. Huebner (Heidelberg: Springer Berlin), 1 [Cited on pages 10 and 13.]
- Huebner, W. F., & Carpenter, C. W. 1979, LA-8085-MS, Informal Report (Los Alamos Scientific Laboratory) [Cited on page 73.]
- Huebner, W. F., & Giguere, P. T. 1980, *The Astrophysical Journal*, 238, 753 [Cited on page 30.]
- Huebner, W. F., Keady, J. J., & Lyon, S. P. 1992, Astrophysics and Space Science, 195, 1 [Cited on pages 38, 54, and 73.]
- Huebner, W. F., & McKay, C. P. 1990, in *Physics and Chemistry of Comets*, ed.W. F. Huebner (Heidelberg: Springer Berlin), 305 [Cited on page 31.]
- Huebner, W. F., & Mukherjee, J. 2015, *Planetary and Space Science*, 106, 11 [Cited on pages 44, 54, 73, 84, and 87.]
- Hui, M.-T., Jewitt, D., & Clark, D. 2018, The Astronomical Journal, 155, 25 [Cited on page 10.]
- Hui, M.-T., Jewitt, D., Yu, L.-L., & Mutchler, M. J. 2022, The Astrophysical Journal Letters, 929, L12 [Cited on page 7.]
- Hunter, E. P. L., & Lias, S. G. 1998, Journal of Physical and Chemical Reference Data, 27, 413 [Cited on pages xiii and 42.]

Ip, W. H. 1983, The Astrophysical Journal, 264, 726 [Cited on pages 30 and 55.]

- Ip, W. H., & Axford, W. I. 1982, in *Comets*, ed. L. L. Wilkening (Tucson, AZ: University of Arizona Press), 588 [Cited on page 14.]
- —. 1990, in *Physics and Chemistry of Comets*, ed. W. F. Huebner (Heidelberg: Springer Berlin), 177 [Cited on page 11.]
- Ip, W. H., & Mendis, D. A. 1977, *Icarus*, 30, 377 [Cited on page 97.]
- Ip, W. H., Schwenn, R., Rosenbauer, H., et al. 1987, Astronomy & Astrophysics, 187, 132 [Cited on page 16.]
- Irvine, W. M. 1998, Origins of Life and Evolution of Biospheres, 28, 365 [Cited on page 4.]
- Irvine, W. M., Schloerb, F. P., Crovisier, J., Fegley, B., J., & Mumma, M. J. 2000, in *Protostars and Planets IV*, ed. V. Mannings, A. P. Boss, & S. S. Russell (Tucson, AZ: University of Arizona Press), 1159 [Cited on page 31.]
- Irvine, W. M., Bockelee-Morvan, D., Lis, D. C., et al. 1996, *Nature*, 383, 418 [Cited on page 113.]
- Itikawa, Y. 2002, Journal of Physical and Chemical Reference Data, 31, 749 [Cited on page 68.]
- —. 2015, Journal of Physical and Chemical Reference Data, 44, 013105 [Cited on pages 68, 70, and 89.]
- Itikawa, Y., & Mason, N. 2005, Journal of Physical and Chemical Reference Data, 34, 1 [Cited on pages 68 and 89.]
- Jaber, A. A., Ceccarelli, C., Kahane, C., & Caux, E. 2014, The Astrophysical Journal, 791, 29 [Cited on page 154.]
- Jackson, W. M., Blunt, V., Lin, H., et al. 1996, Astrophysics and Space Science, 236, 29 [Cited on page 84.]

- Jalbout, A. F., Abrell, L., Adamowicz, L., et al. 2007, Astrobiology, 7, 433 [Cited on page 112.]
- Jewitt, D., Agarwal, J., Hui, M.-T., et al. 2019, *The Astronomical Journal*, 157, 65 [Cited on page 33.]
- Jewitt, D., Hui, M.-T., Kim, Y., et al. 2020, The Astrophysical Journal Letters, 888, L23 [Cited on pages 80 and 85.]
- Jewitt, D., Hui, M.-T., Mutchler, M., et al. 2017, The Astrophysical Journal Letters, 847, L19 [Cited on page 10.]
- Jewitt, D., & Luu, J. 2019, The Astrophysical Journal Letters, 886, L29 [Cited on page 23.]
- Jiménez-Serra, I., Vasyunin, A. I., Caselli, P., et al. 2016, The Astrophysical Journal Letters, 830, L6 [Cited on page 154.]
- Kaneda, E., Ashihara, O., Shimizu, M., Takagi, M., & Hirao, K. 1986, Nature, 321, 297 [Cited on page 11.]
- Kaps, P., & Rentrop, P. 1979, Numerische Mathematik, 33, 55 [Cited on page 77.]
- Kareta, T., Andrews, J., Noonan, J. W., et al. 2020, The Astrophysical Journal Letters, 889, L38 [Cited on pages vi, 80, and 82.]
- Karpas, Z., & Mautner, M. 1989, The Journal of Physical Chemistry, 93, 1859 [Cited on pages 51 and 176.]
- Keller, H. U. 1990, in *Physics and Chemistry of Comets*, ed. W. F. Huebner (Heidelberg: Springer Berlin), 13 [Cited on pages 8, 10, and 11.]
- Keller, H. U., Britt, D., Buratti, B. J., & Thomas, N. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 211 [Cited on page 9.]
- Keller, H. U., Delamere, W. A., Reitsema, H. J., Huebner, W. F., & Schmidt,
 H. U. 1987, Astronomy & Astrophysics, 187, 807 [Cited on page 9.]

- Keller, H. U., & Meier, R. R. 1976, Astronomy & Astrophysics, 52, 273 [Cited on page 12.]
- Kobayashi, H., Hidaka, H., Lamberts, T., et al. 2017, *The Astrophysical Journal*, 837, 155 [Cited on page 153.]
- Kobayashi, H., Kimura, H., & Yamamoto, S. 2013, Astronomy & Astrophysics, 550, A72 [Cited on page 10.]
- Koenders, C., Glassmeier, K. H., Richter, I., Ranocha, H., & Motschmann, U. 2015, *Planetary and Space Science*, 105, 101 [Cited on pages 74 and 75.]
- Koenders, C., Goetz, C., Richter, I., Motschmann, U., & Glassmeier, K. H. 2016, Monthly Notices of the Royal Astronomical Society, 462, S235 [Cited on page 62.]
- Körösmezey, A., Cravens, T. E., Gombosi, T. I., et al. 1987, Journal of Geophysical Research, 92, 7331 [Cited on pages 31 and 55.]
- Kriegel, H., Simon, S., Meier, P., et al. 2014, Journal of Geophysical Research: Space Physics, 119, 2740 [Cited on page 75.]
- Kuiper, G. P. 1951, in Astrophysics: A Topical Symposium Commemorating the Fiftieth Anniversary of the Yerkes Observatory and a Half Century of Progress in Astrophysics, ed. J. A. Hynek (New York: McGraw-Hill), 357 [Cited on page 24.]
- Kulyk, I., Korsun, P., Rousselot, P., Afanasiev, V., & Ivanova, O. 2016, *Icarus*, 271, 314 [Cited on page 10.]
- Kwok, S. 2016, The Astronomy and Astrophysics Review, 24, 8 [Cited on page 4.]
- Lamy, P. L., Toth, I., Weaver, H. A., et al. 2000, in AAS/Division for Planetary Sciences Meeting Abstracts, Vol. 32, 36.04 [Cited on page 7.]
- Landau, L. D., & Lifshitz, E. M. 1987, Fluid Mechanics: Volume 6 of Course of Theoretical Physics, 2nd edn. (Oxford: Pergamon Press) [Cited on page 56.]

- Läuter, M., Kramer, T., Rubin, M., & Altwegg, K. 2019, Monthly Notices of the Royal Astronomical Society, 483, 852 [Cited on page 16.]
- Le Roy, L., Altwegg, K., Balsiger, H., et al. 2015, Astronomy & Astrophysics, 583, A1 [Cited on pages 4, 20, and 60.]
- Lee, C.-H., Lin, H.-W., Chen, Y.-T., & Yen, S.-F. 2020, The Astronomical Journal, 160, 132 [Cited on page 85.]
- Levison, H. F., Dones, L., & Duncan, M. J. 2001, The Astronomical Journal, 121, 2253 [Cited on page 24.]
- Levison, H. F., & Duncan, M. J. 1994, *Icarus*, 108, 18 [Cited on page 25.]
- Levison, H. F., Duncan, M. J., Brasser, R., & Kaufmann, D. E. 2010, *Science*, 329, 187 [Cited on page 169.]
- Li, J., Shen, Z., Wang, J., et al. 2017, The Astrophysical Journal, 849, 115 [Cited on page 112.]
- Li, J.-Y., A'Hearn, M. F., Belton, M. J. S., et al. 2007, *Icarus*, 191, 161 [Cited on page 10.]
- Lien, D. J. 1990, The Astrophysical Journal, 355, 680 [Cited on page 17.]
- Lin, H. W., Lee, C.-H., Gerdes, D. W., et al. 2020, The Astrophysical Journal Letters, 889, L30 [Cited on pages vi, 80, 82, 83, and 84.]
- Linnartz, H., Ioppolo, S., & Fedoseev, G. 2015, International Reviews in Physical Chemistry, 34, 205 [Cited on page 153.]
- Lippi, M., Villanueva, G. L., Mumma, M. J., et al. 2020, The Astronomical Journal, 159, 157 [Cited on pages xiv and 116.]
- Lis, D. C., Keene, J., Young, K., et al. 1997, *Icarus*, 130, 355 [Cited on pages xiv, 113, and 116.]
- Lisse, C. M., Cravens, T. E., & Dennerl, K. 2004, in *Comets II*, ed. M. C. Festou,
 H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 631
 [Cited on page 17.]

- Loison, J.-C., Wakelam, V., & Hickson, K. M. 2014, Monthly Notices of the Royal Astronomical Society, 443, 398 [Cited on pages 52, 53, 178, 179, and 182.]
- Loison, J.-C., Agúndez, M., Wakelam, V., et al. 2017, Monthly Notices of the Royal Astronomical Society, 470, 4075 [Cited on page 181.]
- Luca, A., Voulot, D., & Gerlich, D. 2002, in WDS'02 Proceedings of Contributed Papers Part II, ed. J. Šafránková (Prague: Matfyzpress), 204 [Cited on page 49.]
- Luspay-Kuti, A., Hässig, M., Fuselier, S. A., et al. 2015, Astronomy & Astrophysics, 583, A4 [Cited on page 115.]
- Mackay, G. I., Betowski, L. D., Payzant, J. D., Schiff, H. I., & Bohme, D. K. 1976, The Journal of Physical Chemistry, 80, 2919 [Cited on page 179.]
- Madanian, H., Cravens, T. E., Rahmati, A., et al. 2016, Journal of Geophysical Research: Space Physics, 121, 5815 [Cited on page 106.]
- Mandt, K. E., Eriksson, A., Beth, A., Galand, M., & Vigren, E. 2019, Astronomy & Astrophysics, 630, A48 [Cited on page 15.]
- Mandt, K. E., Eriksson, A., Edberg, N. J. T., et al. 2016, Monthly Notices of the Royal Astronomical Society, 462, S9 [Cited on pages 15 and 16.]
- Manion, J. A., Huie, R. E., Levin, R. D., et al. 2008, NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.09 (Gaithersburg, MD: National Institute of Standards and Technology) [Cited on page 53.]
- Marconi, M. L., & Mendis, D. A. 1982a, *The Astrophysical Journal*, 260, 386 [Cited on pages 30 and 61.]
- —. 1982b, The Moon and the Planets, 27, 27 [Cited on page 31.]
- —. 1983, The Astrophysical Journal, 273, 381 [Cited on pages 29, 30, 55, and 86.]
- -. 1986, Earth, Moon, and Planets, 36, 249 [Cited on pages 30, 55, 59, and 86.]

- Martínez, L., Santoro, G., Merino, P., et al. 2020, Nature Astronomy, 4, 97 [Cited on page 153.]
- Marty, B., Avice, G., Sano, Y., et al. 2016, Earth and Planetary Science Letters,441, 91 [Cited on pages 3 and 4.]
- Marty, B., Altwegg, K., Balsiger, H., et al. 2017, *Science*, 356, 1069 [Cited on page 7.]
- Matrà, L., MacGregor, M. A., Kalas, P., et al. 2017, *The Astrophysical Journal*, 842, 9 [Cited on page 22.]
- McClintock, W. E., Rottman, G. J., & Woods, T. N. 2005, *Solar Physics*, 230, 225 [Cited on page 74.]
- McElroy, D., Walsh, C., Markwick, A. J., et al. 2013, Astronomy & Astrophysics, 550, A36 [Cited on pages 51, 53, 176, 177, and 179.]
- McKay, A. J., Cochran, A. L., Dello Russo, N., & DiSanti, M. A. 2020, *The Astrophysical Journal Letters*, 889, L10 [Cited on pages vi, 80, and 81.]
- McKay, A. J., DiSanti, M. A., Kelley, M. S. P., et al. 2019, The Astronomical Journal, 158, 128 [Cited on pages 33, 98, and 171.]
- McPhate, J. B., Feldman, P. D., Weaver, H. A., et al. 1996, in Bulletin of the American Astronomical Society, Vol. 28, 1093 [Cited on pages xiv, 113, and 116.]
- Meech, K. J., Hainaut, O. R., & Marsden, B. G. 2004, *Icarus*, 170, 463 [Cited on page 8.]
- Meech, K. J., & Svoren, J. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 317 [Cited on page 23.]
- Meech, K. J., Pittichová, J., Bar-Nun, A., et al. 2009, *Icarus*, 201, 719 [Cited on pages 3 and 10.]

- Meech, K. J., Weryk, R., Micheli, M., et al. 2017a, *Nature*, 552, 378 [Cited on page 23.]
- Meech, K. J., Kleyna, J. T., Hainaut, O., et al. 2017b, The Astrophysical Journal Letters, 849, L8 [Cited on page 10.]
- Meierhenrich, U. J., Muñoz Caro, G. M., Schutte, W. A., et al. 2005, *Chemistry– A European Journal*, 11, 4895 [Cited on page 148.]
- Mendis, D. A., Flammer, K. R., Rème, H., et al. 1989, *Annales Geophysicae*, 7, 99 [Cited on page 15.]
- Miotello, A., Testi, L., Lodato, G., et al. 2014, Astronomy & Astrophysics, 567, A32 [Cited on page 152.]
- Mitchell, G. F., Prasad, S. S., & Huntress, W. T. 1981, The Astrophysical Journal, 244, 1087 [Cited on page 30.]
- Morbidelli, A., Levison, H. F., & Gomes, R. 2008, in *The Solar System Beyond Neptune*, ed. M. A. Barucci, H. Boehnhardt, D. P. Cruikshank, A. Morbidelli, & R. Dotson (Tucson, AZ: University of Arizona Press), 275 [Cited on page 4.]
- Mukai, T., Miyake, W., Terasawa, T., Kitayama, M., & Hirao, K. 1986, Nature, 321, 299 [Cited on pages 14 and 15.]
- Mumma, M. J., & Charnley, S. B. 2011, Annual Review of Astronomy and Astrophysics, 49, 471 [Cited on pages 18, 27, 31, and 32.]
- Mumma, M. J., Disanti, M. A., dello Russo, N., et al. 1996, Science, 272, 1310 [Cited on pages xiv, 19, 113, 115, and 153.]
- Mumma, M. J., Weissman, P. R., & Stern, S. A. 1993, in *Protostars and Planets III*, ed. E. H. Levy & J. I. Lunine (Tucson, AZ: University of Arizona Press), 1177 [Cited on page 31.]
- Needham, J. 1959, Science and Civilisation in China, Vol. III, Mathematics and the Sciences of the Heavens and the Earth (Cambridge: Cambridge University Press) [Cited on page 14.]

- Neubauer, F. M. 1988, *Journal of Geophysical Research*, 93, 7272 [Cited on page 16.]
- Neubauer, F. M., Glassmeier, K. H., Pohl, M., et al. 1986, *Nature*, 321, 352 [Cited on pages 14 and 16.]
- Oberg, K. I. 2016, *Chemical Reviews*, 116, 9631 [Cited on page 152.]
- Oberg, K. I., Garrod, R. T., van Dishoeck, E. F., & Linnartz, H. 2009, Astronomy
 & Astrophysics, 504, 891 [Cited on pages 112 and 152.]
- O'dell, C. R., Robinson, R. R., Krishna Swamy, K. S., McCarthy, P. J., & Spinrad, H. 1988, *The Astrophysical Journal*, 334, 476 [Cited on page 30.]
- Olm, C., Varga, T., Valkó, É., et al. 2016, International Journal of Chemical Kinetics, 48, 423 [Cited on page 174.]
- Oort, J. H. 1950, Bulletin of the Astronomical Institutes of the Netherlands, 11,91 [Cited on pages 6 and 24.]
- —. 1990, in *Physics and Chemistry of Comets*, ed. W. F. Huebner (Heidelberg: Springer Berlin), 235 [Cited on pages 23 and 24.]
- Ootsubo, T., Kawakita, H., Hamada, S., et al. 2012, *The Astrophysical Journal*, 752, 15 [Cited on pages 18, 23, and 33.]
- Opitom, C., Jehin, E., Manfroid, J., et al. 2015a, Astronomy & Astrophysics, 574, A38 [Cited on page 114.]
- —. 2015b, Astronomy & Astrophysics, 584, A121 [Cited on page 114.]
- Opitom, C., Fitzsimmons, A., Jehin, E., et al. 2019, Astronomy & Astrophysics,
 631, L8 [Cited on pages vi, 80, 81, and 82.]
- Opitom, C., Jehin, E., Hutsemékers, D., et al. 2021, Astronomy & Astrophysics,
 650, L19 [Cited on pages vi, 80, and 81.]

Oppenheimer, M. 1975, The Astrophysical Journal, 196, 251 [Cited on page 30.]

- Oro, J., Mills, T., & Lazcano, A. 1991, Origins of Life and Evolution of Biospheres, 21, 267 [Cited on pages 4 and 112.]
- 'Oumuamua ISSI Team, Bannister, M. T., Bhandare, A., et al. 2019, *Nature Astronomy*, 3, 594 [Cited on page 79.]
- Pagani, L., Favre, C., Goldsmith, P. F., et al. 2017, Astronomy & Astrophysics, 604, A32 [Cited on page 112.]
- Pagani, L., Steinacker, J., Bacmann, A., Stutz, A., & Henning, T. 2010, Science, 329, 1622 [Cited on page 152.]
- Paganini, L., Mumma, M. J., Villanueva, G. L., et al. 2014a, The Astrophysical Journal, 791, 122 [Cited on pages xiv, 113, and 116.]
- Paganini, L., DiSanti, M. A., Mumma, M. J., et al. 2014b, The Astronomical Journal, 147, 15 [Cited on pages xiv and 116.]
- Paradowski, M. L. 2020, Monthly Notices of the Royal Astronomical Society, 492,
 4175 [Cited on pages xiv and 115.]
- Pesnell, W. D., Thompson, B. J., & Chamberlin, P. C. 2012, Solar Physics, 275, 3 [Cited on page 74.]
- Plessis, S., Carrasco, N., & Pernot, P. 2010, Journal of Chemical Physics, 133, 134110 [Cited on pages 52, 178, and 181.]
- Pontoppidan, K. M., Salyk, C., Bergin, E. A., et al. 2014, in *Protostars and Planets VI*, ed. H. Beuther, R. S. Klessen, C. P. Dullemond, & T. Henning (Tucson, AZ: University of Arizona Press), 363 [Cited on page 152.]
- Press, W. H., Teukolsky, S. A., Vetterling, W. T., & Flannery, B. P. 1992, Numerical Recipes in FORTRAN: The Art of Scientific Computing (Cambridge: Cambridge University Press) [Cited on page 77.]
- Prialnik, D., & Bar-Nun, A. 1992, Astronomy & Astrophysics, 258, L9 [Cited on page 11.]

- Qasim, D., Fedoseev, G., Chuang, K. J., et al. 2020, Nature Astronomy, 4, 781 [Cited on page 153.]
- Quirico, E., Moroz, L. V., Beck, P., et al. 2015, in 46th Lunar and Planetary Science Conference, 2092 [Cited on page 10.]
- Raghuram, S., & Bhardwaj, A. 2013, *Icarus*, 223, 91 [Cited on page 54.]
- Raghuram, S., Bhardwaj, A., Hutsemékers, D., et al. 2021, Monthly Notices of the Royal Astronomical Society, 501, 4035 [Cited on page 97.]
- Raghuram, S., Hutsemékers, D., Opitom, C., et al. 2020, Astronomy & Astrophysics, 635, A108 [Cited on page 54.]
- Raksit, A. B., & Bohme, D. K. 1984, International Journal of Mass Spectrometry and Ion Processes, 57, 211 [Cited on page 179.]
- Reach, W. T., Kelley, M. S., & Vaubaillon, J. 2013, *Icarus*, 226, 777 [Cited on page 26.]
- Reme, H., Mazelle, C., D'Uston, C., et al. 1994, Journal of Geophysical Research,99, 2301 [Cited on page 15.]
- Rodgers, S. D., & Charnley, S. B. 2002, Monthly Notices of the Royal Astronomical Society, 330, 660 [Cited on pages xiii, 31, 57, 66, and 67.]
- 2005, Monthly Notices of the Royal Astronomical Society, 356, 1542 [Cited on page 61.]
- Rodgers, S. D., Charnley, S. B., Huebner, W. F., & Boice, D. C. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 505 [Cited on pages 31 and 59.]
- Rosenbrock, H. H. 1963, The Computer Journal, 5, 329 [Cited on page 76.]
- Rottman, G. 2005, Solar Physics, 230, 7 [Cited on page 74.]
- Rowe, B. R., Dupeyrat, G., Marquette, J. B., & Gaucherel, P. 1984a, Journal of Chemical Physics, 80, 4915 [Cited on page 41.]

- Rowe, B. R., Dupeyrat, G., Marquette, J. B., et al. 1984b, Journal of Chemical Physics, 80, 241 [Cited on page 41.]
- Ruaud, M., Loison, J. C., Hickson, K. M., et al. 2015, Monthly Notices of the Royal Astronomical Society, 447, 4004 [Cited on pages 49 and 175.]
- Rubin, M., Bekaert, D. V., Broadley, M. W., Drozdovskaya, M. N., & Wampfler,
 S. F. 2019, ACS Earth and Space Chemistry, 3, 1792 [Cited on pages 7, 18, 22, 32, 54, and 167.]
- Rubin, M., Combi, M. R., Daldorff, L. K. S., et al. 2014, The Astrophysical Journal, 781, 86 [Cited on pages 45, 74, and 106.]
- Rubin, M., Altwegg, K., Balsiger, H., et al. 2015, Science, 348, 232 [Cited on page 115.]
- Sagdeev, R. Z., Szabo, F., Avanesov, G. A., et al. 1986, *Nature*, 321, 262 [Cited on page 9.]
- Saitta, A. M., & Saija, F. 2014, Proceedings of the National Academy of Science, 111, 13768 [Cited on page 112.]
- Saladino, R., Botta, G., Pino, S., Costanzo, G., & Di Mauro, E. 2012, Chemical Society Reviews, 41, 5526 [Cited on page 112.]
- Sander, S., Abbatt, J., Barker, J. R., et al. 2011, *JPL Publication 10-06* (Pasadena: California Institute of Technology) [Cited on page 177.]
- Sauer, K., Bogdanov, A., & Baumgartel, K. 1995, Advances in Space Research, 16, 153 [Cited on page 15.]
- Schleicher, D. G., & Bair, A. N. 2016, in AAS/Division for Planetary Sciences Meeting Abstracts, Vol. 48, 308.04 [Cited on pages 25 and 26.]
- Schleicher, D. G., & Farnham, T. L. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 449 [Cited on page 11.]

- Schmidt, H. U., & Wegmann, R. 1982, in *Comets*, ed. L. L. Wilkening (Tucson, AZ: University of Arizona Press), 538 [Cited on page 14.]
- Schmidt, H. U., Wegmann, R., Huebner, W. F., & Boice, D. C. 1988, Computer Physics Communications, 49, 17 [Cited on pages xiv, 31, 53, 55, 59, and 71.]
- Schuhmann, M., Altwegg, K., Balsiger, H., et al. 2019, Astronomy & Astrophysics, 630, A31 [Cited on pages 4, 20, and 172.]
- Schulz, R. 2009, Solar System Research, 43, 343 [Cited on page 17.]
- Schunk, R., & Nagy, A. 2009, Ionospheres: Physics, Plasma Physics, and Chemistry (Cambridge: Cambridge University Press) [Cited on pages vii, 106, and 107.]
- Sekanina, Z. 1976, *Icarus*, 27, 123 [Cited on page 22.]
- Senay, M. C., & Jewitt, D. 1994, Nature, 371, 229 [Cited on pages 23 and 33.]
- Shimizu, M. 1976, Astrophysics and Space Science, 40, 149 [Cited on page 71.]
- Simon Wedlund, C., Behar, E., Nilsson, H., et al. 2019, Astronomy & Astrophysics, 630, A37 [Cited on page 106.]
- Sivaramakrishnan, R., Su, M.-C., Michael, J. V., et al. 2010, The Journal of Physical Chemistry A, 114, 9425 [Cited on pages 49 and 174.]
- Skouteris, D., Balucani, N., Ceccarelli, C., et al. 2018, *The Astrophysical Journal*, 854, 135 [Cited on pages 49, 51, 53, 160, 171, 174, 175, 176, 178, and 183.]
- Smith, I. W. M., Herbst, E., & Chang, Q. 2004, Monthly Notices of the Royal Astronomical Society, 350, 323 [Cited on page 41.]
- Soderblom, L. A., Becker, T. L., Bennett, G., et al. 2002, *Science*, 296, 1087 [Cited on pages 10 and 17.]
- Sorkhabi, O., Blunt, V. M., Lin, H., et al. 1997, Planetary and Space Science, 45, 721 [Cited on page 84.]

- Su, T., & Chesnavich, W. J. 1982, Journal of Chemical Physics, 76, 5183 [Cited on page 46.]
- Sung Lee, H., Drucker, M., & Adams, N. G. 1992, International Journal of Mass Spectrometry and Ion Processes, 117, 101 [Cited on pages 51 and 175.]
- Sunshine, J. M., Groussin, O., Schultz, P. H., et al. 2007, *Icarus*, 191, 73 [Cited on page 7.]
- Szegö, K., Glassmeier, K.-H., Bingham, R., et al. 2000, Space Science Reviews, 94, 429 [Cited on page 14.]
- Thomas, P. C., Veverka, J., Belton, M. J. S., et al. 2007, *Icarus*, 191, 51 [Cited on page 7.]
- Tielens, A. G. G. M. 1992, in *Chemistry and Spectroscopy of Interstellar Molecules*, ed. D. K. Bohme (Tokyo: University of Tokyo Press), 237 [Cited on page 153.]
- Tsang, W. 1987, Journal of Physical and Chemical Reference Data, 16, 471 [Cited on pages 49 and 178.]
- Vaisberg, O. L., Smirnov, V. N., Gorn, L. S., & Iovlev, M. V. 1987, Kosmicheskie Issledovaniia, 25, 867 [Cited on page 16.]
- Van Doren, J. M., Barlow, S. E., DePuy, C. H., et al. 1986, The Journal of Physical Chemistry, 90, 2772 [Cited on page 175.]
- Vasyunin, A. I., Caselli, P., Dulieu, F., & Jiménez-Serra, I. 2017, The Astrophysical Journal, 842, 33 [Cited on page 171.]
- Vasyunin, A. I., & Herbst, E. 2013, The Astrophysical Journal, 769, 34 [Cited on page 171.]
- Waite, J. H., J., & Cravens, T. E. 1981, *Planetary and Space Science*, 29, 1333 [Cited on page 70.]
- Wakelam, V., Smith, I. W. M., Herbst, E., et al. 2010, Space Science Reviews, 156, 13 [Cited on pages 41 and 46.]

- Wakelam, V., Herbst, E., Loison, J. C., et al. 2012, The Astrophysical Journal Supplement Series, 199, 21 [Cited on page 46.]
- Wakelam, V., Loison, J. C., Herbst, E., et al. 2015, *The Astrophysical Journal Supplement Series*, 217, 20 [Cited on pages 44, 48, 49, 50, 51, 52, 53, 174, 175, 176, 177, 179, 180, 181, 182, and 183.]
- Watanabe, N., & Kouchi, A. 2002, The Astrophysical Journal Letters, 571, L173 [Cited on page 100.]
- Wegmann, R., Schmidt, H. U., Huebner, W. F., & Boice, D. C. 1987, Astronomy & Astrophysics, 187, 339 [Cited on page 31.]
- Weidenschilling, S. J. 2004, in *Comets II*, ed. M. C. Festou, H. U. Keller, & H. A. Weaver (Tucson, AZ: University of Arizona Press), 97 [Cited on page 3.]
- Weiler, M. 2006, PhD thesis, Technischen Universität Berlin, Germany [Cited on pages xiii, 45, 54, 61, 62, 66, and 67.]
- Weiler, M. 2012, Astronomy & Astrophysics, 538, A149 [Cited on page 31.]
- Weissman, P. R. 1991, in International Astronomical Union Colloquium 116: Comets in the post-Halley era, ed. J. Newburn, R. L., M. Neugebauer, & J. Rahe (Cambridge: Cambridge University Press), 463 [Cited on page 24.]
- Weissman, P. R., Bottke, W. F., J., & Levison, H. F. 2002, in Asteroids III, ed. W. F. Bottke, A. Cellino, P. Paolicchi, & R. P. Binzel (Tucson, AZ: University of Arizona Press), 669 [Cited on page 3.]
- Weissman, P. R., & Lowry, S. C. 2008, *Meteoritics & Planetary Science*, 43, 1033 [Cited on page 8.]
- Whipple, F. L. 1950, *The Astrophysical Journal*, 111, 375 [Cited on pages 6 and 8.]
- Wierzchos, K., & Womack, M. 2018, The Astronomical Journal, 156, 34 [Cited on pages 97 and 171.]

- Williamson, H. N., Nilsson, H., Stenberg Wieser, G., Moeslinger, A., & Goetz,
 C. 2022, Astronomy & Astrophysics, 660, A103 [Cited on page 15.]
- Wilson, P. F., McEwan, M. J., & Meot-Ner, M. 1994, International Journal of Mass Spectrometry and Ion Processes, 132, 149 [Cited on page 176.]
- Wincel, H., Fokkens, R. H., & Nibbering, N. M. M. 2000, Rapid Communications in Mass Spectrometry, 14, 135 [Cited on page 112.]
- Womack, M., Sarid, G., & Wierzchos, K. 2017, Publications of the Astronomical Society of the Pacific, 129, 031001 [Cited on pages 10, 18, 23, and 33.]
- Woods, T. N., Rottman, G., & Vest, R. 2005, Solar Physics, 230, 345 [Cited on page 74.]
- Woods, T. N., Eparvier, F. G., Hock, R., et al. 2012, *Solar Physics*, 275, 115 [Cited on page 74.]
- Woon, D. E., & Herbst, E. 2009, The Astrophysical Journal Supplement Series, 185, 273 [Cited on pages 46, 48, 49, 52, 174, 175, 178, 179, 180, and 181.]
- Wu, C.-W., Lee, Y.-P., Xu, S., & Lin, M. C. 2007, The Journal of Physical Chemistry A, 111, 6693 [Cited on pages 49 and 174.]
- Wyckoff, S., Tegler, S., & Engel, L. 1989, Advances in Space Research, 9, 169 [Cited on page 84.]
- Wyckoff, S., Tegler, S., Wehinger, P. A., Spinrad, H., & Belton, M. J. S. 1988, *The Astrophysical Journal*, 325, 927 [Cited on page 30.]
- Xing, Z., Bodewits, D., Noonan, J., & Bannister, M. T. 2020, The Astrophysical Journal Letters, 893, L48 [Cited on pages vi, 80, and 81.]