

In the interstellar medium, cosmic rays comprised mostly of high-energy protons can drive fast non-thermal reactions in the ice mantles covering microscopic dust grains. Illustrated here is such a collision, highlighting the tracks (shown in red) of both the cosmic ray and "secondary electrons" that are formed in the ice. This track was generated using the CIRIS program (Shingledecker et al., 2017).

ON COSMIC RAYS IN ASTROCHEMICAL MODELS

Christopher Nelson Shingledecker Virginia Beach, Virginia

B.Sc. Chemistry with Highest Distinction University of Virginia, 2013

A Dissertation Presented to the Graduate Faculty of the University of Virginia in Candidacy for the Degree of

Doctor of Philosophy

Department of Chemistry University of Virginia April 2018

© Copyright by Christopher Nelson Shingledecker All rights reserved May 12, 2018

ABSTRACT

OSMIC rays are known to have significant physicochemical impact on interstellar regions (Indriolo and McCall, 2013). For example, even in the very first astrochemical modeling work of Herbst and Klemperer (1973), cosmic rays were shown to drive the gas-phase chemistry of molecular clouds through the ionization of H_2 and subsequent formation of H_3^+ . Later, Prasad and Tarafdar (1983) demonstrated that cosmic rays - and the secondary electrons they generate - could collisionally excite the Lyman and Werner bands of H₂, leading to the formation of internal UV photons in dense regions where the external interstellar UV radiation field is quickly attenuated. However, despite the central role that the ionization and excitation of H_2 currently plays in astrochemical models, extending the treatment of these types of interactions to other species has proven challenging thanks to both the complexity and variety of underlying microscopic processes, which has stymied the development of suitable theoretical and computational techniques. In spite of these difficulties, radiation chemistry remains astrochemically attractive since, as demonstrated by an extensive body of work in laboratory astrophysics, non-thermal reactions triggered ice irradiation can lead to the formation of even complex organic molecules (Holtom et al., 2005; Hudson and Moore, 2001; Hudson et al., 2008; Rothard et al., 2017). Therefore, we have developed new techniques for modeling solid-phase cosmic ray-induced radiation chemistry in both detailed microscopic Monte Carlo models and more general models utilizing rate equations. Where possible, results from our new models are compared with previous experimental data and found to be in good agreement. Finally, we have incorporated solid-phase radiation chemistry into an existing chemical network in order to examine the impact of such reactions on the abundances of species in cold cores. Our results suggest that cosmic ray-driven chemistry is indeed a powerful formation mechanism which both increases the abundance of complex organic molecules and improves the agreement between models and observations. Thus, given the ubiquity of cosmic rays in the interstellar medium and their substantial physicochemical impact, as shown in part by the new computational results presented here, we conclude that, similar to photochemistry, radiation chemistry - particularly in interstellar ices - should become a standard component of future astrochemical models.

To Anna

ICO igitur, quod necessarium est, quod orbis totius natura aut simplex est, nihil in se habens nisi homogenia quæ unius formæ et unius dispositionis et virtutis sunt, sicut quælibet pars ignis est ignis, aut est naturæ compositæ habens in se diversa secundum formam et dispositionem. Nos autem videmus oculis nostris, quod orbis non est naturæ unius et unius formæ et dispositionis: quoniam sunt in ipso et sphæræ diversæ et partes diversæ: quarum una non est stellata, et altera non suscipit lumen non habens: et talis diversitas formarum et dispositionum non est in eo quod naturæ simplicis et homogenium...

- Sanctus Albertus Magnus

De causis proprietatum elementorum Lib.II, tract.1, cap.1 De elementis cælum componentibus

Committee Members:

Eric Herbst Brooks H. Pate Sergei A. Egorov Robin T. Garrod Robert E. Johnson

PREFACE & Acknowledgements

N the Spring of 2014, about half way through my second year of graduate school, I had yet to really settle on a major project for my dissertation. It was around that time that my research advisor, Eric Herbst, attended the 168th Faraday Discussion on the "Astrochemistry of Dust, Ice, and Gas." Upon returning to Charlottesville, he suggested that I might "study how high-energy protons and electrons interact with grains and what reactions they can cause." The chief inspiration for this endeavor was, I think, the paper presented by Mason et al. (2014) on the astrochemical promise of secondary electrons, which are formed in material exposed to ionizing radiation. In that work, Mason and coworkers remarked that "the astrochemistry community can and should assimilate data from [the experimental radiation chemistry] community relevant to their research." In the context of astrochemistry, radiation chemistry is extremely attractive, since a large body of experimental work has shown it to be a means by which even complex molecules can be formed at low temperatures.

My initial "exposure" to the field of radiation chemistry came in the form of an overstuffed folder containing about a dozen or so papers - including Mason et al. (2014). Carefully going through the contents of that folder - and other works I discovered along the way - constituted how I spent the bulk of my time during the summer of 2014. My initial, and naïve, idea was that it should be possible merely to pluck a ready made radiation chemistry model off the shelf, so to speak, which I could then use to study the bombardment of interstellar ices by cosmic rays. Very quickly however, I realized that, on the one hand, there were very nice radiation track models, and on the other, that there were very nice chemical models, but that there was no single program which satisfactorily combined the two. By the Fall of 2014, after my intensive summer crash course, I became convinced that it was possible to write such a combined model, i.e. one that could calculate both radiation tracks and the chemical evolution of an irradiated solid. About three years and \sim 5,000 lines of Fortran code later, I published Shingledecker et al. (2017), which presented CIRIS, the Chemistry of Ionizing Radiation in Solids program. My work developing this detailed Monte Carlo model as well as collaborations with experimenters further convinced me that a simplified macroscopic generalization of the microscopic events simulated in CIRIS was urgently needed to spur the incorporation of cosmic ray-driven grain chemistry into astrochemical networks. Fortuitously, our group had recently received an invitation to submit a paper to a special issue of *Physical Chemistry Chemical Physics*, which was to be focused on "theory, experiment, and simulations in laboratory astrochemistry." That invitation proved to be the necessary motivation to develop the general theoretical framework described in Shingledecker and Herbst (2018). Finally, in Shingledecker et al. (2018), we made our first attempt to shed light on whether radiation chemistry could drive the formation of large astronomical molecules and found that the bombardment of dust particles by cosmic rays could indeed enhance the abundances of such species.

Reaching this point would have been impossible without the patience, guidance, instruction, and assistance of a veritable cloud of individuals. First and foremost, I wish to express my sincerest gratitude to Eric Herbst. Over my time working with him, first as an undergraduate and later as a graduate student, he has been an invaluable mentor and an amazing research supervisor. His clarity and incisiveness in teaching is the gold standard to which I aspire, and he is also my model for professional collegiality and scientific good taste. In addition, I wish to thank Karin Öberg, another valued mentor and colleague who, along with Eric, introduced me to astrochemistry and helped considerably with my first first-author paper. I've also learned much from the many post-docs who have been with the group during my time at UVa, viz. Anton Vasyunin, Qiang Chang, Tatiana Vasyunina, Ugo Hincelin, Kinsuk Acharyya, and Romane Le Gal - all of whom have my profound thanks for putting up with innumerable naïve questions.

During my time in graduate school, I've had the privilege of working with many fantastic people. First, I wish to thank two of my fellow UVa class of 2013 grads, Ryan Loomis and Jennifer Bergner (Wahoowa!), whom I have had the honor of knowing since the very beginning of my adventures in astrochemistry. Special thanks also to Anthony "Tony" Remijan and the merry band of rabble rousers that comprise the "Kingdom of Remijanistan," in particular Brett McGuire and Andrew Burkhardt. From Tony, I've learned the value of forthrightness in communication, leadership skills, and even some sage relationship advice. He also taught me that, as a modeler, I should have some skin in the game - that I need to go out on a limb and make predictions that observers can test. Brett McGuire - big molecule hunter extrordinaire - has a boundless energy, relentless drive, and infectious enthusiasm that makes science really exciting. Brett is also the most naturally gifted public speaker I know, and his presentations have been, for me, master classes in scientific communication. Finally, Andrew and I started graduate school together and his friendship has made the journey a real joy. Over the last five years, I've come to appreciate his personal qualities - empathy, levelheadedness, and a sense of humor - as much as his work ethic, creativity, and resourcefulness.

In addition to the help I've received from research advisors, group members, and colleagues, I could not have reached this point without the instruction and guidance of my teachers and professors - especially Sergei Egorov, James Demas, Ian Harrison, and Kevin Lehmann. Sergei, in particular, has been a valuable mentor along the way, and it's thanks to his encouragement and advice most of all that I am now a fellow Humboldtian. Also, though I've never had the good fortune to take one of his classes, I feel I must here thank Bob Johnson, whose book, *Energetic Charged-Particle Interactions with Atmospheres and Surfaces*, has been the single most valuable work during my graduate career and has never left my desk since I began my work in radiation chemistry.

I also wish to thank Thomas "TJ" Eldridge, Ellen Speers, Matthew Cline, and Charles McAnany. Their companionship has been a delight during the last five years and our regular game nights have played a major role in keeping me sane during that time!

Last, but certainly not least, I wish to thank my family. My wife Anna, to whom I dedicate this work, has been my closest friend, biggest supporter, and most patient counselor. In these and other roles, she has helped me in countless way, including, but by no means limited to, the following: editing my writing, critiquing my practice presentations, and reminding me to eat (coffee doesn't count as food). Finally, I thank my parents for their constant love and support - in particular my father, who has always nurtured my innate curiosity, and from whom I learned the value of hard work and doing a job well, even - or rather, especially - if it's hard.

Unfortunately, I cannot here thank my cat Maya, since she has persisted at every opportunity in attempting to reduce my work productivity from home, and has exercised her limited powers of creativity in coming up with new and ever more annoying ways of getting between me and my computer.

C. N. Shingledecker

Charlottesville, VA IV.MMXVIII

ix

CONTENTS

Ι	Int	roduction	1
1	Bac 1.1 1.2 1.3 1.4	kground & SummaryCosmic RaysRadiation ChemistryMethodology1.3.1Models Utilizing Rate-Equations1.3.2Monte Carlo ModelsThesis scope	2 5 9 10 11 12 13
II	Re	elevant Published Work	15
2	On	Detailed Radiation Chemistry Modeling	16
	2.1	Introduction	16
	2.2	Model and Theory	19
		2.2.1 Monte Carlo modeling of irradiation effects	19
		2.2.2 Continuous-time random walk chemical modeling	27
		2.2.3 Chemical Network	30
	2.3	Results and Discussion	33
	2.4	Summary and Conclusions	36
3	On	a General Theory for Modeling Radiation Chemistry	39
	3.1	Introduction	39
	3.2	Theory	40
		3.2.1 Energy loss and W values \ldots	40
		3.2.2 <i>G</i> values	44
		3.2.3 Decomposition Pathways	45
		3.2.4 Rate coefficients for radiolysis	48
	3.3	Results & Discussion	52
	3.4	Conclusion	55
	3.5	Acknowledgements	56

4	On	Cosmic Ray-Driven Grain Chemistry in Cold Core Models	57
	4.1	Introduction	57
	4.2	Model	61
	4.3	Network	62
	4.4	Results & Discussion	66
		4.4.1 HOCO	68
		4.4.2 NO_2	69
		4.4.3 HC_2O	71
		4.4.4 $HCOOCH_3$	72
		4.4.5 CH_3CH_2OH	74
		4.4.6 Results Using Enhanced Ionization Rates	75
	4.5	Conclusions	79
Π	ΙΟ	Conclusions	81
5	Con	clusions & Outlook	82
	5.1	Major Conclusions	82
		5.1.1 Chapter Two	82
		5.1.2 Chapter Three	83
		5.1.3 Chapter Four	84
		5.1.4 Summary of Main Conclusions	84
	5.2	Future Work	85
		5.2.1 Improvements to both Monte Carlo and	
		Rate Equation Models	85
		5.2.2 Improvements Specific to Rate Equation Models	86
		5.2.3 Improvements Specific to Monte Carlo Models	86
Bi	bliog	;raphy	89
Aj	ppen	dices	113
A	Rad	iolysis Reactions	114
В	Clas	ss 2 Reactions	116
C	Nev	v HOCO Reactions	117
C	INCV	V HOCO Reactions	11/
D	Tim	e-line of Interstellar Molecule Discovery	119
	D.1	The Optical Absorption Era	119
	D.2	The Post-War Science Boom and Efflorescence of Radio Astronomy	120
	D.3	The Birth of Astrochemical Models	122
	D.4	Astrochemistry in the Age of ALMA	131

LIST OF FIGURES

1	In the interstellar medium, cosmic rays comprised mostly of high-energy protons can drive fast non-thermal reactions in the ice mantles covering microscopic dust grains. Illustrated here is such a collision, highlighting the tracks (shown in red) of both the cosmic ray and "secondary electrons" that are formed in the ice. This track was generated using the CIRIS program (Shingledecker et al., 2017).	0
1.1	The "Pillars of Creation" in NGC 6611. Credit: NASA, ESA, STScI, J. Hester and P. Scowen (Arizona State University)	3
1.2	An example of a Wulf electrometer, manufactured by Gunther & Teget- meyer, Braunschweig (a) (Credit: University of Toronto Scientific Instru- ments Collection), and a diagram, taken from Hörandel (2013), showing the internal structure and gold leaves (b).	6
1.3	The approximate composition of cosmic rays.	7
1.4	Cosmic ray flux spectra proposed by Hayakawa et al. (1961) (dashed line), Spitzer and Tomasko (1968) (dotted line), and Nath and Biermann (1994)	-
	(solid line). Image taken from Rimmer et al. (2012).	8
1.5	Cartoon of a radiation track initiated by a primary ion, in this case a proton, colliding with a solid target, here represented as an O_2 ice	9
1.6	Cartoon depicting the major processes considered in a CTRW chemical model. Blue squares are normal lattice sites, and yellow squares are interstitial sites - white squares are unoccupied. Fig. (A) shows the surface, while (B) shows the bulk. Image taken from Chang and Herbst (2014).	13
		10
2.1	Proton-collision cross-sections using parameters listed in Tables 2.1 and 2.2.	21
2.2	2.3, 2.4, and 2.5.	27
2.3	Hopping times for neutral species as a function of system temperature and diffusion barrier height.	30
2.4	Sample track structure in which a proton collides with a pristine O_2 ice with	
o -	fixed collision distance of $\Delta x = 33$ A	34
2.5	Ozone abundances both as calculated by CIRIS and from B99. Experimen- tal data are shown in blue. Calculated abundances are represented by the vellow green and red curves, which correspond the ices of thicknesses of	
	$0.1 \mu\text{m}$, $1 \mu\text{m}$, and $10 \mu\text{m}$, respectively	35
3.1	Cosmic ray energy distribution from Spitzer and Tomasko (1968)	49

Electronic stopping cross sections for protons in water, calculated using PSTAR.	51
sub-excitation electron energy distribution for water, calculated using equa- tion (3.25).	54
Gas-phase abundances in TMC-1 of HC_3N (solid line), HC_5N (dotted line), HC_7N (dashed line), and HC_9N (dot-dashed line), calculated both with (a)	
Abundances of H_2O in the gas (solid line), on grain surfaces (dotted line), and in the bulk (dashed line), calculated both with (a) and without (b) the	67
new radiation chemistry	67
(dotted line) radiation chemistry	68
(b), and in the ice bulk (c), calculated both with (solid line) and without (dotted line) radiation chemistry. \ldots \ldots \ldots \ldots \ldots \ldots \ldots Simulated TMC-1 abundances of HC ₂ O in the gas (a), on the grain/ice sur-	70
face (b), and in the ice bulk (c), calculated both with (solid line) and without (dotted line) radiation chemistry. $\dots \dots \dots$	71
surface (b), and in the ice bulk (c), calculated both with (solid line) and with- out (dotted line) radiation chemistry.	73
both with (solid line) and without (dotted line) radiation chemistry. \ldots	74
Calculated gas-phase abundances of HOCO (a) NO ₂ (b) HC ₂ O (c), and HCOOC (d) calculated at ionization rates of 10^{-17} s ⁻¹ (solid line), 10^{-16} s ⁻¹ (dotted	H_3
Calculated grain-surface abundances of HOCO (a) NO ₂ (b) HC ₂ O (c), and HCOOCH ₃ (d) calculated at ionization rates of 10^{-17} s ⁻¹ (solid line), 10^{-16}	76
s ⁻¹ (dotted line), 10^{-15} s ⁻¹ (dashed line), and 10^{-14} s ⁻¹ (dot-dashed line) Calculated bulk-ice abundances of HOCO (a) NO ₂ (b) HC ₂ O (c), and HCOOCH	77 [₃
(d) calculated at ionization rates of 10^{-17} s ⁻¹ (solid line), 10^{-16} s ⁻¹ (dotted line), 10^{-15} s ⁻¹ (dashed line), and 10^{-14} s ⁻¹ (dot-dashed line).	78
	Electronic stopping cross sections for protons in water, calculated using PSTAR

LIST OF TABLES

2.1	Proton ionization cross-section parameters	23
2.2	Proton excitation cross-section parameters	23
2.3	Electron ionization cross-section parameters	25
2.4	Electron excitation cross-section parameters for allowed transitions	26
2.5	Electron excitation cross-section parameters for forbidden transitions	26
2.6	Secondary electron reactions	28
2.7	Chemical network. The activation energies and branching fractions are taken	
	from gas-phase studies	31
2.8	Model parameters	33
3.1	Key symbols used.	41
3.2	Ionization, excitation, and sub-excitation energies as well as the resulting G	
	values and rate coefficients for water	52
4.1	Model parameters and physical conditions used	62
4.2	Elemental abundances used in this work.	62
4.3	Parameters used in calculating <i>G</i> values and rate coefficients. Ionization energies were taken from Lias (2018), and average excitation energies from	
	Keller-Rudek et al. (2013).	63
A.1	New solid-phase radiolysis processes	114
B.1	New Class 2 reactions involving suprathermal species	116
C.1	New gas-phase HOCO destruction reactions	118

Part I Introduction

CHAPTER 1

BACKGROUND & SUMMARY

"... And so it was no flight of the imagination really, for me to assume that if you can count cosmic rays that you ought to be able to count pulses, even if they were generated by something which was just a keyboard in which you created pulses to correspond to numbers. Therefore, with fast electronic counters and switches, gates as they call them now, that you could do things in the way of building an electronic counter. It was Eckert then who assured me that you could certainly do this reliably, which was a necessity, of course, for mathematical calculations and commercial accounting both require reliability."

- John Mauchly, on the invention of ENIAC, the first computer, with J. Presper Eckert

EVEN thousand light-years from Earth is an astronomical object known to astronomers as NGC 6611 - more commonly referred to as the Eagle Nebula or M16. Using data from the Hubble Space Telescope (HST), a composite image of the center of the Eagle Nebula, shown in Fig. 1.1, was created in 1995 and has since become iconic for capturing the majestic beauty of the Universe. Through other astronomical observations, primarily using light in the radio and microwave regimes, we know that sources like NGC 6611 can be quite chemically rich. To date, nearly 200 different molecules - as well as many isotopologues - have been discovered in the interstellar medium (ISM) (see Appendix D for a timeline of interstellar molecule detections). These species can range from the simple - like H_2 - to the not-quite-so-simple - such as benzonitrile $C_6H_5(CN)$ (McGuire et al., 2018). Indeed, the sheer number and variety of these interstellar species is remarkable given the extreme physical conditions of the ISM by Terrestrial standards.

It is not clear what the upper limit to interstellar chemical complexity is. Intriguingly, however, prebiotic molecules - i.e. species implicated in the origin of life - have been detected in planetary bodies such as comets and meteorites. For example, amino acids are the building blocks of proteins and are synthesized in the cells of Terrestrial organisms via complex metabolic pathways; yet, as demonstrated by Engel et al. (1990), glycine, alanine, glutamic acid, aspartic acid, proline, and other amino acids have been detected in meteorites and were confirmed to be of extraterrestrial origin based on isotopic analysis. Moreover, Engel and Nagy (1982) found that these meteoritic species showed an L enantiomeric excess - a striking finding given that Terrestrial organisms utilize L amino acids almost exclusively. Amino acids have also been detected in comets by Altwegg et al. (2016), suggesting that these complex molecules were present in the presolar nebula and



Figure 1.1: The "Pillars of Creation" in NGC 6611. Credit: NASA, ESA, STScI, J. Hester and P. Scowen (Arizona State University)

the primordial material out of which both comets and meteorites formed. In addition, both nucleobases (Callahan et al., 2011) and sugars (Cooper and Rios, 2016) have also been detected in meteorites, with the latter also showing an enantiomeric excess of the bio-relevant form - the D enantiomer in this case. The cometary delivery of these prebiotic molecules to planets is one of the efficient causes that could trigger the subsequent development of primitive organisms (Chyba et al., 1990).

Through chemical models, astrochemists attempt to uncover the reactions and processes that might have contributed to the observed abundances of interstellar molecules. For many species, like the cyannopolyynes (HC_nN, $3 \ge n \ge 9$), models agreeably reproduce the observed abundances to within a factor of a few (Hincelin et al., 2011), for others, though, they do a much poorer job. For example, the ketenyl radical (HC₂O), was observed by Agúndez et al. (2015), who noted that it was badly underproduced in their simulations - a fact that led them to posit the existence of a "powerful formation mechanism" hitherto not considered in astrochemical models.

One challenge in using charge-coupled devices (CCDs) to obtain images like Fig. 1.1 - particularly on spacecraft like the HST - is an occasional noise from electrons generated in random pixels. Cosmic rays - a form of very high energy (MeV-TeV) ionizing radiation - are a common form of such noise (Windhorst et al., 1994) and, though not visible in Fig. 1.1, are ubiquitous in interstellar space (Blasi, 2013). These cosmic rays are known to have a significant physicochemical impact on interstellar environments (See Indriolo and McCall (2013) and references therein). For example, cosmic rays drive chemistry in dense molecular clouds via

$$\mathrm{H}_2 \rightsquigarrow \mathrm{H}_2^+ + \mathrm{e}^- \tag{1.1}$$

$$H_2^+ + H_2 \to H_3^+ + H$$
 (1.2)

where the curly arrow implies bombardment by an energetic particle. The central importance of the ion-neutral reactions initiated by H_3^+ in the subsequent formation of polyatomic species motivated Woon (2011) to comment that astrochemistry began, not with the discovery of the first interstellar molecule, but rather when this mechanism was used by Herbst and Klemperer (1973) in the first modeling paper - a claim that observational astronomers might find amusing but which nevertheless underscores the role that cosmic rays play in shaping the chemistry of the ISM. In addition, Lyman and Werner band excitation of H₂ by both cosmic rays and the secondary electrons they produce generate internal UV photons in dense regions where the external UV photon flux is quickly attenuated (Prasad and Tarafdar, 1983). The photoionization, photodissociation, and photodesorption caused by these internal UV photons is known to have a profound chemical impact, particularly in energy-poor environments such as cold cores (van Dishoeck, 1988). Thus, given the central importance of cosmic ray-driven ionization and excitation of H_2 , one might think that similar processes for other species would be a common aspect of astrochemical modeling. However, due to the sheer complexity and variety of the underlying microscopic events, there have not been any suitable theoretical and computational techniques that would facilitate adding radiation chemistry to chemical networks in a general way.

This dissertation documents some recent work we have done to address this shortcoming in astrochemical models, and we have focused on reactions in interstellar ices that could occur as a result of cosmic ray bombardment, since it is in these ices that the fast non-thermal processes triggered by cosmic rays are most likely to lead to complex organic molecules (COMs)- those consisting of more than ~ 5 atoms - and other astrochemically interesting species. Thus, our thesis is as follows:

- A If we could add cosmic ray-driven grain chemistry to astrochemical models, then we could better establish its astrochemical importance
- (S1) B We can add cosmic ray-driven chemistry grain chemistry to astrochemical models.
 - C We can better establish its astrochemical importance

In this Chapter, we will attempt to demonstrate that cosmic rays can indeed drive solidphase radiation chemistry. However, as mentioned, since suitable tools to study this phenomenon have not been previously available, the majority of the rest of this work is aimed at proving the minor premise (S1B) - that we can now add cosmic ray-driven grain chemistry to astrochemical models. To that end, we will describe new methods we have developed that now enable both the microscopic and macroscopic simulation of radiation chemistry, and demonstrate the utility of our new techniques in modeling the chemistry of cold cores. Therefore, via *modus ponens*, we hope to arrive at conclusion (S1C), that we can begin to elucidate the astrochemical role of cosmic ray-dust interactions.

The organization of the rest of this Chapter is as follows: in §1.1 we go into the history of cosmic rays and their physical characteristics. In §1.2 we summarize the physicochemical effects that occur when a particle of ionizing radiation bombards some material. The types of astrochemical models we have utilized - as well as their optimal use cases - are given in §1.3. Finally, in §1.4 we go over the scope of this thesis.

1.1 Cosmic Rays

Cosmic rays, the focus of this work, have been studied for over a century by generations of researchers. Ionizing radiation itself was discovered by Bequerel (1896), who there described experiments involving the fogging of photographic plates that had been exposed to what he called *"les radiations"* emitted by phosphorescent uranium salts. Initially, it was thought that radioactivity was solely a property of Terrestrial materials, and that therefore, the naturally occurring radiation flux would be inversely proportional to the distance from the ground.

In order to test this theory, Wulf (1910) carried out experiments at the Eiffel tower - the tallest human-made structure at the time - using a gold-leaf electroscope as a kind of rudimentary radiation detector. Wulf measured no noticeable drop in the radiation flux at the top of the tower compared with measurements made on the ground. In a follow-up study, Hess (1912) made eletrometer measurements in balloons at altitudes of up to ~ 5 km and found a very clear increase in the radiation flux with altitude, thus surmising an extra-Terrestrial origin for the measured radiation. Based on the assumption that they were comprised primarily of electromagnetic waves, Millikan and Cameron (1928) coined



Figure 1.2: An example of a Wulf electrometer, manufactured by Gunther & Tegetmeyer, Braunschweig (a) (Credit: University of Toronto Scientific Instruments Collection), and a diagram, taken from Hörandel (2013), showing the internal structure and gold leaves (b).

the term "cosmic rays" to describe the phenomena.

Later, measurements of cosmic rays at various latitudes motivated Rossi (1930) to posit that, in fact, cosmic rays consisted mostly of positively charged particles. This chargedparticle theory - and the manner in which these particles interact with the magnetosphere of the Earth - was later elaborated by Lemaître and Vallarta (1933). In that work, Lemaître commented "I think that a possible test of the theory is that, if I am right, cosmic rays cannot be formed uniquely of photons, but must contain, like the radioactive rays, fast beta-rays and alpha-particles, and even new rays of greater masses and charges." However, despite the conclusive evidence against the "ray" theory of cosmic rays, the name persisted - a fact that can result in confusion at times.

Currently, it is thought that cosmic rays are particles with energies in the range of \sim MeV and higher and, as shown in Fig. 1.3, consist of protons ($\sim 90\%$), helium nuclei ($\sim 9\%$), and High atomic number (Z) and Energy (HZE) nuclei ($\sim 1\%$) (Blasi, 2013; Indriolo et al., 2009). Directly measuring the low-energy component of the Galactic cosmic ray



Figure 1.3: The approximate composition of cosmic rays.

energy distribution from Earth is not possible due to the effects of the Solar wind, a local source of ionizing radiation (Baade and Zwicky, 1934). Supernova shocks are thought to be a major formation mechanism for cosmic rays (Axford, 1981; Biermann et al., 2010), which would result in a lower energy limit of ~ 100 MeV (Hayakawa et al., 1961; Ip and Axford, 1985). It is possible that interstellar shocks can re-accelerate thermalized cosmic rays, thus reducing the lower energy limit to ~ 1 MeV (Indriolo et al., 2009; Ip and Axford, 1985). Data from the Pierre Auger cosmic ray observatory indicates that the upper limit to cosmic ray energies can exceed the astonishing value of a few exa-electronvolts (10^{18} eV), or about a Joule per particle (Aab et al., 2017). These so-called "ultra-high energy cosmic rays" almost certainly originate in extragalactic sources, with super-massive black holes at the centers of some galaxies likely being involved in their formation (Aab et al., 2017).

The interaction between cosmic rays and either H or H_2 is critical for understanding the physics and chemistry of the ISM. Take, for example, the ionization of atomic hydrogen

$$H \rightsquigarrow H^+ + e^-. \tag{1.3}$$

The rate of H⁺ production due to cosmic rays is thus

$$\frac{\mathrm{d}[\mathrm{H}^+]}{\mathrm{d}t} = \zeta_{\mathrm{H}}[\mathrm{H}] \tag{1.4}$$

with $\zeta_{\rm H}$ being the cosmic ray-induced ionization rate coefficient of atomic hydrogen. The rate coefficients for the ionization of atomic and molecular hydrogen are related via



Figure 1.4: Cosmic ray flux spectra proposed by Hayakawa et al. (1961) (dashed line), Spitzer and Tomasko (1968) (dotted line), and Nath and Biermann (1994) (solid line). Image taken from Rimmer et al. (2012).

$$\zeta_{\rm H_2} \approx 2\zeta_{\rm H} \tag{1.5}$$

where ζ_{H_2} is the ionization rate coefficient for H₂ (Glassgold and Langer, 1974). Collisions between cosmic rays and atomic and molecular hydrogen are widely thought to have a significant impact on both the physical conditions (Ao et al., 2013; Goldsmith and Langer, 1978; Spitzer and Tomasko, 1968) and chemistry (Indriolo and McCall, 2013) of interstellar environments.

Given our inability to directly measure the low energy component of the Galactic cosmic ray flux from Earth, a number of different energy distributions have been proposed over the years (Hayakawa et al., 1961; Nath and Biermann, 1994; Spitzer and Tomasko, 1968), some of which are shown in Fig. 1.4, taken from Rimmer et al. (2012). Perhaps the most widely used spectrum is that of Spitzer and Tomasko (1968) - represented by the dotted line in Fig. 1.4 - which represents a lower limit in the predicted abundance of MeV cosmic rays and results in an ionization rate of $\sim 10^{-17}$ s⁻¹ - the standard value used in most astrochemical models (Shingledecker et al., 2016). This standard value can be significantly enhanced due to local conditions in some regions. For example, the ionization rate around Sgr A^{*} - the galactic center - has been estimated to be as high as $\sim 10^{-14}$ s⁻¹ (Ao et al., 2013; Yusef-Zadeh et al., 2013).



Figure 1.5: Cartoon of a radiation track initiated by a primary ion, in this case a proton, colliding with a solid target, here represented as an O_2 ice.

1.2 Radiation Chemistry

As a form of ionizing radiation, cosmic rays can trigger significant physicochemical changes in materials. Generally, when a particle of ionizing radiation - also referred to as a "primary" - collides with some material - called the "target" - a series of microscopic events is initiated (Johnson, 1990), as depicted in Fig. 1.5. When species in the target are ionized by the primary, an ion-pair is formed, typically consisting of a cation and a "secondary electron." These secondary electrons may be formed with sufficient energy, in turn, to collisionally excite and ionize other species in the target, thus propagating the physicochemical changes in the target initiated by the primary. When the energy of a secondary electron drops below the excitation threshold of the material, the electron is known as a sub-excitation electron and can continue to cause physicochemical changes in the target via resonant mechanisms like dissociate electron attachment (DEA) (Arumainayagam et al., 2010).

Based on Johnson (1990), we here divide the sequence of events into the following general phases:

Physical Stage (< 10⁻¹³ s): Here, energy is transferred from the energetic primary to the target in discrete elastic and inelastic (ionizing and exciting) collisions. Secondary electrons generated in the target propagate the changes initiated by the primary via yet more collisions.

- **physicochemical Stage** (< 10⁻¹¹ s): Here, electronic recombinations occur between either cations and anions, or cations and electrons. Excited molecular species may dissociate or undergo rearrangements. At the selvedge of solids (Abdulgalil et al., 2013), non-thermal desorption mechanisms, e.g sputtering, may promote species into the gas-phase.
- Luminescence (> 10⁻⁹ s): Here, electronically excited species may either quickly react, dissociate, or be quenched by the material.
- **Chemical Stage** ($\sim 10^{-6}$ s yr): In solids, species react via thermal, diffusive mechanisms.

Where, following Bohr (1913), we have made a distinction between elastic (or nuclear) collisions in which energy is transferred to the target nuclei, and inelastic (or electronic) collisions in which energy is transferred to the target electrons. The net energy loss of some of some particle, *A*, to a target comprised of *B* can be expressed as

$$\frac{\mathrm{d}E}{\mathrm{d}t} \approx n_{\mathrm{B}}(S_{\mathrm{n}} + S_{\mathrm{e}}) \tag{1.6}$$

where here, $n_{\rm B}$ is the number density of the target and $S_{\rm n}$ and $S_{\rm e}$ are the so-called nuclear and electronic stopping cross sections, respectively. The stopping cross sections are also referred to as energy loss functions, which perhaps gives a better sense of what they characterize.

In Chapters 2 and 3, we discuss in detail how the inelastic energy loss of an charged particle can drive chemical changes in a material. Radiation-chemical reactions often involve the suprathermal species, radicals, and molecular fragments formed from the collisionally driven ionization, excitation, and dissociation of target species (Spinks and Woods, 1990). In the often cold, energy-poor environments of interstellar space, such reactions are particularly attractive since they represent a promising means by which COMs could be formed, even under the constraints imposed by the physical conditions. The notion is supported by a large body of work in laboratory astrophysics and radiation chemistry, which indicate that the energetic particle bombardment can result in the formation of these COMs, even inside very cold ices. For example, Abplanalp et al. (2016) describe the synthesis of acetaldehyde and vinyl alcohol in mixed CO:CH₄ ices, and work by Holtom et al. (2005), Lafosse et al. (2006), and Hudson et al. (2008) showed that amino acids could be formed in irradiated ice mixtures.

1.3 Methodology

In this work, we have used astrochemical models to simulate chemistry under the physical conditions of interstellar environments. Such models can be grouped into two main categories, viz.

- i Deterministic models based on coupled differential equations
- ii Stochastic Monte Carlo models

Each of these has its own uses and advantages, which we will discuss in this section.

1.3.1 Models Utilizing Rate-Equations

The quantitative study of the abundance of interstellar molecules began with work by Bates and Spitzer (1951), in which the chemistry of CH and CH⁺ were examined. That seminal work considered a number of processes that are still critical in modern astrochemical models - such as radiative association and dissociative recombination. Building on the work of Bates and Spitzer (1951), McCrea and McNally (1960) studied the effects of H₂ formation on grains, which also remains a key element in simulations of interstellar environments.

Perhaps the most important breakthrough in the quantitative study of the abundances of interstellar molecules was made by Herbst and Klemperer (1973). That work marked the first used of an astrochemical model based on coupled nonlinear equations, which they used to study the chemistry of cold cores. To illustrate the general method behind rate equation-based simulations, consider a hypothetical pure gas-phase toy model in which the rate of change in the abundance of some species, x, is given by

$$\frac{\mathrm{d}n(x)}{\mathrm{d}t} = \sum_{y} \sum_{z} k_{yz} n(y) n(z) - n(x) \sum_{y} k_{xy} n(y)$$
(1.7)

where here, n(x), n(y), and n(z) are the number densities of x, y, and z, respectively. The first term on the right hand side of Eq. (1.7) describes the production of x from the reaction of y and z, which occurs with a rate coefficient given by k_{yz} . The second term describes the destruction of x via its reaction with y, occurring with rate coefficients of k_{xy} .

In astrochemical models with $N_{\rm sp}$ different species, there are therefore the same number of differential equations. Each of these rates equations has the same basic form as Eq. (1.7), though of course the individual production and destruction reactions will be unique to each species. Since, as on can see from Eq. (1.7), the rate of change for x depends on the abundances of other species - here y and z - these $N_{\rm sp}$ differential equations are thus necessarily coupled, resulting in a highly non-linear dynamical system. The abundances of species on grain surfaces or in ice-mantles can be added through the inclusion of additional terms to the basic differential equations to describe the interactions between neighboring phases - an often difficult task given the differences between gas-phase and surface chemistry (Garrod, 2008, 2013).

One of the major advantages of this type of model is the efficiency with which results can be calculated, since such systems of equations can be solved using the techniques of linear algebra and there are very efficient numerical libraries for this kind of task, such as BLAS, the Basic Linear Algebra Subprograms (Blackford et al., 2002; Lawson et al., 1979),

which have been continually updated since the late 70's. Thus, "0-D", i.e. isotropic, homogeneous models of the chemical evolution of interstellar sources over more than 10⁸ yr can be run in less than a minute on modern desktop computers. Since these basic models are so efficient, one can link these basic 0-D models together to account for spatial variations in physical conditions, resulting in higher dimensional - and thus more accurate simulations of astronomical environments. For even more physical realism in simulations, rate-equation based models can be coupled to radiative transfer (Le Petit et al., 2006) or hydrodynamics codes (Hincelin et al., 2013). Despite these advantages, models based on rate equations suffer a number of non-trivial drawbacks. For example, one of the most serious of these arises in two-phase models that include surface reactions - a fact that has lead to the development of modified rate equation approaches to chemical modeling (Garrod, 2008).

1.3.2 Monte Carlo Models

Monte Carlo models originated in the 1940s based on work by Ulam, von Neumann, and Metropolis (Harrison, 2010), who were inspired by the recent invention of ENIAC, the Electronic Numerical Integrator and Computer, which was the first electronic digital computer and was designed and built by Mauchly and Eckert. Stochastic calculations involving many random numbers had been considered exceedingly tedious and time-consuming, however, very early on, it was realized by Ulam and coworkers that computers were ideally suited for such problems (Metropolis and Ulam, 1949). One of the first applications of the Monte Carlo method was in studying radiation shielding materials (see Harrison (2010), and references therein, for an historical overview). These techniques have continued to prove well-suited for detailed studies of energetic particles. Indeed, as noted by Wilson and Paretzke (1981), "At present, the only tractable method for handling particle transport in charged-particle track structure with such res- olution and retaining the inherent stochastics is the Monte Carlo method." As shown later in this work, Monte Carlo methods remain a natural choice for modeling radiation tracks.

In this work, we have used the continuous time random walk (CTRW) Monte Carlo technique for our detailed, microscopic chemical models, which was originally developed by Montroll and Weiss (1965) and later applied to astrochemically relevant solids by Chang et al. (2005) based on the work of Akiyama et al. (1987). This approach follows the random thermal diffusion of every individual species in a system. As we discuss in detail in Chapter 2, in a CTRW model, the time between movements for some species, *x*, is influenced by the temperature of the system and the strength of the interactions between *x* and its neighbors. Reactions can occur when two randomly diffusing reactants encounter one another in the material (Chang and Herbst, 2014).

As shown in Fig. 1.6, the Monte Carlo method naturally accounts for many microscopic details - e.g. adsorption, desorption, and diffusion - that may be difficult to accurately generalize in models utilizing rate equations. For example, a CTRW (and similar) approach, easily captures the fact that species in a material randomly diffuse in a way that has been



Figure 1.6: Cartoon depicting the major processes considered in a CTRW chemical model. Blue squares are normal lattice sites, and yellow squares are interstitial sites - white squares are unoccupied. Fig. (A) shows the surface, while (B) shows the bulk. Image taken from Chang and Herbst (2014).

compared to a "drunken sailor" (Pelleg, 2016) in which particles often "back-diffuse" and do not move along straight trajectories; however, as noted by Willis and Garrod (2017), accurately incorporating even this seemingly simple microscopic phenomenon into a rate equation-based model is a non-trivial problem. Similar difficulties involved in generalizing microscopic phenomena related to radiation chemistry will be discussed in Chapter 3 of this work.

Another challenge when using a stochastic Monte Carlo approach is the computational expense. Since only one species moves at a time in a typical stochastic chemical simulation, such stochastic codes do not lend themselves to parallelization, unlike those that rely on linear algebra. The presence of species that move at significantly faster rates than others can result in a serious loss in performance and poses another computational challenge. In astrochemical models, atomic hydrogen poses such a problem, necessitating the use of various computational workaround in order to simulate chemistry over astronomical timescales (Chang and Herbst, 2014; Chang et al., 2017). Despite these technical limitations, when fine-grained physical detail is desired, the innate properties of stochastic Monte Carlo models often make them the best choice.

1.4 Thesis scope

This thesis is focused on the development of theoretical and computational tools to facilitate simulating radiation chemistry, and the application of these tools to better understanding the importance of cosmic ray-induced chemistry in the ISM. We have concentrated on an examination of this non-thermal chemistry in solids, which in the ISM consists primarily of the ice-mantles that coat dust grains, since

- i The effects of these non-thermal reactions are perhaps most pronounced in ices, given the very diffuse gas densities of even "dense" interstellar regions
- ii Based on previous experimental studies, such solid-phase chemistry is most likely to lead to COMs, since the surrounding material can act as a third-body to stabilize products

Here, we have made extensive use of both detailed microscopic Monte Carlo models, and faster, more general codes based on rate equations. As previously mentioned, both types of models have unique strengths and weaknesses, but together, they can reveal a fuller picture of the effects of radiation bombardment in interstellar space than either could individually.

Since the microscopic physicochemical changes initiated by the bombardment of a particle of ionizing radiation are stochastic in nature, they are very naturally amenable to modeling using Monte Carlo methods. In Chapter 2, we describe the first such model of an irradiated solid¹, CIRIS: the Chemistry of Ionizing Radiation in Solids. Using this program, we successfully simulated a laboratory experiment in which ozone was synthesized in an irradiated O_2 ice. In developing CIRIS, we gained key insights into key importance of suprathermal, i.e. electronically excited, species that are generated in solids via the radiolytic decomposition of bulk species.

Based on insights gleaned from our detailed models, we developed a general method for incorporating radiation chemistry into macroscopic models, which we describe in Chapter 3. This theory enables the estimation of radiolytic decomposition pathways, radio-chemical yields, and rate coefficients suitable for inclusion in chemical networks.

The methods described in 3 were then incorporated into an existing macroscopic astrochemical model, and simulations of regions known as cold cores were run. The results of these models, described in Chapter 4, showed that the inclusion of cosmic ray-driven radiation chemistry could efficiently drive the formation of COMs and other astrochemically interesting species without degrading the accuracy with which the abundances of well-known interstellar molecules could be reproduced.

Finally, in Chapter 5, we review both the results presented in this work and our arguments for the necessity of including solid-phase cosmic ray-driven radiation chemistry in future astrochemical models. We further summarize the tools we have developed to facilitate these advances and their optimal use cases. Finally, we point to fruitful avenues of future work in this area, particularly highlighting other physical processes associated with radiation bombardment that could further enhance the astrochemical importance of non-thermal cosmic ray chemistry.

¹To the best of our knowledge!

Part II Relevant Published Work

CHAPTER 2

ON DETAILED RADIATION CHEMISTRY MODELING

The collisions between high-energy ions and solids can result in significant physical and chemical changes to the material. These effects are potentially important for better understanding the chemistry of interstellar and planetary bodies, which are exposed to cosmic radiation and the solar wind, respectively; however, modeling such collisions on a detailed microscopic basis has thus far been largely unsuccessful. To that end, a new model, entitled CIRIS: the Chemistry of Ionizing Radiation in Solids, was created to calculate the physical and chemical effects of the irradiation of solid materials. With the new code, we simulate O_2 ice irradiated with 100 keV protons. Our models are able to reproduce the measured ozone abundances of a previous experimental study, as well as independently predict the approximate thickness of the ice used in that work.¹

2.1 Introduction

RRADIATION by charged particles is well-known to cause substantial physicochemical changes in condensed matter. Beyond its more obvious connections to medical and material science, a detailed understanding of the effects of irradiation induced processes is of great astrochemical interest, since the galaxy is bathed in cosmic rays. Cosmic rays are a particularly high-energy form of ionizing radiation (MeV -TeV) (Ikhsanov, 1991) comprised mostly of protons, which are thought to be created in supernovae (Baade and Zwicky, 1934) or by the super-massive black holes at the centers of galaxies (Abraham et al., 2007). In the interstellar medium, cosmic rays are known to have a strong influence on the chemistry of molecular clouds (Grenier et al., 2015). One component of such environments is dust, which, in cold dense regions, is covered by an ice mantle mainly composed of water (Hasegawa et al., 1992; Herbst and van Dishoeck, 2009). Based on the substantial body of experimental studies showing the complexity of irradiation chemistry, such processes represent promising means by which large interstellar molecules could be formed (Abplanalp et al., 2016), particularly in cases where observational results are difficult to reproduce with current astronomical models (Corby et al., 2015) and possible drivers of complex molecule synthesis are not obvious. In the case of interstellar clouds such as TMC-1, which have temperatures of around 10 K and densities of

¹Originally published as Shingledecker et al. (2017)

 $\sim 10^4$ cm⁻³, a better understanding of cosmic ray induced irradiation chemistry is particularly required since the interiors of these regions are shielded from most of the interstellar UV radiation field. Though cosmic ray ionization rates are reduced by roughly two orders of magnitudes in these regions (Rimmer et al., 2012), a steady-state is reached at which ionization rates stabilize. Thus, particularly in dense cold interstellar environments, it is possible that cosmic ray induced chemical processes represent a potentially very efficient pathway to produce complex and even prebiotic molecules.

Although the interstellar chemistry following cosmic ray bombardment of grains has rarely been studied theoretically, Monte Carlo techniques have been used to give a detailed, microscopic view of the chemistry of solids with, however, only a cursory treatment of the role of ion bombardment. The first such stochastic grain chemistry model utilizing a Monte Carlo approach was reported by Chang et al. (2005). This and later models have utilized in particular the continuous-time random-walk Monte Carlo approach of Montroll and Weiss (1965), such as the simulation of Chang and Herbst (2014).

Due to its many practical applications, prior interest in modeling irradiated matter is well known. Most of this previous computational research has focused on simulating particle tracks in the material, which result from the collisions between species in the solid and the irradiating particles. Due to the stochastic nature of these collisions, Monte Carlo methods are a natural choice for such simulations. Well-known models of this type include MOCA (Paretzke, 1974), MARLOWE (Robinson and Torrens, 1974), TRIM (Ziegler and Manoyan, 1988), and that of Pimblott et al. (1996). The subsequent irradiation-induced chemistry that occurs has been followed in a large number of laboratory experiments on ices and bare solids using both high-energy protons and electrons. In spite of this interest, there has been only limited success in combining track calculations with the subsequent chemistry. One of the most detailed of such attempts was the model of Pimblott and LaVerne (2002). In that work, the authors were able to combine realistic track calculations with a simplified chemical network representing the aqueous solution of a Fricke dosimeter; however, in spite of approximations to the chemistry, such as treating the solute as an infinite continuum, they were only able to simulate the radiation induced chemistry for $\sim 1\mu$ s, due to the computational expense.

The computational expense of these models reflects the many complex physical and chemical processes associated with the bombardment of solids, which must be considered when using a detailed microscopic approach like molecular dynamics or one of the Monte Carlo methods. The physical processes are initiated when a moving energetic particle collides with some material, which we call the target. In this work, the particles we consider are protons and we refer to these as primary ions; however, if the incoming particle is an electron it is sometimes called the primary electron. These primaries transfer energy to atomic or molecular species in the target through collisions. Some of these collisions ionize species in the material, resulting in the formation of "secondary" electrons, which, in turn, transfer energy collisionally to target species and compound the effects of the primary particle, in large part by causing the formation of additional charged species and secondary electrons (Johnson, 1990). Subsequent charge recombination reactions help drive the formation of radicals and other highly reactive species (Mason et al., 2014), which

can react via thermal diffusive mechanisms in the solid, albeit much more slowly than the non-thermal irradiation induced processes (Johnson, 1990).

In this paper, we present a code that is designed to simulate these processes over simulated irradiation exposures relevant to experiments and other real-world applications where a better understanding of the resulting effects on the material is desired. This program, with the acronym CIRIS, which stands for the Chemistry of Ionizing Radiation in Solids, represents an initial attempt at the development of a simulation including a unified model of atomic physics and chemistry. Here, we report the use of our code to simulate the chemistry of the experimental system studied by Baragiola et al. (1999), hereafter referred to as B99. In that work, solid O_2 ice cooled to 5 K under ultra-high vacuum (UHV) conditions was irradiated with 100 keV protons and ozone was synthesized via proton-induced chemical processes.

This system is particularly well-suited as an initial test of our new code. Due to the novelty of this kind of model, well-constrained experiments such as the one reported by B99 allow for a reasonable comparison with our theoretical data. This comparison is aided by the relative simplicity of the irradiated oxygen ice system. One example of this relative simplicity is the upper limit to the size of observable molecules produced via irradiation; namely, ozone, as found by experimental studies, not only of B99, but also those of Ennis and Kaiser (2012) and Lacombe et al. (1997). In other systems, such as those containing carbon, it may not be obvious to determine the limit of chemical complexity obtainable through these processes and some arbitrary upper limit in molecular size may have to be set in the chemical network.

Molecular oxygen ice is present, not only in the Solar System on icy Jovian moons such like Ganymede (Calvin and Spencer, 1997; Spencer et al., 1995) but also in comets. Recently, interest in cometary O_2 ice has increased following the detection of gas-phase O_2 around comet 67P/Churyumov-Gerasimenko (Bieler et al., 2015). It has been speculated by Taquet et al. (2016) and Mousis et al. (2016) that this molecular oxygen was liberated from the icy body of the comet. If that is indeed true, then this represents a possible immediate application of the current results, since comets experience irradiation from the Solar wind, made up mostly of protons with energies mostly between 1.5 and 10 keV (Schwenn, 2001), and cosmic rays with energies above ~ 1 MeV (Spitzer and Tomasko, 1968) that are not stopped by the Solar wind. Moreover, it is possible that cometary ices are relatively pristine remnants of the parent pre-solar nebula (Taquet et al., 2016). Since observations of interstellar O₂, either in the gas or frozen in ice, have thus far proved mainly unsuccessful (Goldsmith et al., 2000; Pagani et al., 2003; Yldz et al., 2013), cometary ice chemistry may provide a crucial window into an as yet poorly understood aspect of interstellar chemistry. Therefore, it is possible that a better understanding of the irradiation chemistry of cometary ices in our Solar system can provide clues as to its possible importance in and contribution to more remote interstellar environments.

The format of the following sections of the paper is as follows. In Section 2 we discuss our model in more detail and give the theory behind the atomic physics and chemistry calculations. In Section 3, we give the results and discuss how these compare with prior experimental work. Finally, in Section 4, we present our summary and conclusions.

2.2 Model and Theory

In our approach, solids are approximated as a lattice, represented in the program by a three-dimensional array. This structure is comprising two types of sites: strongly bound regular lattice sites on the surface and in the bulk of the solid, and more weakly bound internal interstitial sites (Akiyama et al., 1987). At the start of a simulation, we assume a regular lattice comprised of some material, which in this work is solid O_2 . The simulation begins when the first irradiating proton collides with the pristine ice. The primary ion strikes a random surface site at a 90° angle and, as it travels through the solid, the code calculates the relevant physical changes to the material, as described below in Section 2.2.1. The calculations described there are repeated for every subsequent particle arrival. As given in Section 2.2.2, in the model times between particle arrivals, neutral species can thermally diffuse through the solid and chemical reactions in Section 2.2.3 can occur. The model ends when the target material has been exposed to some total amount of irradiation, known as the fluence.

2.2.1 Monte Carlo modeling of irradiation effects

Collisions between energetic particles, such as protons and electrons, with target species occur randomly along the track of the particle through the solid and are thus well-suited to modeling using Monte Carlo techniques. For so-called "fast" incident ions with energies greater than $\sim 1 \text{ keV}/\text{amu}$ (Johnson, 1990), the timescale for these collisions is very short, relative to the chemical timescale (Johnson, 1990). Because the physical irradiation processes occur much faster than the subsequent chemistry, the model decouples the track calculations from the chemistry while the ion is traveling through the target.

In our code, the arrival rate, in s^{-1} , for incoming primary ions is given by

$$k_{\rm ion} = \phi_{\rm ion} A_{\rm solid} \tag{2.1}$$

where ϕ_{ion} is the radiation flux in cm⁻² s⁻¹ and A_{solid} is the surface area of the solid being irradiated. We assume a Poisson distribution of waiting times and calculate the next ion arrival using the stochastic relation

$$\tau_{\rm ion} = -\frac{\ln(R_{\rm n})}{k_{\rm ion}} \tag{2.2}$$

where R_n is a pseudorandom number between 0 and 1. When an ion hits the ice, thermal diffusion is halted until a special set of calculations, described in section 2.2.1, is completed to determine the changes to the solid caused by the incoming ion.

Track Calculations

Following Bohr (1913), we divide collisions between a moving energetic ion and stationary target into two broad categories: those in which energy is transferred to the target nuclei,

which are customarily called nuclear, or elastic, collisions, and those in which energy is transferred to the target electrons, which are called electronic, or inelastic, collisions. The inelastic collisions can be further subdivided into ionizations, in which enough energy is imparted to liberate a secondary electron, and electronic excitations of the target atom or molecule. Here, rotational and vibrational excitations are not considered.

Our code calculates the distance to the next collision, Δx , based on the mean-free-path, Λ_{tot} for an energetic ion with some energy, *E*, given by

$$\Lambda_{\rm tot} = \frac{1}{n_{\rm target} \,\sigma_{\rm tot}} \tag{2.3}$$

where n_{target} is the number density of the target and σ_{tot} is the total cross-section (Pimblott et al., 1996), which is given by

$$\sigma_{\rm tot} = \sigma_{\rm elastic} + \sigma_{\rm inelastic} = \sigma_{\rm elastic} + \sigma_{\rm ion} + \sigma_{\rm ex} \tag{2.4}$$

where σ_{ion} and σ_{ex} are the cross-sections for ionization and excitation of the target, respectively (Pimblott et al., 1996). We stochastically determine which of these three types of collisions occurs next based on the relative sizes of the cross-sections using:

To obtain the distance to the next collision event, we sample from another Poisson distribution using

$$R_{\rm n} = 1 - e^{-\Delta x / \Lambda_{\rm tot}} \tag{2.6}$$

where here, a different random number, R_n , is used and is equivalent to the probability of the particle traveling a distance of Δx to the next collision, given a mean-free-path of Λ_{tot} (Pimblott et al., 1996).

Protons

For protons, we calculate the three key cross-sections for elastic collisions, ionizations and excitations, given in eq. (2.4) before the first collision, and again after every subsequent one, until the particle leaves the system or its energy falls below an arbitrary cutoff of 100 eV, which is the lower limit to the applicability of our method (Biersack and Haggmark, 1980). The average energy loss per unit path length of an ion, labeled A, in a material made of either atoms or molecules, labeled B, is called the stopping, or stopping power (Johnson, 1990), and is given, in the laboratory coordinate system, by

$$\frac{dE}{dx} = n_{\rm B}(S_{\rm n}(E) + S_{\rm e}(E))$$
(2.7)



Figure 2.1: Proton-collision cross-sections using parameters listed in Tables 2.1 and 2.2.

where S_n and S_e are the so-called stopping cross-sections for nuclear (elastic) and electronic (inelastic) collisions, respectively, in units of $eV cm^2$, and n_B is the number density of the material. Here, A refers to protons only, and where B is a molecule, we follow Bragg's rule in approximating the stopping powers as linear combinations of the stopping powers of its constituent atoms (Ziegler and Biersack, 1985; Ziegler and Manoyan, 1988).

Our code uses the stopping cross-section, S_n , to calculate the collisional cross-section, σ_{elastic} . There are many semi-empirical expressions for calculating S_n (Johnson, 1990); we utilize the formalism developed by Ziegler and Biersack (1985) and used in the TRIM program (Ziegler and Biersack, 1985; Ziegler and Manoyan, 1988) which is valid for ions with energies between ~0.1 keV and several MeV. For an elastic collision between ion A, with energy, E_A , and atom B, this is given by

$$S_{\rm n}(E) = 2\pi \frac{\mathcal{A}^2}{\gamma E_{\rm A}} [2\epsilon \, s_{\rm n}(\epsilon)].$$
(2.8)
Here, γ is the mass fraction, defined as

$$\gamma = \frac{4m_{\rm A}m_{\rm B}}{(m_{\rm A} + m_{\rm B})^2},\tag{2.9}$$

and \mathcal{A} is a quantity given by

$$\mathcal{A} = \left(\frac{2m_{\rm A}}{m_{\rm A} + m_{\rm B}} Z_{\rm A} Z_{\rm B} e^2\right) \tag{2.10}$$

where Z_A and Z_B are the nuclear charges of A and B. In equation (2.8), ϵ is the Lindhard-Scharff-Schiott (LSS) reduced energy (Lindhard et al., 1963), calculated as

$$\epsilon = \frac{32.53 \, m_{\rm B} E_{\rm A}}{Z_{\rm A} \, Z_{\rm B} \, (m_{\rm A} + m_{\rm B}) (Z_{\rm A}^{0.23} + Z_{\rm B}^{0.23})} \tag{2.11}$$

and $s_n(\epsilon)$ is the reduced stopping, which has a value of

$$s_n(\epsilon) = \begin{cases} \frac{\ln(\epsilon)}{2\epsilon} & \text{when } \epsilon > 30, \\ \frac{\ln(1+1.1383\epsilon)}{(\epsilon+0.01321\epsilon^{0.21226} + 0.19593\epsilon^{0.5})} & \text{otherwise.} \end{cases}$$
(2.12)

We thus calculate the elastic collisional cross-section from the stopping cross-section using

$$\sigma_{\text{elastic}} = \frac{2S_{\text{n}}(E)}{\gamma E_{\text{A}}}.$$
(2.13)

These elastic cross-sections typically have values of less than $\sim 10^{-20}$ cm⁻² at energies above approximately 100 keV and approach values of 10^{-16} cm⁻² as the incident ion energy decreases.

The kinetic energy transferred from the ion to the target in the elastic collision is found from elementary classical scattering theory (Ziegler and Manoyan, 1988) to be

$$E_{\rm kin} = \frac{4E_{\rm A}m_{\rm A}m_{\rm B}}{m_{\rm A} + m_{\rm B}} \sin^2 \frac{\Theta}{2}$$
(2.14)

where Θ , the center-of-mass (CM) scattering angle, is obtained using the "Magic Formula" of Biersack and Haggmark (1980) and the "universal" potential for ion-target scattering of Ziegler and Biersack (1985). It should be noted that the scattering angles are all assumed to be small and thus tracks of the primary ions are approximated with straight line trajectories; however, we calculate these angles explicitly in the code to allow for more accurate modeling of the energy lost in such nuclear-elastic collisions.

¹Data taken from Edgar et al. (1975)

²Data extracted from Newson et al. (1995)

³Data extracted from Sweeney and Shyn (1996)

State	a	J(eV)	ν	Ω	I(eV)
		Atomic Ox	ygen ¹		
$^{3}P_{2}$	20.40	6.15×10^4	0.82	0.75	13.6
		Molecular O	xygen ¹		
$X^2 \Pi_q$	9.56	$4.58 imes 10^4$	0.61	1.26	12.1
U		Ozone	2		
$X^{1}A_{1}$	40.00	1.05×10^5	1.00	0.75	12.43

Table 2.1: Proton ionization cross-section parameters

Excited State	a	J(eV)	ν	Ω	W(eV)
		Atomic Oxyg	en ¹		
$^{1}\mathrm{D}$	0.51	5.40×10^{3}	1.0	1.0	1.85
$^{1}\mathrm{S}$	0.075	$8.70 imes 10^3$	1.0	1.0	4.18
$^{3}\mathrm{S}$	0.38	3.72×10^4	1.0	1.0	9.53
$^{5}\mathrm{S}$	0.55	$1.61 imes 10^6$	1.0	1.0	9.20
		Molecular Oxy	gen ¹		
$a^1\Delta_{\rm g}$	0.092	2.50×10^3	0.5	3.0	0.98
$b^1 \Sigma^+_{\circ}$	0.11	4.19×10^3	0.5	3.0	1.64
$A^3 \Sigma_{\mu}^+$	0.57	1.76×10^4	0.5	0.9	4.5
$B^3\Sigma_{\mu}^{-}$	4.73	$5.17 imes 10^4$	0.5	0.75	8.4
9.9 eV peak	0.83	$8.07 imes 10^4$	0.5	0.85	9.9
1		Ozone ³			
$^{1}B_{2}$	0.84	20.00	0.30	35.00	4.9

Table 2.2: Proton excitation cross-section parameters

For protons, ionization and excitation cross-sections are calculated using the semiempirical Green-McNeal formula (Green and McNeal, 1971; Miller and Green, 1973)

$$\sigma_{\text{inelastic}} = \sigma_0 \frac{(Z_{\text{B}} a)^{\Omega} (E_{\text{A}} - I)^{\nu}}{J^{\Omega + \nu} + (E_{\text{A}} - I)^{\Omega + \nu}}$$
(2.15)

where $\sigma_0 = 10^{-16} \approx \pi r_0^2 \text{ cm}^2$, Z_B is the number of electrons in the target atom or molecule, and *I* is the ionization threshold. For excitations between bound states, we replace *I* with *W*, the energy threshold for the particular transition. Listed in Tables 2.1 and 2.2 are the species-dependent values of the unit-less parameters Ω , ν , and *a*, as well as those of the parameter *J*, which is given in units of energy.

In the O_2 ice system considered here, ionization of neutrals by protons, as well as secondary electrons, leads to the formation of the following cation-secondary electron product pairs:

$$O \to O^+ + e^- \tag{2.16}$$

$$O_2 \to O_2^+ + e^-$$
 (2.17)

$$O_3 \to O_3^+ + e^-.$$
 (2.18)

For ionization, the energy deducted from the colliding ion is equal to the sum of the ionization threshold, plus an amount equal to the energy of the resulting secondary electron, which is selected randomly from a skewed Gaussian probability density function(Pimblott et al., 1996) with a mean value of 33 eV, the average energy per ion pair for O_2 (Dalgarno, 1962).

Shown in Fig. 2.1 are the cross-sections as a function of proton energy for collisions with the neutral species we consider in this work, O, O₂, and O₃ using the parameters listed in Tables 2.1 and 2.2. For atomic and molecular oxygen, we have used data from Edgar et al. (1975). Due to the lack of proton-ozone collisional data, in this work, we have fit measured electron impact ionization (Newson et al., 1995) and electron impact excitation cross-sections (Sweeney and Shyn, 1996) to Eq. (2.15) for use in both proton-ozone and secondary electron-ozone ionization and excitation collisions. As can be seen in Fig. 2.1, for all of the neutral species considered, the ionization cross-sections of protons for all energies above 100 eV are at least about an order of magnitude larger than either the excitation or elastic collisional cross-sections. Below this energy, elastic collisions are dominant. Fig. 2.1 also shows the well-known inverse relationship between primary ion energy and total collisional cross-section, i.e. that colliding particles with more energy interact less as they travel through materials than do those with lower energies. This illustrates partially why attempts to measure the galactic cosmic ray energy spectrum are thwarted by the effects of Sun, since the lower energy cosmic rays interact more strongly with the Solar wind (Parker, 1958).

Secondary Electrons

Once formed, secondary electrons are placed on a random lattice site next to their parent cations and diffuse away until they are stopped by the solid through energy lost in inelastic collisions. To calculate their trajectories in the material, we utilize a hybrid approach which combines elements of proton travel with our treatment of the hopping of neutral species. As with protons, we calculate a mean-free-path between inelastic collisions; however, in the case of electrons, we use this distance to determine the number of instantaneous jumps from one neighboring lattice site to the next until ionization or excitation occurs. The value used in determining these distances is the sum of the total inelastic collisional crosssection and a constant elastic cross-section equal to the geometrical hard-sphere value of $\sigma_{\text{elastic}}^e = 10^{-16} \text{ cm}^2$. The actual distance a secondary electron travels between collisions, Δx , is then calculated as in Eq. (2.6). Energy loss due to elastic collisions of electrons is not treated rigorously since, for the purposes of chemical changes in the solids, such collisions are of comparatively less importance than excitations and ionizations, due to the mass difference between electrons and bulk species.

The secondary electrons formed by the primary ion are known as "first-generation" secondary electrons and these can, in turn, ionize other species in the bulk, resulting in the formation of later generations of secondary electrons. In this way, a cascade of a few to up to $\sim 10^4$ ion-pairs can be formed from a single primary ion (Mason et al., 2014). For electron-impact ionization cross sections, we use the semi-empirical formala described in Green and Stolarski (1972) given by:

$$\sigma_{i}(E) = \sigma_{0} A(E) \Gamma(E) \left[\arctan\left(\frac{T_{m}(E) - T_{0}(E)}{\Gamma(E)}\right) + \arctan\left(\frac{T_{0}(E)}{\Gamma(E)}\right) \right]$$
(2.19)

where, σ_0 is 10^{-16} cm² and A(E) is the differential cross-section with respect to energy, calculated using

$$A(E) = \left(\frac{K}{E} + K_{\rm B}\right) \ln\left(\frac{E}{J} + J_{\rm B} + \frac{J_{\rm C}}{E}\right).$$
(2.20)

The values $\Gamma(E)$ and $T_0(E)$ are what Green and Stolarski (1972) refer to as width and resonance factors, respectively, and are given by

$$\Gamma(E) = \Gamma_{\rm S} \frac{E}{E + \Gamma_{\rm B}}$$
(2.21)

$$T_0(E) = T_{\rm S} - \left(\frac{T_{\rm A}}{E + T_{\rm B}}\right) \,\mathrm{eV}.$$
(2.22)

We assume the more energetic electron, post collision, to be the particle which caused the ionization. Thus, $T_{\rm m}$, the maximum energy of the new secondary electron, is half the remaining energy of the parent electron after the ionization, i.e. $T_{\rm m} = 1/2(E - I)$, where E the energy of the colliding secondary electron and I the ionization threshold. Values used in calculating these cross-sections are given in Table 2.3.

Table 2.3: Electron ionization cross-section parameters

State	K (eV)	$K_{\rm B}$	J (eV)	$J_{\rm B}$	$J_{\rm C}~({ m eV})$	$\Gamma_{\rm S}$ (eV)	$\Gamma_{\rm B}$ (eV)	$T_{\rm S}~({\rm eV})$	$T_{\rm A}$ (eV)	$T_{\rm B}~({\rm eV})$
					Molecula	r Oxygen ⁴	4			
$X^2 \Pi_{\rm g}$	0.48	0.00	3.76	0.00	0.00	18.50	12.10	1.86	1000.00	24.20
0					Atomic	Oxygen ⁴				
$^{3}P_{2}$	1.03	0.00	1.81	0.00	0.00	13.00	- 0.81 ₅	6.41	3450.00	162.00

For electron-impact excitations of bulk species from the ground state to the j-th state, we use the formalism developed by Porter (1976) for allowed transitions, in which the cross-section is given by

$$\sigma_{j}(E) = \left(\frac{q_{0} F_{j} \left[1 - \left(\frac{W}{E}\right)^{\alpha}\right]^{\beta}}{E W}\right) \ln\left(\frac{4E C}{W} + e\right).$$
(2.23)

Here $q_0 = 4\pi a^2 R^2$, where is *R* the Rydberg energy for atomic hydrogen, F_j is the optical oscillator strength, and α and β dimensionless values which Porter (1976) extracted from experiment. *W* is again the excitation energy threshold and ensures proper shape in the low-energy regime while *C* ensures proper high-energy falloff. Species-specific values used in this work for calculating these excitation cross-sections can be found in Tables 2.4 and 2.5.

Excited State	W(eV)	α	β	C	F
		Atomic Oxy	gen ⁴		
$^{3}\mathrm{S}$	9.53	0.86	1.44	0.32	0.056
		Molecular Ox	ygen ⁵		
$B^3\Sigma_{\mathrm{u}}^-$	8.4	1.19	2.31	0.037	0.25
9.9 eV peak	9.9	1.38	3.44	0.62	0.029

Table 2.4: Electron excitation cross-section parameters for allowed transitions

Table 2.5: Electron excitation cross-section parameters for forbidden transitions

Excited State	W(eV)	α	β	Ω	F
		Atomic Oxy	gen ⁴		
$^{1}\mathrm{D}$	1.96	1.00	2.00	1.00	0.010
$^{1}\mathrm{S}$	4.18	0.50	1.00	1.00	0.0042
$^{5}\mathrm{S}$	10.60	19.20	10.50	2.69	0.013
		Molecular Ox	xygen ⁵		
$a^1\Delta_{ m g}$	0.98	3.00	1.00	3.00	0.0005
$b^1 \Sigma^+_{\sigma}$	1.64	3.00	1.00	3.00	0.0005
$A^3 \Sigma_{\mathrm{u}}^{+}$	4.50	1.00	1.00	0.90	0.021

Our calculated values for the electron cross-sections, using the parameters given in Tables 2.3, 2.4, and 2.5, are shown in Fig. 2.2. Comparison with Fig. 2.1 shows that the cross-sections for electron impact are generally smaller than the equivalent values for protons at the same energy.

Energy is deducted from secondary electrons until a lower threshold of 4 eV is reached, at which point a secondary electron enters the sub-excitation regime. Sub-excitation secondary electrons are thought to be the delivery mechanism for ~10-20% of the energy deposited in the solid by the primary ion (Fano and Stephens, 1986), and affect the chemistry through a variety of mechanisms, such as the resonant process of dissociative electron attachment (DEA) (Arumainayagam et al., 2010). We choose 4 eV as our lower energy threshold since it corresponds approximately to the low energy limit of the resonance which leads to DEA in O_2 (Arumainayagam et al., 2010).

⁴Data taken from Jackman et al. (1977)

⁵Data taken from Porter (1976)



Figure 2.2: Electron-collision cross-sections calculated using parameters from Tables 2.3, 2.4, and 2.5.

As listed in Table 2.6, we assume that sub-excitation electrons are destroyed in one of two ways. One possibility is through charge recombination with a neighboring cation. The other is by reaction with a randomly chosen neighboring neutral species via DEA to form an anion. These anions then react with nearby cations formed in previous ionization collisions at the end of the track calculation phase, at which time all remaining charged species are neutralized by such fast ion-ion reactions (Johnson, 1990).

2.2.2 Continuous-time random walk chemical modeling

In the chemical phase of the model, ground-state neutral species in the bulk can diffuse throughout the crystal lattice of the solid and reactions can occur. The Monte Carlo technique used for modeling the chemistry of the solid is the continuous-time random walk method initially developed by Montroll and Weiss (1965), which was further developed by

ID#	Electron Attachment ⁶	$f_{ m branching}$	Source
1	$O + e^- \rightarrow O^-$	1.00	(Phelps, 1969)
2	$O_2 + e^- \to O^- + O$	1.00	(Arumainayagam et al., 2010)
3	$O_3 + e^- \rightarrow O^- + O_2$	1.00	(Senn et al., 1999)
ID#	Electron Recombination	$f_{\rm branching}$	Source
4	$O^+ + e^- \rightarrow O(^1D)$	1.00	(Garrod et al., 2008)
5	$O_2^+ + e^- \rightarrow 2O$	0.20	(Peverall et al., 2001)
6	$O_2^+ + e^- \rightarrow 2O(^1D)$	0.36	(Peverall et al., 2001)
7	$O_2^+ + e^- \rightarrow O + O(^1D)$	0.44	(Peverall et al., 2001)
8	$O_3^+ + e^- \rightarrow O_2 + O$	0.06	(Zhaunerchyk et al., 2008)
9	$O_3^+ + e^- \rightarrow 3O$	0.26	(Zhaunerchyk et al., 2008)
10	$O_3^+ + e^- \rightarrow 3O(^1D)$	0.0094	(Zhaunerchyk et al., 2008)
11	$O_3^+ + e^- \rightarrow O + 2O(^1D)$	0.20	(Zhaunerchyk et al., 2008)
12	$\mathbf{O}_3^{+} + e^- \to 2\mathbf{O} + \mathbf{O}(^1\mathbf{D})$	0.47	(Zhaunerchyk et al., 2008)

Table 2.6: Secondary electron reactions

Chang et al. (2005) and others (Chang and Herbst, 2014, 2016; Hincelin et al., 2015; Lauck et al., 2015) for studying molecular formation on interstellar dust grains. In this scheme, the interstitial sites facilitate bulk diffusion by allowing species to hop from one interstitial site to another with a low barrier. Normal lattice species are, effectively, immobile and do not become interstitial species; however, if a species on a normal lattice site dissociates or reacts, the products can become interstitial. Moreover, an interstitial species can hop to a lattice defect site to become a normal lattice species. A cartoon representation of these possible moves is given in Fig. 1 of Chang and Herbst (2014).

Hopping rates are parameterized by three species-specific values: the binding energy for surface species, $E_{\rm D}$; the barrier against diffusion for surface species, $E_{\rm b1}$; and, the barrier against diffusion for bulk species, $E_{\rm b2}$. We approximate the surface barrier against diffusion as being $E_{\rm b1} = 0.5E_{\rm D}$ following the approximation used in Garrod and Herbst (2006). The bulk barrier against diffusion is assumed to be $E_{\rm b2} = 0.7E_{\rm D}$ (Chang and Herbst, 2014).

For any surface species, the rate coefficient for hopping, b_1 , given by

$$b_1 = \nu \exp\left(-\frac{E_{\rm b1}}{T}\right) \tag{2.24}$$

where *T* is the temperature of the solid and ν is the trial frequency, which has a value of $1.0 \times 10^{12} \text{ s}^{-1}$ (Chang and Herbst, 2014; Hasegawa et al., 1992). Similarly, the rate coefficient for bulk species is

$$b_2 = \nu \exp\left(-\frac{E_{\rm b2}}{T}\right). \tag{2.25}$$

Moreover, on the surface, our Monte Carlo technique allows for the possibility of desorption into the gas phase with a rate coefficient of

$$b_3 = \nu \exp\left(-\frac{E_{\rm D}}{T}\right). \tag{2.26}$$

Whether a surface species hops or desorbs is based on a competitive mechanism based on a random number, R_D , to determine the outcome:

Outcome
$$\begin{cases} \text{Desorption for } 0 < R_{\rm D} \le \frac{b_3}{b_3 + b_1} \\ \text{Diffusion for } \frac{b_3}{b_3 + b_1} < R_{\rm D} \le 1 \end{cases}$$
(2.27)

Because the primary focus of this work is on modeling the chemistry of the irradiated O_2 system, and because the model is not coupled to any gas-phase chemical system, we have disabled the desorption of surface species. Even when enabled, however, such thermal desorption is negligible, given the low ice temperature of 5 K and the high reactivity of the most weakly bound species, atomic oxygen.

Reactions in the model are assumed to proceed via the diffusive (Langmuir-Hinshelwood) mechanism, and can occur when species hop to sites occupied by possible co-reactants, and products can be formed. If the reaction has a barrier, a competitive mechanism is also utilized to determine whether the reaction proceeds or the hopping species diffuses away. If one of the co-reactants occupies a normal bulk lattice site and there are multiple products, the one with the higher binding energy will be placed at the site, with the rest being randomly placed in the surrounding interstitial sites. On the surface, only the normal lattice sites can be occupied, i.e. it is assumed that there are no available interstitial sites on the surface.

The waiting time between hops, τ , for a species on the surface is given by

$$\tau_{\rm surf} = -\frac{\ln(R_{\rm D})}{b_1 + b_3},$$
(2.28)

while for bulk species, the time is

$$\tau_{\rm bulk} = -\frac{\ln(R_{\rm D})}{b_2}.$$
(2.29)

As shown in Fig. 2.3, bulk hopping times are affected by both the system temperature and the height of the diffusion barrier. Above about 100 K, further increases in temperature have little or no effect on the hopping time; however, there is a strong temperature dependence below 10 K and this effect becomes larger with increasing diffusion barriers. As described in detail in Chang and Herbst (2014), the waiting time until the next action is stored in a data structure that also contains the type and current coordinates of each species in the system. After a hop, the model searches the waiting list and the species associated with the shortest waiting moves next.

⁶Only applicable for sub-excitation electrons



Figure 2.3: Hopping times for neutral species as a function of system temperature and diffusion barrier height.

2.2.3 Chemical Network

In their work, B99 fit their experimental data with a simplified chemical network consisting of:

$$O_2 \rightarrow 2O$$
 (2.30)

$$O_3 \to O + O_2 \tag{2.31}$$

$$O + 2O_2 \rightarrow O_3 + O_2 \tag{2.32}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{2.33}$$

where here, reactions (2.30) and (2.31) are irradiation induced dissociations, and reactions (2.32) and (2.33) are assumed to proceed via thermal diffusion in the solid. Our network expands on the work of B99, in part, by including electronically excited neutral species, as shown in Table 2.7. We are able to do this since our method of calculating the tracks of the proton and secondary electrons allows us to determine the final state of a species after undergoing an excitation collision; however, our ability to do so is limited by the scarcity of data on the reactivity and product pathways of species in most of these excited states. For instance, though we explicitly consider excitation of O₂ from its triplet ground state to both excited singlet and triplet states, as shown by the cross-sectional parameters in Tables 2.2-2.5, the available theoretical and experimental kinetic data is almost entirely for the ${}^{1}\Delta$ state. Given this discrepancy between the available cross-sectional and kinetic data, in our network, we denote all electronically excited O₂ as O₂(${}^{1}\Delta$). We similarly denote the other

ID#	Neutral-Neutral Reactions	$f_{\rm branching}$	$E_{\rm A}(\rm kJ/mol)$	Source
13	$O + O \rightarrow O_2(^1\Delta)$	1.00	0.00	(Warnatz, 1984)
14	$\mathrm{O} + \mathrm{O}_2 \to \mathrm{O}_3(^1\mathrm{B}_2)$	1.00	0.00	(DeMore et al., 1997)
15	$O + O_3 \rightarrow 2O_2$	1.00	17.12	(Atkinson et al., 2004)
16	$O_3 + O_3 \rightarrow 3O_2$	1.00	77.41	(Pshezhetskii et al., 1959)
17	$O(^{1}D) + O \rightarrow 2O$	0.50	0.00	(Sobral et al., 1993)
18	$O(^{1}D) + O \rightarrow O_{2}(^{1}\Delta)$	0.50	0.00	See text
19	$O(^{1}D) + O_{2} \rightarrow O + O_{2}$	0.50	0.00	(DeMore et al., 1997)
20	$O(^1D) + O_2 \rightarrow O_3(^1B_2)$	0.50	0.00	See text
21	$O(^{1}D) + O_{3} \rightarrow 2O_{2}$	1.00	0.00	(Brasseur and Solomon, 1984)
22	$O_2(^1\Delta) + O \to O + O_2$	0.50	0.00	(Doroshenko et al., 1992)
23	$O_2(^1\Delta) + O \rightarrow O_3(^1B_2)$	0.50	0.00	See text
24	$O_2(^1\Delta) + O_2 \to 2O_2$	1.00	0.00	(Klopovskiy et al., 1999)
25	$O_2(^1\Delta) + O_3 \rightarrow 2O_2 + O$	1.00	23.61	(DeMore et al., 1997)
26	$O(^{1}D) + O(^{1}D) \rightarrow 2O$	0.50	0.00	See text
27	$O(^{1}D) + O(^{1}D) \rightarrow O_{2}(^{1}\Delta)$	0.50	0.00	See text
28	$O(^{1}D) + O_{2}(^{1}\Delta) \rightarrow O + O_{2}$	0.50	0.00	(Doroshenko et al., 1992)
29	$O(^1D) + O_2(^1\Delta) \rightarrow O_3(^1B_2)$	0.50	0.00	See text
30	$O(^{1}D) + O_{3}(^{1}B_{2}) \rightarrow 2O_{2}$	1.00	0.00	See text
31	$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow 2O_2$	1.00	3.23	(Heidner, 1981)
32	$O_2(^1\Delta) + O_3(^1B_2) \rightarrow 2O_2 + O$	1.00	23.61	See text
33	$O_3(^1B_2) + O_3(^1B_2) \to 3O_2$	1.00	77.41	See text
34	$O_3(^1B_2) + O \rightarrow 2O_2$	1.00	17.12	See text
35	$O_3(^1B_2) + O_2 \rightarrow 2O_2 + O$	1.00	23.61	See text
36	$O_3(^1B_2) + O_3 \rightarrow 3O_2$	1.00	77.41	See text
ID#	Ion Recombinations	$f_{\rm branching}$	$E_{\rm A}(\rm kJ/mol)$	Source
37	$O_2^+ + O_2^- \rightarrow O_2(^1\Delta) + O_2$	1.00	0.00	(Fridman, 2008)
38	$O_2^+ + O^- \to O_2(^1\Delta) + O$	1.00	0.00	(Fueki and Magee, 1963)
39	$O_2^- + O^+ \to O_2(^1\Delta) + O$	1.00	0.00	(Fueki and Magee, 1963)
40	$O^+ + O^- \rightarrow 2O(^1D)$	1.00	0.00	See text
41	$O^+ + O_3^- \to O(^1D) + O_3(^1B_2)$	1.00	0.00	See text
42	$O^+ + O_3^- \rightarrow 2O_2(^1\Delta)$	1.00	0.00	See text
43	$O^- + O_3^+ \to O(^1D) + O_3(^1B_2)$	1.00	0.00	See text
44	$O^- + O_3^+ \to 2O_2(^1\Delta)$	1.00	0.00	See text
45	$O_2^- + O_3^+ \to O_3(^1B_2) + O_2(1\Delta)$	1.00	0.00	See text
46	$O_2^+ + O_3^- \to O_3(^1B_2) + O_2(1\Delta)$	1.00	0.00	See text
47	$O_3^+ + O_3^- \to 3O_2(^1\Delta)$	1.00	0.00	See text

Table 2.7: Chemical network. The activation energies and branching fractions are taken from gas-phase studies.

excited neutral species in our network using the term symbol of the best studied higher state.

In our code, we assume that neutrals in excited electronic states either react immediately with a neighboring species or relax back to the ground state if there are no possible nearest neighbor co-reactants. The important role excited species play in the chemistry of the irradiated oxygen ice system is illustrated by the following two reactions:

$$O(^{3}P) + O_{3} \rightarrow 2O_{2}$$

 $O(^{1}D) + O_{3} \rightarrow 2O_{2}.$

Here, the reaction between ozone and the triplet ground state of atomic oxygen has been measured to have a barrier of about 0.2 eV (Atkinson et al., 2004), whereas no barrier has been reported for the reaction between excited singlet atomic oxygen and ozone (DeMore et al., 1997).

Following B99, we have drawn heavily on previous research in atmospheric chemistry in compiling our network (Atkinson et al., 2004; Brasseur and Solomon, 1984; DeMore et al., 1997); however, in some cases we have been unable to find data on certain reactions, particularly for those involving two electronically excited species. For these, we have based the product channels and branching fractions on similar reactions. Since the chemistry here is occurring in an ice, we have added additional pathways to some of the gas-phase reactions to account for solid-phase effects. For instance, to the previously studied (Sobral et al., 1993) gas-phase reaction

$$O + O(^{1}D) \rightarrow 2O$$

we have added the additional product channel

$$O + O(^{1}D) \rightarrow O_{2}$$

to account for the trapping and stabilization of products in the ice.

Ion-ion recombinations present unique challenges in our model, since there are a number of product channels involving species that can be formed in a number of different excited states. For simplicity, where we have been unable to find data on these processes, we base the product channels on the corresponding neutral-neutral reactions, but with products assumed to be electronically excited, as with:

$$O^- + O_3^+ \to 2O_2(^1\Delta)$$
$$O^+ + O_3^- \to 2O_2(^1\Delta),$$

which were based on the reaction between singlet atomic oxygen and ozone.

One class of reactions not present in our network consists of those between ions and neutral species. These are often barrier-less and are known to be of significant astrochemical importance (Wakelam et al., 2010). We do not include these since we assume in this work that ions are quickly neutralized via charge recombination reactions, as suggested by previous theoretical and experimental studies (Baragiola et al., 1999; Johnson, 1990). This is due to the uncertain diffusion barriers of charged species in solids, and the significant influence of effects which we do not consider in this work, such as Coulombic forces.

2.3 **Results and Discussion**

As an initial test of our approach, we simulated the experiment described in B99 in which O_2 is partially converted to O_3 . Listed in Table 2.8 are the physical conditions we take from that work. We assume an initial pure O_2 ice at a constant temperature of 5 K, connected to a helium cryostat. The ice studied in B99 had a thickness of $\sim 10 \ \mu m$. In this work we model a $\sim 0.1 \ \mu m$ thick ice, due both to computational expense and because our interest is ultimately in the chemistry of the ice mantles of interstellar dust grains, which are thought to reach a maximum thickness on the order of $\sim 0.01 \ \mu m$ (Herbst, 2014). We here use the thicker ice, since in this work, we wanted to better model the experiment, rather than an actual interstellar ice mantle. In our code, the simulation begins when the first proton collides with the pristine ice. Following B99, we assume an initial proton energy of 100 keV and a flux of $10^{11} \mbox{ cm}^{-2} \mbox{ s}^{-1}$. The model continues to follow subsequent proton arrivals and hopping of species in the ice until an upper fluence limit of $10^{17} \mbox{ protons/cm}^2$ is reached, where fluence is defined as the total irradiation exposure per unit surface area. It is used in comparing the results of irradiation in a way that is less dependent on the specific flux of particles to which the material is exposed.

Table 2.8: Model parameters

Physical Conditions from B99	Value
Temperature	5 K
Ice Density [O ₂]	$1.313 \times 10^{22} \text{ cm}^{-3}$
Initial Proton Energy	100 keV
Proton Flux	$1.0 \times 10^{11} \mathrm{~cm^{-2}~s^{-1}}$
Species	Binding Energy to O_2 (eV)
0	2.15×10^{-2}
O_2	7.85×10^{-2}
O_3	6.41×10^{-2}

Using the parameters listed in Table 2.8, our code predicts that each proton undergoes a collision in the bulk of the ice approximately every 300 Å, or about three times, given the thickness of the simulated ices in this work. On average, protons in these simulations lose on the order of $\sim 10^2$ eV, or 0.1% of their initial energy, by the time they exit the system. We can, however, arbitrarily fix the distance between proton collisions to be some smaller value. By thus increasing the number of collisions, and thus the energy deposited in the system by each proton, we can approximate the effects of having a thicker ice. From the formula for the stopping power, given in Eq. (2.7), one can derive the energy lost by a proton traveling in a straight path through any given solid to be

$$\Delta E = \Delta x \sum_{n} \frac{Q_n}{\Lambda_n},\tag{2.34}$$

where Δx is some path length and the sum is over *n* inelastic processes, with each resulting



Figure 2.4: Sample track structure in which a proton collides with a pristine O_2 ice with fixed collision distance of $\Delta x = 33$ Å.

in an average energy loss, Q_n , by the primary ion and having a mean-free-path of Λ_n . If Δx is the total thickness of the solid, ΔE approximates the total energy lost by the primary ion, which is proportional to ice thickness and inversely proportional to the mean-free-path between energy loss events.

Shown in Fig. 2.4 is an example of a track calculation in which, starting with pristine O_2 ice, we fixed the distance between collisions to be 33 Å, corresponding to a total cross-section larger than the real value by about an order of magnitude. Here the proton enters the ice at z = 0 Å, with an entry angle of 90° relative to the surface, and travels in a nearly straight path through the material until it exits at z = 1000 Å. In Fig. 2.4 the path of the proton is represented by a red line and secondary electron paths are given in blue. CIRIS performs such a track calculation for every proton arrival. Given the simulated size of our ice, to reach a fluence of 10^{17} protons/cm², our code calculates more than 10^6 such proton arrivals.



Figure 2.5: Ozone abundances both as calculated by CIRIS and from B99. Experimental data are shown in blue. Calculated abundances are represented by the yellow, green, and red curves, which correspond the ices of thicknesses of 0.1 μ m, 1 μ m, and 10 μ m, respectively.

Between track calculations, neutral species diffuse through the solid and can react with their neighbors. The rate of this diffusive chemistry is governed, in part, by the hopping rates of each of the reactants. In our code, we calculate these hopping rates using Eqs. (2.24) - (2.26). These values are functions of both the temperature of the solid and the barrier against diffusion, which we approximate as 50% and 70% of the desorption energy, $E_{\rm D}$, of the relevant adsorbate-substrate pair for surface and bulk diffusion, respectively. For O₂-O₂, we have a measured value of $E_{\rm D}^{\rm O_2} = 7.85 \times 10^{-2}$ eV from an experimental study by Acharyya et al. (2007). Lacking other data, one could make the crude assumption that atomic oxygen desorption is ~ 0.5 times this value, and ozone desorption as 1.5 times this value, giving $E_{\rm D}^{\rm O} = 3.92 \times 10^{-2}$ eV and $E_{\rm D}^{\rm O_3} = 1.18 \times 10^{-1}$ eV for O and O₃, respectively. Unfortunately, we were unable to find much other previous work on O-O₂ or O_3 - O_2 desorption energies; however, Cuppen and Herbst (2007) estimate these values to be $E_D^O = 4.74 \times 10^{-3}$ eV and $E_D^{O_3} = 1.03 \times 10^{-2}$ eV for O and O₃ adsorbed on an O₂ substrate. Here, we assume that the values derived from the work of Acharyya et al. (2007) represent a rough upper limit, while those in Cuppen and Herbst (2007) represent a lower limit, and use the average of the two. This gives values of $E_{\rm D}^{\rm O} = 2.15 \times 10^{-2}$ eV for O and $E_{\rm D}^{\rm O_3} = 6.41 \times 10^{-2}$ eV for O₃. B99 assumed that the concentration of atomic oxygen in their ice remained very low throughout the experiment, given its reactivity with molecular oxygen. We find that, in our models at 5 K, values for the $O-O_2$ diffusion barriers above $E_{\rm B}^{\rm O} \sim 2.60 \times 10^{-2}$ eV lead to a large buildup of atomic oxygen in the ice which is most likely unphysical. Values lower than this, such as the one used here, result effectively in a constant near-zero concentration of atomic oxygen in the ice, as it reacts quickly with surrounding species.

Plotted in Fig. 2.5 are ozone abundances as a function of proton fluence for the ex-

perimental data of B99, as well as several calculated abundance curves. Shown in yellow are data from Model A, in which the distances between proton collisions are calculated on-the-fly based on the magnitude of the energy-dependent cross-sections, as given by Eq. (2.3). A comparison between the experimental data and this model shows that, in both, ozone abundances increase at roughly the same rate before reaching $\sim 7 \times 10^{-4}$ mol cm⁻³. After abundances have reached this quasi steady-state value, further irradiation results in only marginal increases in ozone. The fluence at which such an inflection in growth occurs, however, is much larger in the model than measured in B99. This discrepancy is likely due to the differing ice thicknesses considered. Since the ices used in the experimental study were roughly two orders of magnitude thicker than the $\sim 0.1 \ \mu m$ ice considered in this work, each proton which hit the surface deposited less energy in our base model simulation. To illustrate this effect, we include simulations in Fig. 2.5, Models B and C, in which the distance between proton collisions was artificially reduced from our calculated value of ~ 300 Å, to 3.3 and 33 Å, respectively. These data show that, as more energy per proton is transferred to the solid, the theoretical results approach the experimental values. From Fig. 2.5, one can also see that the best agreement between our model and the experiment is obtained when $\Delta x = 3.3$ Å. Given the thickness of our simulated ice, this means that the proton collides ~ 300 times before exiting the system. If one uses the Model A results for protons of ~ 300 Å between collisions, this corresponds to an ice ~ 10^5 Å, or 10 μ m, thick - approximately equal to the actual thickness of the ice studied in B99.

The chemistry behind the ozone abundances given in Fig. 2.5 begins with the arrival of the first proton. The secondary electrons which form along the track of this primary ion are the main drivers of atomic oxygen production through both dissociative attachment with O_2 and dissociative recombination with O_2^+ . Atomic oxygen is mainly depleted through reaction with O_2 , resulting in the formation of the ozone which begins to build up in the ice. This reaction between triplet O and triplet O_2 continues to be the primary formation route for ozone throughout the simulation. Once formed, ozone is destroyed through two main non-thermal pathways which occur as a result of continued irradiation. The first of these is through direct ionization by both the primary ion and secondary electrons, resulting in O_3^+ , which is destroyed via the charge neutralizations with either secondary electrons or anions, which occur at the end of each track calculation phase of the code. The other main destruction mechanism for ozone is reaction with singlet atomic and molecular oxygen, both of which are formed either through direct excitation or as a product of ion-ion and ion-electron recombinations.

2.4 Summary and Conclusions

In this work, we have presented a new stochastic model which calculates the physical and chemical changes of solids exposed to high-energy protons. Beginning with pure O_2 ice we are able to follow, on a collision-by-collision basis, the tracks of energetic protons and secondary electrons. The reactive species, such as atomic oxygen, which form as a result of the non-thermal processes induced by the irradiation cause significant chemical changes in

the ice, even at the very low temperatures considered in this work where thermal diffusive chemistry is inefficient. As shown in Fig. 2.5, we are able to reproduce both the quasi-steady-state abundances of ozone in such an irradiated material, as well as reproduce the approximate thickness of the ice studied by B99.

Though our ultimate goal is to better understand the degree to which interactions between cosmic rays and interstellar grain ice mantles contribute to the formation of complex molecules, the techniques presented here are not specific to the chemistry of these extreme environments, and can be applied to other systems as well. One area of practical interest where CIRIS can compliment experimental work is in modeling irradiated polymers, such as poly(vinyl chloride) or PVC. These materials are widely used in environments in which they are exposed to ionizing radiation (Nicholson, 2006). Previous experimental work has investigated PVC radiolysis (LaVerne et al., 2008), and our code could compliment such studies by providing a means to investigate possible radiolysis pathways, or to simulate the system under physical conditions and exposures not practical or obtainable in the laboratory. Ionizing radiation also poses serious health and safety risks for any future missions to Mars and the Moon, and our code could be used to evaluate potential radiation shielding materials, such as those composed of polymers. This type of shielding is generally more effective at stopping energetic ions than metals, but poses a greater risk of structural failure due to prolonged exposure or flammability, in part, from radiolysis products like gaseous H_2 (Barghouty and Thibeault, 2006; LaVerne et al., 2008). By allowing for simulations of the physicochemical evolution of potential shielding materials, use of CIRIS could aid mission planners in selecting the safest, most effective solutions.

A major consideration for future applications to other systems is the availability, or lack thereof, of relevant experimental data. In calculating tracks and collisional probabilities for each neutral species considered in this work, our code draws on cross-sectional data for electron and proton impact ionization and excitation. For the chemistry, we rely on desorption energies to calculate hopping rates, and kinetic studies to determine the branching fractions. Unfortunately, there is often significant uncertainty in desorption energies, as is the case for $O-O_2$ binding. For the kinetics of charge recombination processes such as ion-ion and ion-electron reactions, the unique properties of storage rings allow for experiments, such as the one reported by Zhaunerchyk et al. (2008), that can furnish exactly the kind of data which can be directly used in our code, i.e. dissociation pathways, the electronic states of products, and branching fractions. Though we have had to rely mostly on previous gas-phase studies in modeling the comparatively simple O_2 ice system, this approach is not equally applicable for all systems. For instance, Ribeiro et al. (2015) irradiated CH_3CN ice and observed products with notably different abundances from what would be expected in the gas phase, likely because of the influence of the condensed medium on the non-thermal ion and electron induced chemistry. Such experimental work is of significant value when considering irradiation chemistry on a microscopic level and future applications should focus on systems where solid state

Nevertheless, this model may represent a first-step towards a better understanding of complex, interconnected phenomena. Future versions of our code will focus on improvements that will enable us to examine other aspects of the irradiation of a solid in more

38

detail, despite the promising results reported here of our simulations of the O_2 ice system. First, we would like to consider displacement of lattice species due to elastic collisions in more detail. Improving these aspects will allow us to better model the changes to the ice lattice caused by collisions between bulk species and the primary ion, as well as to begin examining additional processes associated with ion-solid collisions, such as sputtering, in which bound species on or near the surface of the target material are released into the gas phase. Another aspect of the model that is important to continue developing is electron transport. This aspect is treated in more detail by the CASINO (Hovington et al., 1997) and PENELOPE (Salvat et al., 2006) models, and it may be possible to incorporate the theory they employ into future versions of CIRIS. Related to this, electrostatic effects such as Coulombic forces could be incorporated that could allow for a better picture of the motion of charged species in the solid. Improvements such as these will enable us to better investigate irradiation induced non-thermal desorption mechanisms. In addition to sputtering, these improvements include desorption induced by electronic transitions (DIET), Auger stimulated ion desorption (ASID), and electron stimulated ion desorption (ESID) (Ribeiro et al., 2015). These processes are of particular astrochemical interest, because they represent a means by which the complex molecules formed on interstellar dust grain surfaces can be

C.N.S. wishes to thank the Advanced Research Computing Services (ARCS) center at the University of Virginia for use of the RIVANNA supercomputer. E.H. wishes to thank the National Science Foundation for continuing to support the astrochemistry program at the University of Virginia. This research has made use of NASA's Astrophysics Data System Bibliographic Services.

CHAPTER 3

ON A GENERAL THEORY FOR MODELING RADIATION CHEMISTRY

In this chapter, we propose a general formalism that allows for the estimation of radiolysis decomposition pathways and rate coefficients suitable for use in astrochemical models, with a focus on solid phase chemistry. Such a theory can help increase the connection between laboratory astrophysics experiments and astrochemical models by providing a means for modelers to incorporate radiation chemistry into chemical networks. The general method proposed here is targeted particularly at the majority of species now included in chemical networks for which little radiochemical data exists; however, the method can also be used a starting point for considering better studied species. We here apply our theory to the irradiation of H_2O ice and compare the results with previous experimental data.¹

3.1 Introduction

NTERSTELLAR space is permeated by the highly energetic particles known as cosmic rays. These particles, which are over 90% protons and typically have energies of MeV-TeV, are formed in supernovæ (Baade and Zwicky, 1934) or active galactic nuclei (see review by Blasi (2013) and references therein). Unlike external UV photons, cosmic rays are not quickly attenuated in regions with high visual extinctions (>10) and can undergo a large number of collisions before being fully stopped (Padovani et al., 2009; Rimmer et al., 2012). The interaction between these ionizing particles and the gas and dust of the interstellar medium can have significant effects on the physical and chemical properties of a source (Caselli et al., 1998; Ceccarelli et al., 2011; Guelin et al., 1977; Hasegawa et al., 1992; Ivlev et al., 2015; Leger et al., 1985) and are thus of great astrochemical interest.

In addition to the production of gas-phase ions, which leads to ion-molecule chemistry, cosmic rays have two main roles in astrochemical simulations. The more important is in generating internal UV photons, following the work of Prasad and Tarafdar (1983), which drive photoionization and photodissociation. In many astrochemical models, cosmic rays can also non thermally desorb grain-surface species (Ruaud et al., 2016), following work by Hasegawa et al. (1992). In addition to these functions, however, cosmic rays can also have a substantial impact on the chemistry of interstellar ices, particularly in cold cores such as

¹Originally published as Shingledecker and Herbst (2018)

TMC-1 where there is very little thermal energy to drive the normal diffusive chemistry of grain species.

In this work, we will refer to the chemical changes induced by ionizing particles by the historical and still widely used, though somewhat confusing, name of "radiation chemistry (Spinks and Woods, 1990)," which was originally coined by Burton (Magee, 1988) and meant to distinguish the field from photochemistry. One key characteristic of radiation chemistry is the production of "secondary electrons" which are produced in ionizing collisions in an irradiated material and typically have energies below ~ 50 eV (Johnson, 1990).

A large body of work in laboratory astrophysics exists on the action of ionizing radiation on astrophysically relevant ices (Boyer et al., 2016; Rothard et al., 2017), and some experiments have shown that complex organic molecules, even amino acids, can be produced in irradiated ice mixtures (Abplanalp et al., 2016; Lafosse et al., 2006). However, despite the abundance of such studies, astrochemical models largely omit any solid-phase radiation chemistry. This deficiency in models has been due, in part, to the complexity of the microscopic processes that contribute to the ultimately measured values in experiments, and the lack of radiochemical data for the majority of the many species now included in astrochemical networks. For instance, the chemical network used in recent work by Ruaud et al. (2016) contains 717 different species.

Recently, in Abplanalp et al. (2016), we made an initial attempt to examine the effects of radiation chemistry in astrochemical simulations. This was, to the best of our knowledge, the first time such processes were incorporated into an astrochemical network, and our results showed that the additions improved the agreement between observed and calculated abundances. A major obstacle to a more thorough implementation of radiation chemistry in astrochemical networks has been the lack of a general theory that can be used to reduce the detail needed in a microscopic model (Shingledecker et al., 2017) to a level more easily implementable in a typical rate equation model. Ideally, such a theory should be (a) applicable to any species, (b) utilize readily available physical values as parameters, and (c) should give results within reasonable agreement of experiments. In this work, we propose a simple, astrochemically relevant formalism for estimating both the major radiolysis decomposition pathways and rate coefficients in a manner suitable for addition to standard chemical networks, which we hope satisfy these criteria. Here, we discuss the theory in §2, and apply our scheme to water ice in §3. A list of key values used in this work is given in Table 3.1.

3.2 Theory

3.2.1 Energy loss and *W* values

Since the early 20th century, it has been known that when a swiftly moving charged particle of ionizing radiation, which we will call the primary ion, encounters some material, called the target, the primary ion loses velocity and physicochemical changes to the target

Value	Units	Description
$\overline{\sigma_{ m tot}}$	cm^2	Total cross section
$\sigma_{ m n}$	cm^2	Nuclear cross section
$\sigma_{ m e}$	cm^2	Electronic cross section
$\sigma_{ m ion}$	cm^2	Ionization cross section
$\sigma_{ m exc}$	cm^2	Excitation cross section
$S_{\rm e}$	$eV cm^2$	Total electronic stopping cross section
$S_{\rm ion}$	$eV cm^2$	Ionization stopping cross section
$S_{\rm exc}$	$eV cm^2$	Excitation stopping cross section
W	eV	Mean energy per ion pair
G	species/100 eV	Radiochemical yield
$E_{\rm ion}$	eV	Ionization potential
E_0	eV	Excitation threshold
$W_{\rm e}$	eV	Total inelastic energy loss
$W_{\rm ion}$	eV	Average ionization energy loss
$W_{\rm exc}$	eV	Average excitation energy loss
$W_{\rm s}$	eV	Average sub-excitation energy loss
ϵ	eV	Secondary electron energy
ζ	s^{-1}	Cosmic ray ionization rate
ξ		Excitation to ionization ratio
$N_{\rm e}$		Total number of inelastic collisions
$N_{\rm ion}$		Total number of ionizing collisions
$N_{\rm exc}$		Total number of excitating collisions
M		Number of species created or destroyed
F		Total number of inelastic processes
Ι		Total number of ionized states
J		Total number of transitions between bound states
$f_{\rm br}$		Branching fraction
$P_{\rm e}$		Electron escape probability
$P_{\rm dis}$		Dissociation probability
$\phi_{\rm st}$		Spitzer & Tomasko cosmic ray flux
$\phi_{\rm ism}$		Scaled cosmic ray flux

Table 3.1: Key symbols used.

occur (Curie, 1910). These changes are driven by collisions in which energy is transferred from the primary to the target (Bethe, 1932; Bohr, 1913). A convenient distinction was made by Bohr (1913) between energy loss by the swiftly moving charged particle to the nuclei and electrons, termed elastic and inelastic collisions, respectively. The inelastic collisions can, in turn, be divided into collisions in which the target species are either ionized or electronically excited. Thus, the total collisional cross section can be represented by

$$\sigma_{\rm tot} = \sigma_{\rm n} + \sigma_{\rm e} = \sigma_{\rm n} + \sigma_{\rm ion} + \sigma_{\rm exc} \tag{3.1}$$

with σ_n and σ_e being the elastic and inelastic cross sections, and σ_{ion} and σ_{exc} being the cross-sections for ionization and excitation. Using this distinction between nuclear and electronic collisions, we can express the "stopping power," or energy loss per unit path length for any energetic particle, as

$$\frac{dE}{dx} = n(S_{\rm n} + S_{\rm e}) \tag{3.2}$$

where *n* is the density of the target and S_n and S_e are the stopping cross sections in units of energy times area, which are also sometimes referred to by the more descriptive term "energy loss functions" (Peterson and Green, 1968). The electronic stopping cross section, S_e , characterizes the energy lost in inelastic collisions by a primary ion hitting some target, and are dependent on the physical properties of both.

The electronic energy loss function, S_e , can be described as the sum of each possible inelastic energy loss, weighted by its cross section. For example, let F be the number of different inelastic collisional processes in which w_f energy is lost by the primary ion traveling through some target. Moreover, let F be composed of (a) the ionization of I different states resulting in an energy loss of w_i^{ion} and (b), J different excitations between bound and unbound states resulting in an energy loss of w_j^{exc} . The electronic energy loss function, $S_{e'}$ is then (Johnson, 1990)

$$S_{\rm e} = \sum_{f}^{F} w_f \sigma_f = \sum_{i}^{I} w_i^{\rm ion} \sigma_i^{\rm ion} + \sum_{j}^{J} w_j^{\rm exc} \sigma_j^{\rm exc} + \dots$$
(3.3)

where here, we have neglected higher order processes such as double ionizations.

Consider now the case of the bombardment of a target by a single primary ion where we approximate the inelastic energy loss function to be $S_e = S_{ion} + S_{exc}$. Now, let N_e be the total number of inelastic collisions that occur between target species in the material and both the primary ion and secondary electrons. Moreover, let N_{ion} be the total number of ionizing collisions and N_{exc} be the total number of exciting collisions such that the total number of inelastic collisions is $N_e = N_{ion} + N_{exc}$. The average energy lost in exciting collisions, W_{exc} , is then

$$W_{\rm exc} = \frac{1}{N_{\rm exc}} \sum_{j}^{N_{\rm exc}} w_j^{exc}$$
(3.4)

where w_j^{exc} is the energy lost in each excitation. One can also define an average excitation cross section, $\overline{\sigma_{exc}}$ as

$$\overline{\sigma_{\text{exc}}} = \frac{\sum_{j}^{N_{\text{exc}}} \sigma_{j}^{\text{exc}} w_{j}^{\text{exc}}}{\sum_{j}^{N_{\text{exc}}} w_{j}^{\text{exc}}}$$
(3.5)

The remainder of the inelastic collisions, $N_{ion} = N_e - N_{exc}$, result in ionization of species in the target. One can similarly define the average ionization energy loss to be

$$W_{\rm ion} = \frac{1}{N_{\rm ion}} \sum_{i}^{N_{\rm ion}} w_i^{ion}$$
(3.6)

and the average ionization cross section

$$\overline{\sigma_{\text{ion}}} = \frac{\sum_{i}^{N_{\text{ion}}} \sigma_{i}^{\text{ion}} w_{i}^{\text{ion}}}{\sum_{i}^{N_{\text{ion}}} w_{i}^{\text{ion}}}.$$
(3.7)

In equations (3.5) and (3.7), we have averaged the cross sections of both the primary ion and secondary electrons. Such an approach is physically meaningful, since the cross sections for both have similar peak values - around 10^{-16} cm⁻² for collisions in solid O₂ and typically remain within an order of magnitude of each other at high energies (Shingledecker et al., 2017). For every ionizing collision some energy $w_i^{ion} = E_{ion} + \epsilon$ is lost, where E_{ion} is the ionization potential of the target species and ϵ is the energy of the newly liberated secondary electron. If $\epsilon > E_{ion}$, following Fano (1946), we assume that it contributes to the total number of ionizing collisions, N_{ion} . Unlike Fano, however, if ϵ is less than $E_{\rm ion}$ but greater than some electronic excitation threshold of the target, E_0 , we will assume it contributes to the total number of exciting collisions, N_{exc} . Secondary electrons with energies below the excitation threshold of the target are known as sub-excitation electrons (Platzman, 1955) and contribute neither to the total number of ionization or excitation collisions, though are thought to play a critical role in irradiation induced chemistry (Arumainayagam et al., 2010). We will assume (a) that all N_{ion} secondary electrons produced in ionizing collisions either are formed with energies in the sub-excitation regime, or lose sufficient energy via subsequent ionization or excitation collisions to become sub-excitation electrons, and (b), that these sub-excitation electrons have an average energy of $W_{\rm s}$.

As an example, consider the case of a secondary electron with energy ϵ in a molecular hydrogen gas, where $E_{\text{ion}} = 15.4 \text{ eV}$ and $E_0 = 11.2 \text{ eV}$ (Philip et al., 2004). Here, ϵ can be either the initial energy, ϵ_0 , of the secondary electron, or a subsequent value after the electron has undergone some number of inelastic collisions. If ϵ is greater than 15.4 eV, we assume it further ionizes other H₂ molecules. If the energy is in the range $11.2 \text{ eV} \le \epsilon \le 15.4 \text{ eV}$, we similarly assume that the electron would cause electronic excitations in H₂. Finally, if $\epsilon < 11.2 \text{ eV}$, we consider it a sub-excitation electron.

For every ionizing collision, there will be some number of excitation collisions. Let ξ be the average excitation to ionization ratio, i.e.

$$\xi = \frac{N_{\rm exc}}{N_{\rm ion}}.\tag{3.8}$$

Thus, W_{e} , the total energy transferred to the target via inelastic collisions with either the primary ion or secondary electrons is

$$W_{\rm e} = N_{\rm ion}W_{\rm ion} + \xi N_{\rm ion}W_{\rm exc} = N_{\rm ion}(E_{\rm ion} + W_{\rm s}) + \xi N_{\rm ion}W_{\rm exc}.$$
(3.9)

One can also express the inelastic energy loss per ionization as *W*, where

$$W = E_{\rm ion} + W_{\rm s} + \xi W_{\rm exc} \tag{3.10}$$

is an important quantity in experimental nuclear physics and radiation chemistry (Bethe and Ashkin, 1953) and typically has a value of ~ 30 eV (Dalgarno and Griffing, 1958; Simon Wedlund et al., 2011).

3.2.2 *G* values

Some of the inelastic collisions by the primary ion or secondary electrons result in the dissociation of species in the target material. The number of species created or destroyed per 100 eV of energy transferred to the system by irradiating particles is known as the G value, which is another important quantity in radiation chemistry. This radiochemical yield has a typical value between 0.1-3 molecules/100 eV for bombardment by protons.

The G value has a long history in radiation chemistry, and was proposed by Burton (Dewhurst et al., 1952). As an example, consider the radiolysis of some species, A, described by

$$aA \rightsquigarrow bB + cC + \dots \tag{3.11}$$

where the curly arrow implies bombardment by either a primary ion or secondary electron, and the lowercase values represent the stoichiometric coefficients of the reactants and products. The corresponding *G*-value for the destruction of *A*, as it might be measured, would then be

$$G(-A) = a f_{\rm br} \left(\frac{100}{W}\right) \left(\frac{M^{\rm (A)}}{N_{\rm ion}}\right)$$
(3.12)

where *a* is the stoichiometric coefficient of *A*, f_{br} is the branching fraction where there are multiple product channels, $M^{(A)}$ is the number of *A* molecules destroyed, and N_{ion} is the number of ion-pairs produced. The negative value of *A* in G(-A) implies that *A* is here being destroyed. The *G* values for the destruction of the reactant and production of the products can then be related via

$$\frac{G(-A)}{a} = \frac{G(B)}{b} = \frac{G(C)}{c}.$$
 (3.13)

It should be noted that, strictly speaking, the measured *G* values characterize a system in steady state, and are dependent on the physical conditions and nature of the target (Johnson, 2011). Also, as will be discussed later in this work, the *G* values of the immediate production or destruction are not identical to the measured values due to processes that impact the actual number of species measured.

3.2.3 Decomposition Pathways

The ultimately reported experimental G values characterize the steady state yields of the irradiated system. These yields are effective values that reflect the cumulative physicochemical changes that occur in the target as a result of bombardment by many primary ions. Though complex, the series of events caused by a single primary ion can be divided into several major phases. During the initial "physical" stage of irradiation, the ionizing and exciting collisions between the target and both the primary ion and secondary electrons occur. Subsequently, during the "physicochemical" stage, radiolysis products are formed through the dissociation of excited species and the charge neutralization of molecular ions (Johnson, 1990). In a detailed microscopic model, for even a relatively simple irradiated system, i.e. a pure O₂ ice, one must consider a large number of possible radiolysis products and decomposition pathways (Shingledecker et al., 2017). This level of detail, however, is not realistically achievable in most widely used astrochemical models, which typically use a rate equation approach of some kind and are quite limited in accommodating physical complexity, particularly for grain surface and bulk chemistry (Garrod and Herbst, 2006; Ruaud et al., 2016; Willis and Garrod, 2017).

Therefore, it is necessary to simplify the microscopic radiochemical processes in a way that is amenable to inclusion into astrochemical models, yet captures the salient features of radiation chemistry that contribute to its astrochemical interest. In this work, we propose that essential astrochemically relevant features of irradiation chemistry are (a) the ionization and excitation of target species, (b) the destruction of the target species via charge neutralization and excitative dissociation, and (c) the formation of radiolysis products, including electronically excited suprathermal species. Thus, for molecular species, *A*, we propose the following basic decomposition pathways that occur after bombardment by an energetic particle

$$aA \rightsquigarrow aA^+ + e \tag{3.14}$$

$$aA \rightsquigarrow aA^+ + e \rightarrow aA^* \rightarrow bB^* + cC^*$$
(3.15)

$$aA \rightsquigarrow aA^* \to bB + cC$$
 (3.16)

$$aA \rightsquigarrow aA^*$$
 (3.17)

where the star superscript indicates an electronically excited species. Here, we will refer to processes (3.14)-(3.17) as ion1, ion2, exc1, and exc2, respectively. If *A* is an atom, we assume that process (3.16) does not occur and that (3.15) is functionally identical to (3.17). Once they are formed, we further assume that these electronically excited, or suprathermal, species rapidly react, are quenched by the solid (Abplanalp et al., 2016; Johnson, 1990; Shingledecker et al., 2017), or dissociate in the case of molecular products (Herbst, 1978). Reactions between ground state species that have a barrier often have little or no barrier when one of the reactants is in one of these electronically excited states, which is in part why such energetic radiolysis products have been of recent astrochemical interest (Shingledecker et al., 2017), and these suprathermal species have been implicated in driving the non-equilibrium low-temperature solid-phase chemistry seen in previous experiments (Abplanalp et al., 2016). In a real system, the measured *G* values will be heavily influenced by the rate of the backwards reactions, e.g. $bB + cC \rightarrow aA$. One advantage of including reactions (3.14) - (3.17) in an astrochemical simulation is that the back reactions can be accounted for separately and explicitly, thus, we here focus on the radiolytic destruction of *A* and show only the forward reactions. It should be emphasized that reactions (3.14)-(3.17) most appropriately describe what occurs in the bulk of the solid, where most of the radiation chemistry is thought to occur (Abdulgalil et al., 2013). Conversely, irradiationinduced processes at the gas-surface interface, also called the selvedge, are more likely to lead to desorption, as also noted in work by Abdulgalil et al. (2013).

Having described the major decomposition routes for A via radiolysis, we now turn our attention to determining the products, which we have here called B and C. We first examine the products of the excitative dissociation given in (3.16), where A dissociates after being electronically excited due to an inelastic collision with a primary ion or secondary electron. One can use the dissociation products from photochemistry Okabe (1978) as a guide in this regard (Spinks and Woods, 1990), since there is typically no distinction whether the species absorbed w_i^{exc} eV from an inelastic collision from a particle or a photon of $E = w_i^{\text{exc}}$ when considering a single event. Care must be taken, however, due to two key differences between photochemistry and radiation chemistry. First, in photochemistry selection rules govern the possible excitations and product channels. Secondly, since photochemical experiments often use monochromatic light, only a few, or even one, electronic transition may result, moreover, not all species in a photochemical target of mixed composition will absorb light of the utilized frequency to the same degree, and the chemical changes observed can be dominated by the dissociation of a single constituent. Conversely, for ionizing radiation, a larger number of electronic excitations are possible in the target species, and in mixed materials all components can be physio-chemically altered (Wishart, 1998).

The products of the dissociative recombination reaction given in (3.15) can be more difficult to estimate. For polyatomic species there exist statistical theories, such as the one proposed by us in a previous work (Herbst, 1978), in which the excited intermediate is treated as a complex of excited atoms and the product channels are assumed to be independent of the entrance channel. This statistical method works best for molecules with \sim 3 or more atoms (Chabot et al., 2010). For smaller species, the dissociative recombination mechanism can be non-statistical; however, since these are typically better studied than larger species, there is likely to be more relevant experimental and theoretical work which could be used in determining the nature and energetics of the products. For both excitative dissociation and dissociative recombination, where there are multiple known product channels, the corresponding *G* values for the formation of the products can be multiplied by a branching fraction, as in equation (3.12).

What, though, are the *G* values for reactions (3.14)-(3.17)? Consider the case of $N_{ion} = 1$

and $N_{\text{exc}} = \xi$. Based on processes (3.14)-(3.16), we propose the following forms for the *G* values describing the effects of an inelastic collision resulting in the ionization or excitation of some species, *A*:

$$G_{\text{ion1}}(-A) = a P_{\text{e}} \left(\frac{100}{W}\right) M_{\text{ion}}^{(A)}$$
(3.18)

$$G_{\rm ion2}(-A) = a \left(1 - P_{\rm e}\right) \left(\frac{100}{W}\right) M_{\rm ion}^{(A)}$$
 (3.19)

$$G_{\text{exc1}}(-A) = a P_{\text{dis}} \left(\frac{100}{W}\right) M_{\text{exc}}^{(A)}$$
(3.20)

$$G_{\rm exc2}(-A) = a \left(1 - P_{\rm dis}\right) \left(\frac{100}{W}\right) M_{\rm exc}^{\rm (A)}$$
 (3.21)

where *a* is the stoichiometric coefficient, $P_{\rm e}$ is the electron escape probability and $P_{\rm dis}$ is the dissociation probability. The electron escape probability can be estimated using the formalism of Elkomoss and Magee (1962), based on which we approximate $P_{\rm e} = 0$ for solids, which means that $G_{\rm ion1} = 0$, i.e. that all charged species formed in ionizations are neutralized. Regarding the dissociation probability, we here set $P_{\rm dis} = 0.5$ in the absence of any experimental or theoretical data for *A*.

For each process given in Eq. (3.14)-(3.17), we determine the corresponding value of $M^{(A)}$ from our expression for the *W* value given in (3.10). Thus, for each ionization

$$M_{\rm ion}^{\rm (A)} = 1$$
 (3.22)

while the number of excitations that occur per ion-pair is then

$$M_{\rm exc}^{\rm (A)} = \xi. \tag{3.23}$$

Following Fueki and Magee (1963) we estimate an average value of ξ from the energy per ion-pair, *W* using

$$\xi = \frac{W - (E_{\rm ion} + W_{\rm s})}{W_{\rm exc}}.$$
(3.24)

In solids with large band gaps, excitons, electron-hole pairs formed due to the electronic excitation of species in the material, have been noted as being both a promising link between photochemistry and radiation chemistry and an additional initiator of physic-ochemical changes (Cuppen et al., 2014). These excitons could increase the number of excited species and thereby amplify the radiochemical yield. Though a consideration of these effects is beyond the scope of the present work, they could be included via an extra factor in equation (23) which would take into account the increased number of affected species.

Since *W* is typically ~ 30 eV (Bethe and Ashkin, 1953; Dalgarno and Griffing, 1958; Lind, 1961), G_{ion1} and G_{ion2} will be similar for most species. Thus, the relative stability of some electronically excited species, A^* , is reflected more by ξ . From equation (3.24), one can see that ξ is inversely proportional to W_{exc} , and thus, the smaller the average excitation energy, the more excitation collisions that will occur per ion-pair (Johnson, 2011).

To obtain values for E_{ion} and W_{exc} we assume a solid composed of pure *A*. For solids, E_{ion} and by extension, *W* will typically be lower than the corresponding gas phase values. Here, for species in interstellar ices, we take E_{ion} to be the ionization potential from the ground state. The average excitation energy, W_{exc} , can be approximated as the peak UV/vis absorption energy, corresponding to the most likely electronic transition (Fueki and Magee, 1963). Obtaining solid-phase values for W_{exc} can be difficult; however, gas-phase values can be easily obtained for many species from online databases such as the MPI-Mainz UV/Vis spectral atlas² or the Leiden database for astrophysical molecules³. The average sub-excitation energy, W_s , can be obtained from the distribution of sub-excitation electron energies given in Elkomoss and Magee (1962), which is a function of E_{ion} and E_0 and is given by

$$f(\epsilon) = \left(\frac{1}{\left[1 + \left(\frac{\epsilon}{E_{\rm ion}}\right)\right]^3}\right) \left(\frac{\left[1 + \left(\frac{E_0}{E_{\rm ion}}\right)\right]^2}{E_0 \left[1 + \left(\frac{E_0}{2E_{\rm ion}}\right)\right]}\right) \quad 0 \le \epsilon \le E_0$$
(3.25)

where ϵ is the sub-excitation energy. The average sub-excitation electron energy can be obtained from

$$W_{\rm s} = \frac{\int_0^{E_0} f(\epsilon)\epsilon \, d\epsilon}{\int_0^{E_0} \epsilon \, d\epsilon}.$$
(3.26)

In cases where the value of E_0 is not accurately known, one can approximate this energy as $E_0 \approx W_{\text{exc}}$ (Fueki and Magee, 1963).

3.2.4 Rate coefficients for radiolysis

Being thus equipped to estimate *G* values, we can now use them in determining rate coefficients for use in standard astrochemical models. From basic kinetic theory, one can express the first-order rate coefficient for the bombardment of some species by some particles with a flux of ϕ as $k(s^{-1}) = \sigma \phi$.

In the interstellar medium, cosmic rays are a ubiquitous form of ionizing radiation. Due to the effects of the Sun, directly measuring the interstellar flux from Earth is not possible (Parker, 1958), and there are a number of energy distributions in the literature which differ mainly in the abundance of cosmic rays with energies below ~ 1 GeV (see Indriolo et al.

²http://satellite.mpic.de/spectral_atlas

³http://home.strw.leidenuniv.nl/ ewine/photo/



Figure 3.1: Cosmic ray energy distribution from Spitzer and Tomasko (1968).

(2009) and references therein). We here estimate j(E), the cosmic ray intensity, using the widely used energy distribution of Spitzer and Tomasko (1968), given by

$$j(E) = \frac{0.90}{(0.85 + E_{\rm G})^{2.6}} \frac{1}{(1 + 0.01/E_{\rm G})}$$
(3.27)

where $E_{\rm G}$ is the cosmic ray energy in GeV. This distribution is shown in Fig. 3.1 and, when integrated for particle energies between 0.3 MeV to 100 GeV, corresponding to the lower limit of the Spitzer and Tomasko (1968) theory and a conservative upper cosmic ray energy, one obtains a flux of 8.6 particles cm⁻² s⁻¹, which changes only negligibly when the upper energy limit is increased. This integrated value of the interstellar cosmic ray flux, which we shall refer to as $\phi_{\rm st}$, was used in determining what has become the canonical molecular hydrogen ionization rate of $\zeta = 1.36 \times 10^{-17} \text{ s}^{-1}$ (Spitzer and Tomasko, 1968). This ionization rate is a common input parameter in astrochemical simulations, though is thought to be significantly enhanced in some sources (Indriolo et al., 2009; Oka, 2011; Shingledecker et al., 2016), particularly those near the galactic center (Oka, 2011). Thus, we will introduce a scaling factor, relative to $\phi_{\rm st}$, that can suitably adjust the cosmic ray flux based on the chosen value of ζ for the source being simulated, i.e.

$$\phi_{\rm ism} = \phi_{\rm st} \left(\frac{\zeta}{10^{-17}}\right) \tag{3.28}$$

where we have assumed here that increasing the ionization rate relative to the standard value increases the flux but preserves the overall energy distribution.

Thus, the rate coefficients for processes (3.14)-(3.17) are

$$k_{\rm ion1} = \sigma_{\rm ion1} \phi_{\rm ism} \tag{3.29}$$

$$k_{\rm ion2} = \sigma_{\rm ion2} \phi_{\rm ism} \tag{3.30}$$

$$k_{\rm exc1} = \sigma_{\rm exc1} \phi_{\rm ism} \tag{3.31}$$

$$k_{\rm exc2} = \sigma_{\rm exc2}\phi_{\rm ism}.\tag{3.32}$$

Where there are no experimental or theoretical data on the cross sections, these can be estimated using the appropriate G value from equations (3.18)-(3.21). If one expresses S_{e} , the inelastic stopping cross section, as the sum of the average ionization and excitation energy losses, then division by the average ionization cross section yields

$$\frac{S_{\rm e}}{\overline{\sigma_{\rm ion}}} \approx \frac{1}{\overline{\sigma_{\rm ion}}} \left(\overline{\sigma_{\rm ion}} W_{\rm ion} + \overline{\sigma_{\rm exc}} W_{\rm exc} \right) \\
= \frac{1}{\overline{\sigma_{\rm ion}}} \left(\overline{\sigma_{\rm ion}} E_{\rm ion} + \overline{\sigma_{\rm ion}} W_{\rm s} + \overline{\sigma_{\rm exc}} W_{\rm exc} \right) \\
= W$$
(3.33)

and one can then solve for the ionization cross section, i.e.

$$\overline{\sigma_{\rm ion}} = \frac{S_{\rm e}}{W} = \left(\frac{G_{\rm ion}}{100}\right) S_{\rm e}.$$
(3.34)

By substituting one of the *G* values given in Eq. (3.18)-(3.21) the rate coefficient for the corresponding process can be estimated (Baragiola et al., 1999). The first-order rate coefficients for processes n = 3.14-3.17, as can be used in astrochemical models, are therefore,

$$k_{\rm n} = \left(\frac{G_{\rm n}}{100}\right) S_{\rm e} \phi_{\rm ism} \tag{3.35}$$

where here, G_n is the *G* value for process (3.14)-(3.17). Equation (3.35) more strongly characterizes the disappearance of the reactants than the formation of the products as a result of the correlation between the rate coefficient and the assumptions made here about dissociation and branching fractions. In order to illustrate an extreme case, we here assume a total absence of relevant theoretical and experimental data for values like P_{dis} and f_{bf} ; however, this will not necessarily be true, particularly for common interstellar molecules.

One advantage of Eq. (3.34) is that there exist well known methods for calculating $S_e(E)$ (Bethe, 1932; Johnson, 1990; Ziegler and Biersack, 1985), particularly for high energy particles with energies above 1 MeV/nucleon (Ziegler and Biersack, 1985). The most commonly used formula for high energy electronic stopping cross sections is the Bethe equation (Bethe, 1932), also referred to as the Bethe-Born (Johnson, 1990) or Bethe-Bloch



Figure 3.2: Electronic stopping cross sections for protons in water, calculated using PSTAR.

equation (Ziegler and Biersack, 1985). For some primary ion, x with a velocity of v colliding with target atom y, the formula is

$$S_{\rm e}(E) = \frac{4\pi Z_{\rm x}^2 Z_{\rm y} e^4}{m_{\rm e} v^2} \left[ln \left(\frac{2m_{\rm e} v^2}{E_{\rm ion}} \right) - 1 - \frac{C}{Z_{\rm y}} \right]$$
(3.36)

where m_e is the electron mass, Z_x is the atomic number of x, Z_y is the atomic number of y, and e is the elementary charge. The factor C/Z_y is the shell correction term and accounts for cases where v is much greater than the bound electron velocities of y. The Bethe equation is also used in the popular SRIM program (Ziegler and Manoyan, 1988). This widely used model is particularly good at calculating energy loss, and can simulate other physical effects as well, such as lattice damage and surface sputtering; however, it neither considers the chemical changes that result from inelastic energy loss, nor does it explicitly distinguish between different kinds of electronic energy loss. We here circumvent these limitations through our use of the G values, which allows us to connect specific kinds of inelastic energy loss with specific chemical changes, i.e. radiolytic decomposition pathways.

For radiolysis processes in solids, we here use the stopping cross section for water, which is typically the primary constituent of astrochemical ices (Allamandola et al., 1999; Ruaud et al., 2016). Using the PSTAR program ⁴, we obtained the values for $S_{\rm e}$ shown in Fig. 3.2. A mean value of $S_{\rm e} = 1.287 \times 10^{-15} \, {\rm cm}^{-2} \, {\rm eV}$ was obtained using

⁴http://physics.nist.gov/PhysRefData/Star/Text/PSTAR.html

$$S_{\rm e} = \frac{\sum S_{\rm e}(E)j(E)}{\sum j(E)}$$
(3.37)

where here, we have used the Spitzer and Tomasko (1968) cosmic ray energy distribution for weighting.

Table 3.2: Ionization, excitation, and sub-excitation energies as well as the resulting Gvalues and rate coefficients for water.⁵ParameterValueSource

Parameter	value	Source
W	27 eV	Johnson (2011)
$E_{ m ion}$	12.62 eV	Lias (2018)
$W_{ m exc}$	11.12 eV	Keller-Rudek et al. (2013)
$W_{\rm s}$	3.85 eV	See text
$G_{ion2a}(-H_2O)$	1.85 species/100 eV	See text
$G_{ion2b}(-H_2O)$	1.85 species/100 eV	See text
$G_{\rm exc1}$ (-H ₂ O)	1.75 species/100 eV	See text
$G_{\rm exc2}$ (-H ₂ O)	1.75 species/100 eV	See text
$k_{ m ion2a}$	$2.05 \times 10^{-16} \mathrm{s}^{-1}$	See text
$k_{ m ion2b}$	$2.05 imes 10^{-16} \ \mathrm{s}^{-1}$	See text
$k_{ m exc1}$	$1.93 imes 10^{-16} \ \mathrm{s}^{-1}$	See text
$k_{ m exc2}$	$1.93 imes 10^{-16} \ { m s}^{-1}$	See text
$P_{\rm e}$	0.0	See text
$P_{\rm dis}$	0.5	See text

3.3 Results & Discussion

We will now apply our theory to the radiolysis of water ice. The resulting *G* values we obtain using our method are listed in Table 3.2. It should be noted that water is not an understudied species by any means in the context of radiation chemistry (Johnson, 1991, 2011), rather, it is the existence of such data that allows us to estimate the utility of the approximate treatment we propose here. Again, since we are considering solid-phase species, we will approximate $P_e = 0$, i.e. that electron recapture occurs with unit probability. For the remaining radiolysis pathways we will consider the following product channels:

$$H_2O \rightsquigarrow H_2O^+ + e \to OH^* + H^*$$
 (3.38a)

$$\rightarrow \mathrm{O} + \mathrm{H} + \mathrm{H}^* \tag{3.38b}$$

$$H_2O \rightsquigarrow H_2O^* \to OH + H$$
 (3.39)

⁵Rate coefficients were calculated assuming a cosmic ray ionization rate of $\zeta = 1.3 \times 10^{-17} \text{ s}^{-1}$.

$$H_2 O \rightsquigarrow H_2 O^*$$
 (3.40)

where products for reaction (3.39) are based on photo products (Roberge et al., 1991) and those shown in (3.38) are taken from previous water ice radiolysis studies (Johnson, 2011). We further denote processes (3.38a)-(3.40) as ion2a, ion2b, exc1, and exc2, respectively. For the sake of illustration, we let $f_{\rm br}^{(\rm ion2a)} = f_{\rm br}^{(\rm ion2b)} = 0.5$. Thus, the cosmic ray driven dissociation rate for water, $R_{\rm H_2O}^{(\rm CR)}$, is

$$R_{\rm H_2O}^{\rm (CR)} = k_{\rm ion2a} n({\rm H_2O}) + k_{\rm ion2b} n({\rm H_2O}) + k_{\rm exc1} n({\rm H_2O}) + k_{\rm exc2} n({\rm H_2O})$$
(3.41)

and the time dependent abundances of the suprathermal species are

$$\frac{d n(\mathrm{H}^*)}{dt} = k_{\mathrm{ion2a}} n(\mathrm{H}_2\mathrm{O}) + k_{\mathrm{ion2b}} n(\mathrm{H}_2\mathrm{O}) - \sum k n(\mathrm{H}^*) n(X)$$
(3.42)

$$\frac{d n(\mathrm{OH}^*)}{dt} = k_{\mathrm{ion2a}} n(\mathrm{H}_2\mathrm{O}) - \sum k n(\mathrm{OH}^*) n(X)$$
(3.43)

$$\frac{d n(H_2O^*)}{dt} = k_{\text{exc}2}n(H_2O) - \sum k n(H_2O^*)n(X)$$
(3.44)

where the sums are over all destruction reactions. In solids the lifetime of these suprathermal species is very short (Abplanalp et al., 2016; Shingledecker et al., 2017) since they will either rapidly react with a nearby species or be quenched by the solid. Thus, the abundance of these suprathermal species at any time will be very low.

In order to calculate the *G* values, and by extension the rate coefficients, we use an ionization energy of 12.62 eV (Lias, 2018) and an excitation energy of 11.12 eV, corresponding to the strong VUV absorption peak at 111.5 nm (Keller-Rudek et al., 2013). These values were then used in equation (3.25) to determine the sub-excitation energy distribution, shown in Fig. 3.3 and a mean sub-excitation electron energy of $W_s = 3.85$ eV using (3.26). Since, *W*, the mean energy per ion-pair is typically around ~ 30 eV, the total ionization *G* value is $100/W \approx 3$ molecules/100 eV. For water ice, we used a value of W = 27 eV (Johnson, 2011) and, assuming complete charge-neutralization, the resulting value we obtain for $G_{ion2} = G_{ion2a} + G_{ion2b}$ is 3.70 molecules/100 eV. Assuming $P_{dis} = 0.5$ means that $G_{exc1} = G_{exc2}$, which for water ice results in *G* values of 1.75 molecules/100 eV.

Direct comparison of our calculated *G* values with experimentally determined ones is complicated by the fact that distinguishing between different radiolysis pathways can be difficult, since excited molecular species either relax, dissociate, or react very quickly upon formation (Abplanalp et al., 2016; Shingledecker et al., 2017) and it is more common to infer these *G* values from the measured abundances of product species (Spinks and Woods, 1990). Hart, E.J. and Platzman, R. L. (1961) determined a value of $G(H_2) \approx 0.7$ molecules/100 eV based on out-gassing of H₂ from water ice irradiated by α particles. In



Figure 3.3: sub-excitation electron energy distribution for water, calculated using equation (3.25).

the water decomposition pathways given in (3.38a)-(3.40), hydrogen is produced in (3.38) and (3.39). Since the canonical value of $G_{\rm ion}$ is typically 3, and since the suprathermal products of the dissociative recombination are likely to be very short lived due to their increased reactivity (Abplanalp et al., 2016), we will focus our comparison on $G_{\rm exc1}$. If one rewrites process (3.39) as $H_2O \rightarrow OH + (1/2)H_2$, then, following the relation given in (3.13), we estimate a *G* value for the formation of H_2 of $G_{\rm exc2}(H_2) = 0.875$ molecules/100 eV, which is ~ 20% larger than the measured value of 0.7 molecules/100 eV. The difference between the measured and calculated *G* values underscores the difference between the *G* values of immediate formation and destruction and the measured quantities, which in this case are likely lower due to some combination of (a) outgassing of unreacted atomic hydrogen (b) competing reaction pathways, or (c) trapping in the ice. In a standard gasgrain astrochemical model, (a) and (b) at least are usually accounted for in some manner (Ruaud et al., 2016). Using Eq. (3.35) with the previously given values for $\phi_{\rm ism}$ and $S_{\rm e}$ results in rate coefficients of $k_{\rm ion2a} = k_{\rm ion2b} = 2.05 \times 10^{-16} \, {\rm s}^{-1}$ and $k_{\rm exc1} = k_{\rm exc2} = 1.93 \times 10^{-16} \, {\rm s}^{-1}$.

How important are these processes, though, in interstellar chemistry? In dense molecular clouds, where external UV photons are quickly attenuated, another possible dissociation mechanism for gas and grain species is via bombardment by internal UV photons, which are formed as a result of cosmic ray ionization of molecular hydrogen (Prasad and Tarafdar, 1983). Gredel et al. (1989) express the cosmic ray induced photodissociation rate, $R_A^{(CRP)}$, for some species, A, as

$$R_A^{(\text{CRP})} = \left(\frac{p_A}{1-\omega}\right) \zeta \ n(A) \tag{3.45}$$

where ω is the grain albedo and p_A is an efficiency factor for species A. From Gredel et al. (1989), we get $\omega = 0.5$ and $p_{\text{H}_2\text{O}} = 971$. Comparing $R_{\text{H}_2\text{O}}^{(\text{CR})}/R_{\text{H}_2\text{O}}^{(\text{CRP})}$, where $R_{\text{H}_2\text{O}}^{(\text{CR})}$ is given in equation (3.41), implies that the "direct" cosmic ray driven process of water radiolysis occurs with $\sim 3\%$ of the rate of "indirect" internal UV photodissociation. By way of further comparison, $R_{\rm H2O}^{\rm (CR)}$ is $\sim 10^9$ times greater than the rate of photodissociation caused by external UV photons (van Dishoeck, 1988) from the interstellar radiation field (Draine, 1978) in a source with visual extinction of $A_v = 10$, typical of dense molecular clouds. As indicated by previous experimental work (Abplanalp et al., 2016; Lafosse et al., 2006), radiolysis is astrochemically attractive, in part, because of the resulting suprathermal products, which can drive the formation of even complex molecules in low temperature ices, in addition to enhancing diffusion and desorption (Hasegawa et al., 1992; Ivlev et al., 2015; Leger et al., 1985). Thus, our calculated rate for the cosmic ray driven radiation chemistry of water is suggestive of the potential importance of these processes for other interstellar species. This conclusion is in line with our preliminary modeling results in which experimental Gvalues were used (Abplanalp et al., 2016). The simulation results presented in Abplanalp et al. (2016) indicated that the importance of direct cosmic ray ice processing is on par with, and in that case even more important than, indirect cosmic ray VUV photon processing.

As previously alluded to in this work, the underlying processes which drive the radiation chemistry are indeed complex (Shingledecker et al., 2017), and interpreting experimental data may require significantly more speculation than is needed in photochemistry (Spinks and Woods, 1990); however, given the level of detail of standard astrochemical models, reducing the complexity to a few key processes, as described here, can at least allow workers to assess the impact of ionizing radiation on the overall abundances predicted with astrochemical models.

3.4 Conclusion

In conclusion, in this work we have presented a general theory for estimating the radiolysis pathways and rate coefficients for any arbitrary species, *A*, which can be utilized by non-experts in irradiation chemistry. This formalism uses readily available physical values as input, and yields *G* values which are within an astrochemically satisfactory level of agreement with experimental data. The size of the calculated rate coefficients compared with the standard interstellar ionization rate point to the potential importance of radiolysis in grain-surface chemical networks, as does the growing body of laboratory astrophysics data showing that non-equilibrium irradiation-induced solid-phase chemistry can drive low-temperature complex organic molecule formation (Abplanalp et al., 2016; Lafosse et al., 2006).

3.5 Acknowledgements

E.H. wishes to thank the National Science Foundation for continuing to support the astrochemistry program at the University of Virginia. This research has made use of NASA's Astrophysics Data System Bibliographic Services.

CHAPTER 4

ON COSMIC RAY-DRIVEN GRAIN CHEMISTRY IN COLD CORE MODELS

In this chapter, we present preliminary results illustrating the effect of cosmic rays on solid-phase chemistry in models of both TMC-1 and several sources with physical conditions identical to TMC-1 except for hypothetically enhanced ionization rates. Using work described in Chapter 3, we calculated the radiochemical yields, called G values, for the primary dust grain ice-mantle constituents. We show that the inclusion of this non-thermal chemistry can lead to the formation of complex organic molecules from simpler ice-mantle constituents, even under cold core conditions. In addition to enriching ice-mantles, we find that these new radiation-chemical processes can lead to increased gas-phase abundances as well, particularly for HOCO, NO₂, HC₂O, methyl formate (HCOOCH₃), and ethanol (CH₃CH₂OH). These model results imply that HOCO - and perhaps NO₂ - might be observable in TMC-1. Future detections of either of these two species in cold interstellar environments could provide strong support for the importance of cosmic ray-driven radiation chemistry. The increased gas-phase abundance of methyl formate can be compared with abundances achieved through other formation mechanisms such as pure gas-phase chemistry and three-body surface reactions.¹

4.1 Introduction

OSMIC rays are a form of high-energy (MeV - TeV) ionizing radiation composed mostly of protons thought to form both in supernovae and galactic nuclei (Baade and Zwicky, 1934; Blasi, 2013; Lemaître and Vallarta, 1933). It has long been speculated that these energetic particles can have significant physicochemical effects on the interstellar medium (ISM) as a result of collisional energy transfer to the matter in a region. For example, in Herbst and Klemperer (1973), cosmic rays were shown to be the drivers of cold core chemistry via

$$\mathrm{H}_2 \rightsquigarrow \mathrm{H}_2^+ + \mathrm{e}^- \tag{4.1}$$

followed by

$$H_2^+ + H_2 \to H_3^+ + H$$
 (4.2)

¹Originally published as Shingledecker et al. (2018)
where the curly arrow implies bombardment by an energetic particle. The ion-molecule reactions initiated by H_3^+ are of central importance in the subsequent formation of polyatomic species. In addition, cosmic rays are thought to play an important role both in source heating (Ao et al., 2013; Goldsmith and Langer, 1978) and in generating internal UV photons in cold cores through the Lyman and Werner band excitation of H_2 (Prasad and Tarafdar, 1983).

The Galactic value of the cosmic ray ionization rate, ζ , cannot be directly measured from Earth due to the effects of the Solar wind (Parker, 1958). It is thought that the most common ionization rate in the ISM is $\zeta \approx 10^{-15} \text{ s}^{-1}$ everywhere but in dense regions (Grenier et al., 2015), where interactions between the dense cloud and the charged particles that comprise cosmic rays result in a reduced ionization rate of $\sim 10^{-17} \text{ s}^{-1}$ (Rimmer et al., 2012). However, even in dense regions, local effects can result in substantially higher fluxes of ionizing radiation leading to ionization rates in the range $\zeta \approx 10^{-15} - 10^{-14} \text{ s}^{-1}$. Such rates arise in Sgr A* (Ao et al., 2013; Yusef-Zadeh et al., 2013,?), and in sources like W51C, which are near supernova remnants (Ceccarelli et al., 2011; Shingledecker et al., 2016).

Collisions between cosmic rays and dust grains are also important in the ISM. For instance, Ivlev et al. (2015) note that cosmic rays affect the net charge on dust particles, which has an influence on grain growth. Cosmic ray collisions have also been implicated in impulsive grain heating (Hasegawa and Herbst, 1993; Ivlev et al., 2015), which can stimulate both diffusive chemistry and desorption. Despite this, the direct chemical effects resulting from cosmic ray bombardment of dust grain ice mantles are not currently considered in astrochemical models. Previous experimental work has shown that the bombardment of low-temperature ices by ionizing radiation can trigger a rich chemistry (Abplanalp et al., 2016; Hudson and Moore, 2001; Rothard et al., 2017) - including the formation of complex organic molecules such as amino acids (Holtom et al., 2005; Hudson et al., 2008; Lafosse et al., 2006).

Following Bohr (1913), the energy lost by an energetic particle per distance travelled - called the stopping power - can be approximated by the sum of two types of energy loss, as seen in the following equation:

$$\frac{dE}{dx} = n(S_{\rm n} + S_{\rm e}) \tag{4.3}$$

where *n* is the density of the target material, while S_n and S_e are so-called stopping cross sections (Johnson, 1990; Ziegler and Biersack, 1985) - also known as energy loss functions, in units of area × energy (Peterson and Green, 1968). Here, S_n characterizes the elastic energy collisionally transferred to nuclei in a material, while S_e characterizes the energy transferred to electrons in inelastic collisions (Bohr, 1913; Johnson, 1990; Spinks and Woods, 1990). Inelastic events, in turn, are typically approximated as consisting of collisions that cause either the ionization or electronic excitation of target species. The ionization of species in a material results in the formation of so-called "secondary electrons" (Spinks and Woods, 1990). Around 10^4 secondary electrons can be produced per MeV transferred to a material, and they play a critical role in propagating physicochemical changes initiated by primary ions (Gerakines et al., 2001; Mason et al., 2014; Spinks and Woods, 1990).

In Abplanalp et al. (2016), we made the first attempt - to the best of our knowledge - to incorporate experimentally determined chemical reactions resulting from radiation processes into an astrochemical model. Based on insights gained both from that work, and from radiation chemistry based on a subsequent detailed microscopic Monte Carlo model (Shingledecker et al., 2017), we developed a general method described in detail in Shingledecker and Herbst (2018) targeted at the great majority of astrochemically relevant radiolysis processes which have not been studied in detail in the laboratory. The basis of this method is that a microscopic collision between a target species, *A*, and either a primary ion or secondary electron is assumed to have one of the following outcomes:

$$A \rightsquigarrow A^+ + e^- \tag{R1}$$

$$A \rightsquigarrow A^+ + e^- \to A^* \to bB^* + cC^* \tag{R2}$$

$$A \rightsquigarrow A^* \to bB + cC \tag{R3}$$

$$A \rightsquigarrow A^*$$
. (R4)

Here, the asterisk indicates an electronically excited species, which can be referred to as "suprathermal" (Abplanalp et al., 2016); *B* and *C* are the dissociation products; and the lowercase letters are the stoichiometric coefficients (Spinks and Woods, 1990). In this work, we will refer to molecular dissociation due to bombardment by ionizing radiation as *radiolysis* (Johnson, 2011; Spinks and Woods, 1990).

In processes (R1) and (R2), A is ionized upon collision with an energetic particle, resulting in the ion-pair $A^+ + e^-$, which can quickly undergo dissociative recombination, as shown in (R2). The relative importance of (R1) and (R2) is characterized by the electron escape probability, $P_{\rm e}$, which we will here assume to be zero for solid-phase processes, so that (R1) is negligible. In processes (R3) and (R4), A is electronically excited after collision with an energetic particle. As with the ionizing processes, (R1) and (R2), the relative importance of (R3) and (R4) is given by $P_{\rm dis}$, the dissociation probability, which we will here assume to be 0.5 in the absence of relevant experimental or theoretical values.

The suprathermal species produced in processes (R2) and (R4) are critical when considering the effects of radiation exposure on a material, particularly in cold regions, because their energies are often sufficient to overcome reaction barriers that are inaccessible to the reactants in their ground electronic states (Spinks and Woods, 1990). Previous experimental work suggests that these electronically excited species can drive the formation of complex organic molecules, even in solids at 5 K (Abplanalp et al., 2016), where they likely either rapidly react with a neighbor or are quenched by the material (Spinks and Woods, 1990).

The overall efficiency of processes (R1)-(R4), called the radiochemical yield, is characterized by the G value (Dewhurst et al., 1952), defined as the number of molecules created

or destroyed per 100 eV deposited by an incident energetic particle into some system. As described in detail in Shingledecker and Herbst (2018), the *G* values for processes (R1)-(R4) can be calculated using the following expressions:

$$G_{\rm R1} = P_{\rm e} \left(\frac{100\,{\rm eV}}{W}\right) \tag{4.4}$$

$$G_{\rm R2} = (1 - P_{\rm e}) \left(\frac{100 \,{\rm eV}}{W}\right)$$
 (4.5)

$$G_{\rm R3} = P_{\rm dis} \left(\frac{100\,{\rm eV}}{W}\right) \left(\frac{W - (E_{\rm ion} + W_{\rm s})}{W_{\rm exc}}\right) \tag{4.6}$$

$$G_{\rm R4} = (1 - P_{\rm dis}) \left(\frac{100 \,\mathrm{eV}}{W}\right) \left(\frac{W - (E_{\rm ion} + W_{\rm s})}{W_{\rm exc}}\right)$$
(4.7)

where *W* is the mean energy per ion-pair (usually ~ 30 eV) (Dalgarno and Griffing, 1958; Edgar et al., 1973), E_{ion} is the ionization energy of *A*, W_{exc} is the average excitation energy of *A*, and W_s is the average sub-excitation energy of the secondary electrons formed via the ionization of *A* (typically ~ 3 eV) (Elkomoss and Magee, 1962; Fueki and Magee, 1963).

By definition, there is one ionization per ion-pair; however, the number of excitations per ionization is a function of the average excitation energy. The average number of excitations per ionization, ξ , is given by

$$\xi = \frac{W - (E_{\rm ion} + W_{\rm s})}{W_{\rm exc}} \tag{4.8}$$

and is the extra factor included in Eqs. (4.6) and (4.7). Physically, for every W eV lost per ion-pair, an amount equal to E_{ion} of that energy is used to generate the ion-pair, and some small amount W_s accounts for the fact that secondary electrons (a) lose energy through inelastic collisions or (b) have insufficient energy upon formation to either ionize or excite species in the material. Thus, the remaining energy per ion-pair available to cause electronic excitations is $W - (E_{ion} + W_s)$, and ξ , the average number of excitations that can result from this amount of energy, is a function of the average excitation energy, W_{exc} .

These *G* values can, in turn, be used to estimate the first-order rate coefficients (s^{-1}) of processes R1-R4 via

$$k_{\rm R1} = G_{\rm R1} \left(\frac{S_{\rm e}}{100 \text{ eV}} \right) \left(\phi_{\rm ST} \left[\frac{\zeta}{10^{-17}} \right] \right)$$
(4.9)

$$k_{\rm R2} = G_{\rm R2} \left(\frac{S_{\rm e}}{100 \text{ eV}} \right) \left(\phi_{\rm ST} \left[\frac{\zeta}{10^{-17}} \right] \right) \tag{4.10}$$

$$k_{\rm R3} = G_{\rm R3} \left(\frac{S_{\rm e}}{100 \text{ eV}} \right) \left(\phi_{\rm ST} \left[\frac{\zeta}{10^{-17}} \right] \right)$$
(4.11)

$$k_{\rm R4} = G_{\rm R4} \left(\frac{S_{\rm e}}{100 \text{ eV}}\right) \left(\phi_{\rm ST} \left[\frac{\zeta}{10^{-17}}\right]\right). \tag{4.12}$$

Here, ϕ_{ST} is the integrated Spitzer-Tomasko cosmic ray flux (8.6 particles cm⁻² s⁻¹) (Spitzer and Tomasko, 1968), ζ is the H₂ ionization rate, and S_e is the electronic stopping cross section (Bethe, 1932; Johnson, 1990; Ziegler and Biersack, 1985). Amorphous H₂O is typically the dominant ice-mantle constituent; thus, we approximate the stopping cross section for protons in amorphous water ice with the more readily available values for liquid water, which were calculated using the PSTAR program². An average value of $S_e = 1.287 \times 10^{-15}$ cm² eV was obtained using the Spitzer-Tomasko cosmic ray flux (Spitzer and Tomasko, 1968). As discussed further in §4.3, when multiplied by the density of the reactant species, Eqs. (4.9)-(4.12) refer to the time dependence of the concentration of products produced by radiolysis - driven mainly by inelastic collisions involving secondary electrons.

We here examine how radiolysis of the primary dust grain ice mantle constituents influences the chemistry of cold cores like TMC-1. The organization of the rest of this paper is as follows: in §4.2 we give details concerning the code and physical conditions used here, while §4.3 contains a description of the reactions and processes added to the network for this work. §4.4 concerns the description and discussion of our major findings, while in §4.5, we summarize our results and point to areas of future development.

4.2 Model

In this work, we focus on the chemistry of cold cores, such as TMC-1. Despite the low temperatures of these regions, their chemical complexity has been highlighted by recent detections of species such as HC_5O (McGuire et al., 2017), HC_7O (Cordiner et al., 2017; McGuire et al., 2017), and the aromatic molecule benzonitrile (McGuire et al., 2018). The effects of radiation chemistry should be more pronounced in these cold interstellar environments since thermal diffusion is inhibited, thus increasing the relative importance of fast solid-phase reactions involving suprathermal species.

We utilized the NAUTILUS-1.1 astrochemical model (Ruaud et al., 2016), in which three phases are simulated, specifically, (a) the gas-phase, (b) the ice/grain-surface, and (c) the ice-mantle bulk. This distinction between the surface and bulk of the ice is helpful here, since it highlights an important aspect of solid-phase radiation chemistry, namely, that bombardment by ionizing radiation can greatly increase the chemical importance of the bulk ice, since this is the phase in which the majority of the physicochemical changes likely occur (Johnson, 1990; Shingledecker et al., 2017; Spinks and Woods, 1990). The degree of penetration into the ice constitutes a major difference between photochemistry and radiation chemistry (Gerakines et al., 2001, 2004). In the absence of bombardment by energetic particles, the surface is significantly more important in astrochemical models, due both to the lower diffusion barriers and direct contact with the surrounding gas. The non-thermal

²https://physics.nist.gov/PhysRefData/Star/Text/PSTAR.html

desorption mechanisms for surface species are (1) chemical desorption with a standard 1% efficiency (Garrod et al., 2007) (2) cosmic ray-induced desorption (Hasegawa and Herbst, 1993), and (3) photodesorption (Bertin et al., 2013).

We ran simulations of two different types of sources, the cold core TMC-1 and a group of hypothetical sources physically identical to TMC-1, other than having higher ionization rates. The latter set of simulations were run in order to identify any trends in our models arising from the included radiation chemistry. The physical conditions used here for both sets of simulations are given in Table 1, and all models utilized the same initial elemental abundances, listed in Table 2.

Parameter	TMC-1	Hypothetical Sources
$n_{\rm H}~({\rm cm}^{-3})$	10^{4}	10^{4}
$n_{ m dust}~(m cm^{-3})$	$1.8 imes 10^{-8}$	$1.8 imes 10^{-8}$
$T_{\rm gas}$ (K)	10	10
T_{grain} (K)	10	10
$A_{\rm v}$ (mag)	10	10
$N_{ m site}~(m cm^{-2})$	$1.5 imes 10^{15}$	$1.5 imes 10^{15}$
ζ (s ⁻¹)	10^{-17}	$10^{-17} - 10^{-14}$

Table 4.1: Model parameters and physical conditions used.

Table 4.2: Elemental abundances used in this work.

Element	Value	Source
$X(H_2)$	5.00×10^{-1}	
X(He)	9.00×10^{-2}	Wakelam and Herbst (2008)
$X(\mathbf{N})$	2.14×10^{-5}	Wakelam and Herbst (2008)
<i>X</i> (O)	1.70×10^{-4}	McGuire et al. (2018)
$X(\mathbf{C}^+)$	1.70×10^{-4}	Jenkins (2009)
$X(S^+)$	8.00×10^{-8}	Graedel et al. (1982)
$X(Si^+)$	8.00×10^{-9}	Graedel et al. (1982)
$X(Fe^+)$	3.00×10^{-9}	Graedel et al. (1982)
$X(Na^+)$	2.00×10^{-9}	Graedel et al. (1982)
$X(Mg^+)$	7.00×10^{-9}	Graedel et al. (1982)
$X(\mathbf{P}^+)$	2.00×10^{-10}	Graedel et al. (1982)
$X(Cl^+)$	1.00×10^{-9}	Graedel et al. (1982)
$X(\mathbf{F})$	6.68×10^{-9}	Neufeld et al. (2005)

4.3 Network

Our three-phase chemical network is based on the one described in Ruaud et al. (2016) to which we have added the gas-phase reactions of Balucani et al. (2015). To this network,

Table 4.3: Parameters used in calculating G values and rate coefficients. Ionization energies were taken from Lias (2018), and average excitation energies from Keller-Rudek et al. (2013).

Species	$E_{\rm ion}$	$W_{\rm exc}$	$W_{\rm s}$
	(eV)	(eV)	(eV)
H ₂ O	12.621	11.190	3.824
O_2	12.070	8.500	3.886
O_3	12.530	4.860	3.815
CO	14.014	13.190	3.947
CO_2	13.777	13.776	3.927
NO	9.264	13.776	3.422
NO_2	9.586	21.377	3.478
O_2H	11.350	5.961	3.694
H_2O_2	10.580	10.332	3.606
CH ₃ OH	10.840	14.760	3.636
NH_3	10.070	9.110	3.542
H_2CO	10.880	7.940	3.641
CH_4	12.610	13.000	3.823
CH_3COCH_3	9.703	6.358	3.494

we have further included both cosmic ray-induced dissociation of the major ice mantle constituents and reactions involving the suprathermal products. Radiochemical yields (G values) and rate coefficients were calculated using the Shingledecker-Herbst method, and are a function of E_{ion} , W_{exc} , and W_s . Values for the ionization energy, E_{ion} , were taken from the NIST Chemistry Webbook (Lias, 2018). The average electronic excitation energies, W_{exc} , were estimated from the strongest UV-Vis absorption for each species (Fueki and Magee, 1963; Shingledecker and Herbst, 2018) based on spectra in the MPI-Mainz UV-Vis Spectral Atlas (Keller-Rudek et al., 2013). Finally, the average sub-excitation electron energies were calculated using the method of Elkomoss and Magee (1962). A list of both the species that undergo radiolysis as well as the associated parameters used in calculating rate coefficients are given in Table **??**, while Table 4 in Appendix A lists the new solid-phase radiolysis pathways for each species.

In our models, we assume the processes in Table 4 occur both on the surface and in the ice mantle and have labeled them Types I, II, and III. Type I radiolysis corresponds to the process given in equation (R2) where species *A* is ionized and recombines with the newly formed electron to produce suprathermal dissociation products. Type II processes correspond to the sequence of events given in equation (R3), where *A* dissociates into thermal products after being collisionally excited by an energetic particle. Finally, Type III processes are characterized by equation (R4), where *A* is collisionally excited, but does not immediately dissociate.

As supported by previous experimental work (Abplanalp et al., 2016; Bennett and

64

Kaiser, 2005; Bergantini et al., 2018), we assume that for a suprathermal species B^* , the lifetime in solids is much shorter (<< 1 s) than the average surface or bulk thermal hopping time, t_{hop}^B (>> 1 s at 10 K) (Hasegawa et al., 1992). As noted by Bennett and Kaiser (2005), the short lifetimes of these suprathermal species, relative to their hopping times at low temperatures, means that their solid-phase chemistry is likely dominated by reactions with neighbors. Therefore, we assume that once formed, suprathermal species only either react or relax back to the ground state. For reactions of the form

$$A + B^* \to \text{products.}$$
 (4.13)

we use the following formula for calculating the rate coefficients, k_{ST} (cm³s⁻¹):

$$k_{\rm ST} = f_{\rm br} \left[\frac{\nu_0^B + \nu_0^A}{N_{\rm site} n_{\rm dust}} \right]$$
(4.14)

where $f_{\rm br}$ is the product branching fraction, $n_{\rm dust}$ is the dust density - here equal to $1.8 \times 10^{-8} \,\mathrm{cm}^{-3}$, $N_{\rm site}$ is the number of physisorption sites on the grain - here equal to $1.5 \times 10^{15} \,\mathrm{cm}^{-2}$, and ν_0^X is the characteristic vibrational frequency for some physisorbed species, X, which is typically in the range of $1-3 \times 10^{-12} \,\mathrm{s}^{-1}$ (Herbst and Millar, 2008). This frequency can be estimated (Landau and Lifshitz, 1976) using the formula

$$\nu_0^X = \sqrt{\frac{2N_{\rm site}E_{\rm b}^X}{\pi^2 m_X}}$$
(4.15)

where m_X is the mass of X and E_b^X is the diffusion barrier, which we here set equal to 40% and 80% - for surface and bulk species, respectively - of the desorption energies used in Ruaud et al. (2016). Since the dominant mechanism for reactions involving suprathermal species in solids is likely not diffusive (Bennett and Kaiser, 2005), Eq. (4.14) is similar to the typical solid-phase bimolecular rate coefficients, but differs from them in that it does not contain either (a) a term characterizing thermal hopping or (b) a factor accounting for tunneling through reaction barriers, since we assume that suprathermal species are sufficiently energetic to react without a barrier (Hasegawa et al., 1992).

In addition to destruction through chemical reactions, we also assume that suprathermal species can be vibrationally quenched by the ice-mantle (Bennett and Kaiser, 2005; Spinks and Woods, 1990). Here, we use the characteristic frequency, ν_0^B , to approximate the rate coefficient of processes of the form

$$B^* + M \to B + M, \tag{4.16}$$

where M is the bulk ice, acting as a third body.

To illustrate how this radiation chemistry is incorporated into our chemical network, consider the formation and destruction of the suprathermal species, B^* , which is produced solely via process (R2) and only reacts with A, as in Eq. (4.13). In this example then, the rate of change of $n(B^*)$ is given by the equation

$$\frac{d n(B^*)}{d t} = k_{\rm R2} n(A) - \nu_0^B n(B^*) - k_{\rm ST} n(A) n(B^*)$$
(4.17)

where the first term on the right gives the production of B^* via the radiolysis of A, the second term gives the quenching rate for B^* , and the third term gives the rate of destruction via reaction with A - with k_{ST} being the rate coefficient for suprathermal reactions given in Eq. (4.14). We emphasize that in our actual network, most suprathermal species are produced from the radiolysis of more than one species, and all have more than one destructive reaction.

The suprathermal reactions we have added to our network can be grouped into two classes. Class 1 refers to those that are similar to reactions involving ground state species already included in the network, while Class 2 refers to novel reactions unlike those currently included for thermal species. To illustrate Class 1 reactions, consider the following example:

$$H(s) + CO(s) \rightarrow HCO(s)$$
 (4.18)

which has an activation energy of 2300 K in the Ruaud et al. (2016) network, in addition to a diffusion barrier. Here, (s) indicates either a surface or bulk species. We will later use (g) to denote gaseous species, and in cases where reactants labeled with (s) lead to products in the gas-phase, the reactants are assumed to be surface species only. Here we include the following Class 1 suprathermal reactions based on (4.18):

$$\mathrm{H}^*(s) + \mathrm{CO}(s) \to \mathrm{HCO}(s) \tag{4.19}$$

$$H(s) + CO^*(s) \to HCO(s).$$
(4.20)

We assume no barrier for both reaction (4.19) and (4.20), as implied by results from ice irradiation experiments (Abplanalp et al., 2016). Rate coefficients for reactions (4.19) and (4.20), as well as for all similar Class 1 suprathermal reactions, are calculated in our model using Eq. (4.14). Another group of Class 1 reactions included in our network are based on work by Hudson (2017), who found ketene (H₂CCO) among the products of acetone irradiation, which could form via

$$CH_3 + CH_3CO \rightarrow H_2CCO + CH_4$$
 (4.21)

where the CH_3 and CH_3CO radicals result from either Type I or II radiolysis of acetone. We have included both the reaction between ground state radicals as well as reactions involving a single suprathermal reactant, similar to reactions (4.19) and (4.20). A full list of these new reactions is available from the authors.

Class 2 is used to categorize novel reactions that are unlike the kinds of thermal reactions typically considered in gas/grain models. To illustrate why this type of chemistry is astrochemically interesting, consider the following Class 2 reaction:

$$O(s) + CH_4(s) \rightarrow CH_3OH(s).$$
 (4.22)

This type of reaction is known as an "insertion" since the oxygen atom is inserted into one of the C-H bonds to form methanol. Reaction (4.22) is highly endothermic, having an activation energy of ~ 4300 K (Baulch et al., 1992); however, Bergner et al. (2017) recently found that $O(^{1}D)$ and methane could efficiently react to form methanol in low temperature ices via this mechanism. Further evidence for the importance of solid-phase irradiation-driven insertion reactions comes from recent work by Bergantini et al. (2018), who found that such processes could lead to ethanol and dimethyl ether formation at lowtemperatures. Thus, Class 2 reactions may contribute to the formation of COMs, even in cold interstellar environments.

In this study, we added Class 2 reactions for both C^{*} and O^{*}, as listed in Table 5 of Appendix B. Many of these new reactions were drawn from combustion chemistry. Since cosmic rays, such as other forms of ionizing radiation, produce highly non-thermal species, some of the endothermic reactions previously considered in the context of high-temperature systems become relevant when considering irradiated low-temperature ices.

We have also included gas-phase destruction reactions for HOCO. In addition to photodissociation by internal and external UV photons, the reactions listed in Table 6 of Appendix C were added to the Ruaud et al. (2016) network, with neutral-neutral rate coefficient parameters given in terms of α , β , and γ using the Arrhenius-Kooij formula

$$k_{\rm AK} = \alpha \left(\frac{T_{\rm gas}}{300\,\rm K}\right)^{\beta} \exp\left(-\frac{\gamma}{T_{\rm gas}}\right) \tag{4.23}$$

where T_{gas} is the kinetic temperature of the gas.

For reactions between the polar neutral HOCO and ions, we use the Su-Chesnavich capture theory (see Woon and Herbst (2009) and references therein). For HOCO, values of $\mu_D = 3.179$ D and $\alpha_p = 2.739$ Å³ were utilized for the dipole and dipole polarizability, respectively (Johnson, 2016).

4.4 **Results & Discussion**

Given the relative novelty of the radiation chemistry we have added to our chemical network, it is natural to question what effect these new reactions will have on the abundances of important cold core species. To that end, in Fig. 4.1 we show the calculated abundances of the cyanopolyynes in our TMC-1 models, both with and without the new reactions listed in Tables 4 and 5. Reassuringly, one can see that there are no significant differences between cyanopolyyne abundances in the two sets of results - a key test since modern astrochemical models are typically able to reproduce the observed abundances of these species quite well (McGuire et al., 2017)

Since cyanopolyynes are formed in the gas-phase (Loomis et al., 2016), and all of the radiolysis processes considered in this work are assumed to take place in or on the surface



Figure 4.1: Gas-phase abundances in TMC-1 of HC_3N (solid line), HC_5N (dotted line), HC_7N (dashed line), and HC_9N (dot-dashed line), calculated both with (a) and without (b) the new radiation chemistry.



Figure 4.2: Abundances of H_2O in the gas (solid line), on grain surfaces (dotted line), and in the bulk (dashed line), calculated both with (a) and without (b) the new radiation chemistry.

of dust-grain ice mantles, a better confirmation of the new chemistry may be to examine the abundance of the primary ice-mantle constituent, namely, water. Therefore, in Fig. 4.2 we show the abundance of water in the gas-phase, ice-surface, and ice-bulk in our TMC-1 models both with and without radiation chemistry. Again, we find that the differences between the two are negligible. Thus, the addition of the novel reactions does not lead to unphysical predictions for common species (e.g. water), nor does it obviously degrade our ability to reproduce the abundances of commonly observed molecules such as the cyanopolyynes.

However, we have found that the addition of cosmic ray-driven reactions does indeed have a significant effect on the abundances of a number of astrochemically interesting species in our model. In the remainder of this section, we will describe how the inclusion of radiation chemistry affects HOCO, NO₂, HC₂O, and HCOOCH₃, which showed the most pronounced enhancements in gas-phase abundance.

4.4.1 HOCO



Figure 4.3: Simulated TMC-1 abundances of HOCO in the gas (a), on the grain/ice surface (b), and in the ice bulk (c), calculated both with (solid line) and without (dotted line) radiation chemistry.

As shown in Fig. 4.3, abundances of HOCO are increased in simulations including

radiation chemistry in the three phases of the model: gas, ice surface, and ice bulk. This increase is due primarily to the following surface reaction

$$OH^*(s) + CO(s) \to HOCO(g)$$
 (4.24)

where the HOCO product undergoes chemical desorption (Garrod et al., 2007). Here, surface abundances of CO are primarily the result of the adsorption from the gas-phase, and OH* is primarily formed via the Type I radiolysis of water

$$H_2O(s) \rightsquigarrow OH^*(s) + H^*(s). \tag{4.25}$$

The fact that HOCO is significantly enhanced in our TMC-1 simulations is notable because this species is more commonly encountered in high-temperature combustion chemistry (McCarthy et al., 2016; Smith and Zellner, 1973); however, in Milligan and Jacox (1971) - perhaps the first work to identify HOCO - this species was detected in a mixed H₂O:CO ice after irradiation by VUV photons, underscoring the similarity between the products of both combustion and radiation (or high-energy photo-) chemistry. Thus, the detection of species like HOCO in a cold interstellar region would be a strong indication of cosmic ray-induced radiation chemistry at work.

As shown in Fig. 4.3a, the peak gas-phase fractional abundance of HOCO is $\sim 10^{-11}$. Assuming a hydrogen column density for TMC-1 of $N(H_2) \approx 10^{22}$ cm⁻² (Gratier et al., 2016) results in a predicted HOCO column of $N(\text{HOCO}) \approx 10^{11}$ cm⁻². Since HOCO has a dipole of ~ 3 Debye (Johnson, 2016), these model results imply that this species is potentially observable in TMC-1.

4.4.2 NO₂

 NO_2 is another species the abundance of which is enhanced in simulations that include radiation chemistry. As shown in Fig. 4.4, as for the case of HOCO, NO_2 abundances are increased in all three model phases, although the connection between these enhancements and radiation chemistry is slightly more complex than in the case of HOCO.

At early times ($< 10^4$ yr), the dominant formation route for gas-phase NO₂ is the reaction

$$\operatorname{NO}(g) + \operatorname{O}_2\operatorname{H}(g) \to \operatorname{NO}_2(g) + \operatorname{OH}(g).$$
 (4.26)

Here, gas-phase O_2H abundances are enhanced via

$$\mathcal{O}(s) + \mathcal{OH}^*(s) \to \mathcal{O}_2\mathcal{H}(g). \tag{4.27}$$

At later times in the TMC-1 simulations, the dominant formation routes for NO₂ are

$$\mathcal{O}(s) + \mathcal{NO}^*(s) \to \mathcal{NO}_2(g) \tag{4.28}$$

$$O^*(s) + NO(s) \to NO_2(g). \tag{4.29}$$



Figure 4.4: Simulated TMC-1 abundances of NO_2 in the gas (a), on the grain/ice surface (b), and in the ice bulk (c), calculated both with (solid line) and without (dotted line) radiation chemistry.

At all simulation times, surface NO^{*} is formed mainly via the Type III excitation of NO:

$$NO(s) \rightsquigarrow NO^*(s)$$
 (4.30)

while O^{*} is formed from the Type I radiolysis of water, CO, and CO₂:

$$\mathrm{H}_{2}\mathrm{O}(s) \rightsquigarrow \mathrm{O}^{*}(s) + \mathrm{H}_{2}^{*}(s), \tag{4.31}$$

$$CO(s) \rightsquigarrow C^*(s) + O^*(s),$$
 (4.32)

$$\operatorname{CO}_2(s) \rightsquigarrow \operatorname{CO}^*(s) + \operatorname{O}^*(s).$$
 (4.33)

As shown in Fig. 4.4a, the peak gas-phase relative abundance of NO₂ in our TMC-1 model is $\sim 4 \times 10^{-11}$, corresponding to a column density of $\sim 4 \times 10^{11}$ cm⁻². Though this is slightly higher than the predicted abundance of HOCO, observations of NO₂ are challenging due to its small permanent dipole of < 1 Debye (Johnson, 2016).

4.4.3 HC₂O



Figure 4.5: Simulated TMC-1 abundances of HC_2O in the gas (a), on the grain/ice surface (b), and in the ice bulk (c), calculated both with (solid line) and without (dotted line) radiation chemistry.

The ketenyl radical, HC₂O, was first observed in the cold ($T_{\rm kin} \approx 15$ K) starless cores Lupus-1A and L483 by Agúndez et al. (2015), who derived a column density of ~ 5×10^{11} cm⁻² for both sources. Chemical simulations were run assuming HC₂O formation via the As shown in Fig. 4.5, the inclusion of radiation chemistry in our TMC-1 simulations results in significant enhancements of HC₂O - roughly four orders of magnitude for the gas, ice surface, and ice bulk. At early simulation times ($< 10^3$ yr), the dominant formation route for gas-phase ketenyl radical is

$$OH^*(s) + CCH(s) \rightarrow HC_2O(g) + H(g).$$
 (4.34)

At all later simulation times (> 10^3 yr), HC₂O is mainly formed via

$$H(s) + CCO(s) \to HC_2O(g).$$
(4.35)

In both TMC-1 simulations with and without radiation chemistry, there is little difference in the CCH abundance at all times and for all phases of the model; however, the ice surface and bulk abundances of CCO are enhanced via the reaction

$$C^*(s) + CO(s) \to CCO(s) \tag{4.36}$$

where the suprathermal carbon atoms are formed mainly via the radiolysis of CO.

Though our simulations still underproduce gas-phase HC_2O compared with observed values of Agúndez et al. (2015), the significant enhancements seen in models run with radiation chemistry suggest that perhaps radiation chemistry is their speculated powerful formation mechanism. Since we have not included any non-thermal desorption mechanisms caused by the direct cosmic ray bombardment of dust grains, such as sputtering, it may be that the impact of radiation chemistry on gas-phase abundances is greater than what is implied by our results here.

4.4.4 HCOOCH₃

As with the other species highlighted thus far, the abundance of methyl formate (HCOOCH₃) is enhanced in all three phases of the model. In simulations including radiation chemistry, the main production pathways for gas-phase methyl formate are

$$\operatorname{HCO}^*(s) + \operatorname{CH}_3\operatorname{O}(s) \to \operatorname{HCOOCH}_3(g)$$
 (4.37)

and

$$HCO(s) + CH_3O^*(s) \rightarrow HCOOCH_3(g).$$
 (4.38)

Here, the suprathermal HCO is produced mainly via the Type I radiolysis of formaldehyde:

$$H_2CO(s) \rightsquigarrow H^*(s) + HCO^*(s)$$
 (4.39)

and the methoxy radical is produced from the Type I decomposition of methanol:



Figure 4.6: Simulated TMC-1 abundances of $HCOOCH_3$ in the gas (a), on the grain/ice surface (b), and in the ice bulk (c), calculated both with (solid line) and without (dotted line) radiation chemistry.

$$CH_3OH(s) \rightsquigarrow H^*(s) + CH_3O^*(s).$$
 (4.40)

Methyl formate has been a focus of several recent studies which likewise examined its formation in cold cores (Balucani et al., 2015; Chang and Herbst, 2016; Vasyunin and Herbst, 2013). In Balucani et al. (2015) gas-phase production via

$$O + CH_3OCH_2 \rightarrow HCOOCH_3 + H$$
 (4.41)

was considered. As shown in Fig. 4.6, our models predict a peak gas-phase relative abundance of $\sim 3 \times 10^{-11}$ for methyl formate. Our peak value here is $\sim 500\%$ larger than than

the $\sim 5 \times 10^{-12}$ obtained by Balucani and coworkers in models where they used the standard chemical desorption fraction of 1%, the efficiency we assume throughout this work. Similarly, Chang and Herbst (2016) achieved somewhat higher gas-phase abundances of methyl formate in a number of their cold core simulations; however, they found that such results required both an enhanced chemical desorption fraction of 10% and the addition of a novel "chain reaction mechanism" that is not easily implemented in the macroscopic model we have utilized.

Though the number of grain-surface formation routes for COMs like methyl formate are limited in our network - compared with those used in hot core simulations (Garrod et al., 2017) - these results suggest radiation-chemical reactions may be able to drive the formation of COMs even under cold core conditions. As shown, the production of these complex species is possible because of the suprathermal reactants which form as a result of the radiolytic dissociation of molecules in dust grain ice-mantles.

4.4.5 CH₃CH₂OH



Figure 4.7: Simulated TMC-1 abundance of gas-phase ethanol (CH₃CH₂OH), calculated both with (solid line) and without (dotted line) radiation chemistry.

Unlike the other species highlighted thus far, surface and bulk abundances of the COM, ethanol, were not significantly enhanced in our simulations including radiation chemistry. However, as shown in Fig. 4.7, the gas-phase abundance is enhanced by ca. an order of magnitude by the Class 2 insertion reaction

$$\operatorname{CH}_{2}^{*}(s) + \operatorname{CH}_{3}\operatorname{OH}(s) \to \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OH}(g).$$
 (4.42)

This insertion reaction, which was recently studied experimentally by Bergantini et al. (2018), was shown to efficiently form both ethanol - as well as dimethyl ether - in low temperature ices. In that work, Bergantini and coworkers found that CH_2^* was formed from the radiolytic decomposition of methane:

$$\operatorname{CH}_4(s) \rightsquigarrow \operatorname{CH}_2^*(s) + \operatorname{H}_2(s).$$
 (4.43)

This process, which we have included in our network, is the dominant formation route of CH_2^* at all model times. The results shown in Fig. 4.7 highlight the effect that Class 2 reactions such as insertions can have on the production of COMs in cold sources. Again, we note that since chemical desorption at the standard 1% efficiency is the dominant non-thermal desorption mechanism in our model, the influence of reaction (4.42), and similar surface reactions, is likely underestimated here.

4.4.6 **Results Using Enhanced Ionization Rates**



Figure 4.8: Calculated gas-phase abundances of HOCO (a) NO₂ (b) HC₂O (c), and HCOOCH₃ (d) calculated at ionization rates of 10^{-17} s⁻¹ (solid line), 10^{-16} s⁻¹ (dotted line), 10^{-15} s⁻¹ (dashed line), and 10^{-14} s⁻¹ (dot-dashed line).



Figure 4.9: Calculated grain-surface abundances of HOCO (a) NO₂ (b) HC₂O (c), and HCOOCH₃ (d) calculated at ionization rates of 10^{-17} s⁻¹ (solid line), 10^{-16} s⁻¹ (dotted line), 10^{-15} s⁻¹ (dashed line), and 10^{-14} s⁻¹ (dot-dashed line).



Figure 4.10: Calculated bulk-ice abundances of HOCO (a) NO₂ (b) HC₂O (c), and HCOOCH₃ (d) calculated at ionization rates of 10^{-17} s⁻¹ (solid line), 10^{-16} s⁻¹ (dotted line), 10^{-15} s⁻¹ (dashed line), and 10^{-14} s⁻¹ (dot-dashed line).

Additional simulations were run in order to examine the effect of the new radiation chemistry at high ζ . As mentioned in §4.2 - and shown in Table 4.1 - we assume that the simulated hypothetical sources are physically identical to TMC-1 except for having higher ionization rates. The results from these model runs for HOCO, NO₂, HC₂O, and HCOOCH₃ are depicted in Figs. 4.8-4.10, which show the gas, surface, and bulk abundances, respectively.

As one can see from a comparison of Figs. 4.8-4.10, several trends emerge as the ionization rate changes. First, since, as previously demonstrated, the abundances of HOCO, NO₂, HC₂O, and HCOOCH₃ are enhanced due to radiochemical processes, it is reasonable that their abundances should tend to increase with increasing ζ . This effect is most obvious at very early times before ~ 10³ yr, with the correlation between the two clearly observable in Figs. 4.8-4.10. At intermediate times however, between ~ 10³-10⁶ yr, the relationship between abundance and ζ begins to break down, particularly in the gas phase. Generally, we find that the higher the ionization rate, the faster the peak abundance is reached, and the lower the peak value - a trend that can most easily be seen in Figs. 4.9 and 4.10, which show the surface and bulk abundances, respectively. After ~ 10⁶ yr, an anti-correlation between ζ and abundance emerges for most of the species shown. The reasons for this behavior are complex, but are driven in part by (a) the increased radiolytic destruction of surface and bulk species into more weakly bound fragments, and (b) the greatly increased gas-phase abundances of ions such as H⁺ and C⁺, reactions with which further reduce the abundance of the neutral species considered here.

4.5 Conclusions

We have utilized the theory described in Shingledecker and Herbst (2018) in an initial attempt to incorporate radiation chemistry into an existing chemical network. Simulations of the cold core TMC-1 were run, both with and without the new cosmic ray-induced reactions. We also modeled several hypothetical sources which were physically identical to TMC-1 other than having enhanced ionization rates. The major results of the simulations described in this work are the following:

- Radiation chemistry can result in substantially enhanced abundances in all three model phases for a variety of species, including COMs.
- These enhancements in abundance occur mainly as a result of reactions involving suprathermal species formed from the radiolytic dissociation of simple ice mantle constituents.
- Even under cold core conditions, these suprathermal species can react quickly by a variety of mechanisms, including insertion, which we found to be particularly important in increasing the abundance of COMs.
- We predict that HOCO, and perhaps NO₂, could be observable in TMC-1, given a sufficiently deep search.

- The addition of radiation chemistry substantially improves agreement between calculated and observed abundances of HC₂O.
- For the neutral species considered here, ionization rates of 10^{-16} s⁻¹ or higher generally resulted in reduced abundances in all model phases at times greater than $\sim 10^3$ yr.

It should be emphasized that these results, while promising, are necessarily preliminary in nature, given the novelty of incorporating radiation chemistry into astrochemical models. More work is needed to better characterize both (a) cosmic ray-induced radiolysis and chemistry and (b) secondary effects such as the non-thermal desorption of grain species triggered by cosmic ray bombardment. These non-thermal desorption mechanisms, such as sputtering, desorption induced by electronic transitions (DIET), electron stimulated ion desorption (ESID), and Auger stimulated ion desorption (ASID) (Ribeiro et al., 2015) are particularly promising since they could provide a means of enriching gasphase abundances at low temperatures, and are therefore a natural complement to the non-thermal chemistry described here.

As we have demonstrated in this work, the addition of cosmic ray-driven solid-phase reactions can improve existing astrochemical models in a number of significant ways. First, the addition of this non-thermal chemistry increases the realism of models, since cosmic ray bombardment of ice mantles certainly occurs in the ISM. Moreover, a consideration of solid-phase radiation chemistry both helps to explain how COMs like methyl formate could efficiently form in cold cores (Balucani et al., 2015; Chang and Herbst, 2016; Vasyunin and Herbst, 2013), and improves the agreement between calculated and observational abundances for HC₂O. Cosmic ray-driven ice chemistry is thus attractive as a component of future astrochemical modeling studies.

E. H. wishes to thank the National Science Foundation for supporting the astrochemistry program at the University of Virginia through grant AST 15 - 14844. C. N. S. thanks V. Wakelam for use of the NAUTILUS-1.1 code. This research has made use of NASA's Astrophysics Data System Bibliographic Services

Part III Conclusions

CHAPTER 5

CONCLUSIONS & OUTLOOK

E have developed new techniques for modeling solid-phase cosmic ray-induced radiation chemistry in both detailed microscopic Monte Carlo models and more general models utilizing rate equations. Where possible, we have compared results from our new models with previous experimental data and found the two to be in good agreement. Using the new methods we have developed, we have incorporated solid-phase radiation chemistry into an existing chemical network in order to examine the impact of such reactions on the abundances of species in cold cores, and have found that cosmic ray-driven chemistry increases the abundance of complex organic molecules and improves the agreement between models and observations. Thus, we conclude that radiation chemistry driven by cosmic rays represents a promising method of improving current and future astrochemical models.

5.1 Major Conclusions

5.1.1 Chapter Two

The collisions between high-energy ions and solids can result in significant physical and chemical changes to the material. These effects are potentially important for better understanding the chemistry of interstellar and planetary bodies, which are exposed to cosmic radiation and the solar wind, respectively; however, modeling such collisions on a detailed microscopic basis has thus far been largely unsuccessful. To that end, a new model, entitled CIRIS: the Chemistry of Ionizing Radiation in Solids, was created to calculate the physicochemical effects of the irradiation of solid materials. With the new code, we simulated an O_2 ice bombarded by 100 keV protons. Our models were able to reproduce the measured ozone abundances of a previous experimental study, as well as independently predict the approximate thickness of the ice used in that work. The major points made in this chapter are

- Detailed Monte Carlo methods have been used to separately simulate both chemistry and particle tracks.
- That these two components can be incorporated into a single simulation that tracks both the physical and chemical effects of energetic particle bombardment.

That the new combined model, CIRIS, agreeably reproduces the abundance of ozone produced in solid O₂ - thus making it the fist microscopic model capable of simulating radiation chemistry over timescales relevant to experiments and real physical environments.

CIRIS, while promising, is only a first-step towards our goal of creating a referenceclass radiation chemistry model that can be widely adopted and used by researchers without a specialized computational background - similar to the widely used SRIM or CASINO programs. To that end, several key improvements are envisioned for future versions of the code, which we will discuss in §5.2.

5.1.2 Chapter Three

In this Chapter, we proposed a general formalism that allowed for the estimation of radiolysis decomposition pathways and rate coefficients suitable for use in astrochemical models, with a focus on interstellar solids. Such a theory can help increase the connection between laboratory astrophysics experiments and astrochemical models by providing a means for modelers to incorporate radiation chemistry into chemical networks. The general method proposed here was targeted particularly at the majority of species now included in chemical networks for which little radiochemical data exists; however, the method can also be used a starting point for considering better studied species. We here applied our theory to the irradiation of H_2O ice and compare the results with previous experimental data. The major points made in this chapter are

- While detailed microscopic models are important computational tools, simpler rate equation-based codes will likely remain the most widely used type of astrochemical model for the foreseeable future.
- That if such models are to treat radiation chemistry in anything approaching a comprehensive way, the microscopic processes underlying radiation chemistry have to be generalized in such a way that the salient aspects are preserved in cases where there are no relevant experimental data.
- That such a "method of last resort" in a manner comparable to the Langevin formula - should give results within reasonable agreement of experimental values, and should do so using readily available physical parameters.

In order to test the impact of our approach on astrochemical models, we incorporated it into an existing chemical network. This newly expanded network was utilized in simulating cold-cores and described in detail in Chapter 4.

5.1.3 Chapter Four

In this paper, we presented preliminary results illustrating the effect of solid-phase radiation chemistry on models of cold cores, including TMC-1 and several TMC-1 like hypothetical sources with increased ionization rates. Using the theory described in Chapter 3, we calculated the radiochemical yields for the primary dust grain ice-mantle constituents. We showed that the inclusion of this novel non-thermal chemistry enriched ice-mantle abundances and lead to increased gas-phase abundances for a number of species, particularly HOCO, NO₂, HC₂O, and methyl formate (HCOOCH₃). Moreover, our data from these simulations imply that HOCO - and perhaps NO₂ - might be detectable in TMC-1. Future observations of either of these species in cold interstellar environments could provide strong support for the importance of cosmic ray-driven radiation chemistry. The major points made in this chapter are

- Radiation chemistry can result in substantially enhanced abundances in all three model phases for a variety of species, including COMs.
- These enhancements in abundance occur mainly as a result of reactions involving suprathermal species formed from the radiolytic dissociation of simple ice mantle constituents.
- Even under cold core conditions, these suprathermal species can react quickly by a variety of mechanisms, including insertion, which we found to be particularly important in increasing the abundance of COMs.
- We predict that HOCO, and perhaps NO₂, could be observable in TMC-1, given a sufficiently deep search.
- The addition of radiation chemistry substantially improves agreement between calculated and observed abundances of HC₂O.

5.1.4 Summary of Main Conclusions

- I That since the groundbreaking work of Herbst and Klemperer (1973), cosmic raydriven chemistry has been a central component of astrochemical models, albeit mostly limited to the ionization (and later, excitation) of H₂ (See Chapter 1).
- II That the reason for this partial treatment of interstellar radiation chemistry has been a lack of appropriate theoretical and computational methods (See Chapters 1 & 4).
- III That we have developed theoretical and computational methods such that radiation chemistry can now be simulated using both detailed Monte Carlo and general rate equation-based astrochemical models (See Chapters 2 and 3).
- IV That radiation chemistry can drive reactions in even very cold solids, which can lead to the formation of a variety of species, including COMs (See Chapters 1-4).

V That the inclusion of solid-phase radiation chemistry in cold core simulations results in improved agreement with observations and new, testable predictions (See Chapter 4).

In light of the above points, we return to the syllogistic expression of our thesis, which we presented in Chapter 1, namely

A If we could add cosmic ray-driven grain chemistry to astrochemical models, then we could better establish its astrochemical importance

· .

- (S2) B We can add cosmic ray-driven chemistry grain chemistry to astrochemical models.
 - C We can better establish its astrochemical importance

In this work, we have attempted to motivate our efforts via I and II and have sought to establish the validity of the minor premise, (S2B), via III. Thus, we feel that enough has now been done to reach our conclusion, (S2C) and, as supported by IV and V, have indeed begun to investigate the astrochemical role of cosmic ray-dust interactions. As we have noted in Chapter 4, the preliminary results are quite promising; however, much work remains to be done, some of which we review below.

5.2 Future Work

5.2.1 Improvements to both Monte Carlo and Rate Equation Models

One of the most important improvements that could be made to astrochemical models described here is the addition of non-thermal desorption mechanisms initiated by energetic particle bombardment. In current models, typical desorption mechanisms include desorption from impulsive grain heating by cosmic rays (Hasegawa and Herbst, 1993; Leger et al., 1985), photo-desorption (Andersson and van Dishoeck, 2008; Bertin et al., 2013), and chemical desorption (Garrod et al., 2007; Ruaud et al., 2016). Mechanisms such as these are critical for promoting grain-surface species into the surrounding gas. Future work in this area might profitably focus on the following cosmic ray-driven desorption mechanisms:

- Image: Sputtering
- Auger-stimulated ion desorption (ASID)
- Electron-stimulated ion desorption (ESID)
- Desorption induced by electronic transitions (DIET)

These non-thermal desorption mechanisms are a natural compliment to the work presented here, since, as shown in Chapter 4, radiation chemistry can greatly enhance the abundances of certain species in the ice. If such desorption mechanisms are important, then the impact of solid-phase radiation chemistry is likely even more pronounced than our work here indicates, and the gas-phase abundances predicted in Chapter 4 are then more likely to be lower-limits.

5.2.2 Improvements Specific to Rate Equation Models

There are two main avenues for improving the treatment of radiation chemistry in standard astrochemical models, viz. (a) expanding existing radiolysis processes to include every grain species included in a chemical network, and (b) extending gas-phase radiation chemistry beyond H_2 . The importance of the latter of these is somewhat uncertain given that the gas densities in interstellar environments are typically very low and thus, suprathermal species are much more likely to dissociate or emit a photon (as is the case with H_2) than to react. Moreover, since H_2 is the dominant species in molecular regions, gas-phase processes involving other species are statistically much less likely and, therefore, important for the overall chemistry of a region. Nevertheless, it is certainly possible that gas-phase cosmic ray-induced dissociations and reactions involving secondary electrons may have a non-negligible chemical impact and thus is worth investigating, if only for the sake of completeness.

5.2.3 Improvements Specific to Monte Carlo Models

As a potential "digital laboratory," future improvements to CIRIS should focus on microscopic processes that ultimately improve its ability to reproduce experimental data and more accurately simulate interstellar ices. These improvements can be grouped into improvements to (a) physics and (b) chemistry.

Our detailed model currently uses an "on-lattice" approximation, i.e. that the solid has a regular crystal structure; however, interstellar ices are typically assumed to be amorphous in most environments (Gärtner et al., 2017; Hollenbach and Salpeter, 1970). As with the Monte Carlo model of Garrod (2013), an off-lattice approach - or even better, a combined MD-MC model - could be implemented and would enable more accurate simulations of amorphous solids as well as allow us to model how cosmic ray bombardment changes the ices structure over time (Dartois et al., 2015) through the evolution of lattice defects and the sputtering of species in the selvedge (Kinchin and Pease, 1955; Norgett et al., 1975; Robinson and Torrens, 1974; Sigmund, 1969).

A major improvement to the chemistry of our detailed model would be the inclusion of ion-neutral reactions. A recent review by Cuppen et al. (2017) on the state of astrochemical grain models noted that despite many recent advances, two largely unexplored frontiers then remained: namely, direct cosmic ray-driven radiation chemistry and solid-phase ion-neutral (ion-ice) reactions. The two areas are actually closely related, since cosmic rays, as

a form of ionizing radiation, can drive the formation of charged species. The ions formed in ices due to cosmic ray bombardment can, in turn, react with neutral species in the ice in a manner analogous to what is widely thought to occur in the gas phase (Cuppen et al., 2017). Since the importance of ion-ice chemistry remains mysterious despite the dominant role of ion-neutral gas-phase reactions, simulating these novel grain processes would be a major advance in astrochemical modeling.



S ICUT enim maius est illuminare quam lucere solum, ita maius est contemplata aliis tradere quam solum contemplari.

- Sanctus Thomas de Aquino

Summa Theologiæ II-II, q. 188 a. 6 co.

BIBLIOGRAPHY

Aab, A. et al. Science 2017, 357, 1266–1270.

- Abdulgalil, A. G. M.; Marchione, D.; Thrower, J. D.; Collings, M. P.; McCoustra, M. R. S.; Islam, F.; Palumbo, M. E.; Congiu, E.; Dulieu, F. *Phil. Trans. R. Soc. A* **2013**, *371*, 20110586.
- Abplanalp, M. J.; Gozem, S.; Krylov, A. I.; Shingledecker, C. N.; Herbst, E.; Kaiser, R. I. *Proceedings of the National Academy of Sciences* **2016**, *113*, 7727–7732.

Abraham, J. et al. *Science* **2007**, *318*, 938–943.

- Acharyya, K.; Fuchs, G. W.; Fraser, H. J.; van Dishoeck, E. F.; Linnartz, H. Astronomy and Astrophysics **2007**, 466, 1005–1012.
- Agundez, M.; Marcelino, N.; Cernicharo, J.; Tafalla, M. Astronomy & Astrophysics **2018**, 611, L1, arXiv: 1802.09401.
- Agúndez, M.; Cernicharo, J.; Guélin, M.; Kahane, C.; Roueff, E.; Kos, J.; Aoiz, F. J.; Lique, F.; Marcelino, N.; Goicoechea, J. R.; González García, M.; Gottlieb, C. A.; McCarthy, M. C.; Thaddeus, P. Astronomy and Astrophysics 2010, 517, L2.
- Agúndez, M.; Cernicharo, J.; Pardo, J. R.; Guélin, M.; Phillips, T. G. Astronomy & Astrophysics 2008, 485, L33–L36.
- Agúndez, M. et al. *Astronomy and Astrophysics* **2015**, 579, L10.
- Agúndez, M.; Cernicharo, J.; Guélin, M. Astronomy and Astrophysics 2015, 577, L5.
- Agúndez, M.; Cernicharo, J.; Guélin, M. *The Astrophysical Journal Letters* **2007**, 662, L91–L94.
- Agúndez, M.; Cernicharo, J.; Guélin, M. Astronomy and Astrophysics 2014, 570, A45.
- Akiyama, A.; Hosoi, T.; Ishihara, I.; Matsumoto, S.; Niimi, T. Computer-Aided Design of Integrated Circuits and Systems, IEEE Transactions on **1987**, *6*, 185–189.
- Allamandola, L. J.; Bernstein, M. P.; Sandford, S. A.; Walker, R. L. In Composition and Origin of Cometary Materials: Proceedings of an ISSI Workshop, 1418 September 1998, Bern, Switzerland; Altwegg, K., Ehrenfreund, P., Geiss, J., Huebner, W. F., Eds.; Springer Netherlands: Dordrecht, 1999; pp 219–232.
- Altwegg, K. et al. Science Advances 2016, 2, e1600285.

- Anderson, J. K.; Ziurys, L. M. The Astrophysical Journal Letters 2014, 795, L1.
- Andersson, S.; van Dishoeck, E. F. Astronomy and Astrophysics 2008, 491, 907–916.
- Ao, Y.; Henkel, C.; Menten, K. M.; Requena-Torres, M. A.; Stanke, T.; Mauersberger, R.; Aalto, S.; Mühle, S.; Mangum, J. *Astronomy and Astrophysics* **2013**, *550*, A135.
- Apponi, A. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. *The Astrophysical Journal Letters* **1999**, *516*, L103–L106.
- Arumainayagam, C. R.; Lee, H.-L.; Nelson, R. B.; Haines, D. R.; Gunawardane, R. P. Surface Science Reports **2010**, 65, 1–44.
- Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmospheric Chemistry and Physics* **2004**, *4*, 1461–1738.
- Avery, L. W.; Broten, N. W.; MacLeod, J. M.; Oka, T.; Kroto, H. W. *The Astrophysical Journal Letters* **1976**, 205, L173–L175.
- Axford, W. I. Annals of the New York Academy of Sciences 1981, 375, 297–313.
- Baade, W.; Zwicky, F. Proceedings of the National Academy of Science 1934, 20, 259–263.
- Ball, J. A.; Gottlieb, C. A.; Lilley, A. E.; Radford, H. E. *The Astrophysical Journal Letters* **1970**, 162, L203.
- Balucani, N.; Ceccarelli, C.; Taquet, V. *Monthly Notices of the Royal Astronomical Society* **2015**, 449, L16–L20.
- Baragiola, R. A.; Atteberry, C. L.; Bahr, D. A.; Jakas, M. M. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **1999**, 157, 233–238.
- Barghouty, A. F.; Thibeault, S. A. NASA/TM-2006-214604 2006, 1–32.
- Barlow, M. J.; Swinyard, B. M.; Owen, P. J.; Cernicharo, J.; Gomez, H. L.; Ivison, R. J.; Krause, O.; Lim, T. L.; Matsuura, M.; Miller, S.; Olofsson, G.; Polehampton, E. T. *Science* 2013, 342, 1343–1345.
- Bates, D. R.; Spitzer, L. The Astrophysical Journal 1951, 113, 441.
- Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *Journal of Physical and Chemical Reference Data* 1992, 21, 411–734.
- Belloche, A.; Garrod, R. T.; Müller, H. S. P.; Menten, K. M.; Comito, C.; Schilke, P. Astronomy and Astrophysics 2009, 499, 215–232.
- Belloche, A.; Menten, K. M.; Comito, C.; Müller, H. S. P.; Schilke, P.; Ott, J.; Thorwirth, S.; Hieret, C. Astronomy and Astrophysics **2008**, 482, 179–196.

- Belloche, A.; Meshcheryakov, A. A.; Garrod, R. T.; Ilyushin, V. V.; Alekseev, E. A.; Motiyenko, R. A.; Margulès, L.; Müller, H. S. P.; Menten, K. M. Astronomy and Astrophysics 2017, 601, A49.
- Belloche, A.; Garrod, R. T.; Müller, H. S. P.; Menten, K. M. Science 2014, 345, 1584–1587.
- Bennett, C. J.; Kaiser, R. I. The Astrophysical Journal 2005, 635, 1362.
- Bequerel, H. Comptes Rendus 1896, 122, 501–503.
- Bergantini, A.; Góbi, S.; Abplanalp, M. J.; Kaiser, R. I. *The Astrophysical Journal* **2018**, *852*, 70.
- Bergman, P.; Parise, B.; Liseau, R.; Larsson, B.; Olofsson, H.; Menten, K. M.; Güsten, R. *Astronomy and Astrophysics* **2011**, 531, L8.
- Bergner, J. B.; Oberg, K. I.; Rajappan, M. The Astrophysical Journal 2017, 845, 29.
- Bernath, P. F.; Hinkle, K. H.; Keady, J. J. Science 1989, 244, 562–564.
- Berné, O.; Mulas, G.; Joblin, C. Astronomy and Astrophysics 2013, 550, L4.
- Bertin, M.; Fayolle, E. C.; Romanzin, C.; Poderoso, H. A. M.; Michaut, X.; Laurent Philippe,; Jeseck, P.; Öberg, K. I.; Linnartz, H.; Fillion, J.-H. *The Astrophysical Journal* **2013**, *779*, 120.
- Bethe, H. Zeitschrift fur Physik 1932, 76, 293–299.
- Bethe, H. A.; Ashkin, J. In *Experimental Nuclear Physics*; Segrè, E., Ed.; Wiley: New York, 1953; Vol. 1.
- Betz, A. L. The Astrophysical Journal Letters 1981, 244, L103–L105.
- Bieler, A. et al. Nature 2015, 526, 678-681.
- Biermann, P. L.; Becker, J. K.; Dreyer, J.; Meli, A.; Seo, E.-S.; Stanev, T. *The Astrophysical Journal* **2010**, 725, 184–187.
- Biersack, J. P.; Haggmark, L. G. Nuclear Instruments and Methods 1980, 174, 257–269.
- Blackford, L. S.; Demmel, J.; Dongarra, J.; Duff, I.; Hammarling, S.; Henry, G.; Heroux, M.; Kaufman, L.; Lumsdaine, A.; Petitet, A.; Pozo, R.; Remington, K.; Whaley, R. C. ACM *Trans. Math. Softw.* 2002, 28, 135–151.
- Blake, G. A.; Keene, J.; Phillips, T. G. The Astrophysical Journal 1985, 295, 501-506.
- Blasi, P. The Astronomy and Astrophysics Review 2013, 21, 70.
- Bohr, N. Philosophical Magazine 1913, 25, 10–31.

- Boyer, M. C.; Rivas, N.; Tran, A. A.; Verish, C. A.; Arumainayagam, C. R. *Surface Science* **2016**, *652*, 26–32.
- Brasseur, G.; Solomon, S. Aeronomy of the middle atmosphere: chemistry and physics of the stratosphere and mesosphere; D. Reidel Pub. Co., 1984.
- Broten, N. W.; MacLeod, J. M.; Avery, L. W.; Irvine, W. M.; Hoglund, B.; Friberg, P.; Hjalmarson, A. *The Astrophysical Journal Letters* **1984**, 276, L25–L29.
- Broten, N. W.; MacLeod, J. M.; Oka, T.; Avery, L. W.; Brooks, J. W.; McGee, R. X.; Newton, L. M. *The Astrophysical Journal Letters* **1976**, 209, L143–L147.
- Broten, N. W.; Oka, T.; Avery, L. W.; MacLeod, J. M.; Kroto, H. W. *The Astrophysical Journal Letters* **1978**, 223, L105–L107.
- Brown, R. D.; Crofts, J. G.; Godfrey, P. D.; Gardner, F. F.; Robinson, B. J.; Whiteoak, J. B. *The Astrophysical Journal Letters* **1975**, *197*, L29–L31.
- Brown, R. D.; Godfrey, P. D.; Cragg, D. M.; Rice, E. H. N.; Irvine, W. M.; Friberg, P.; Suzuki, H.; Ohishi, M.; Kaifu, N.; Morimoto, M. *The Astrophysical Journal* **1985**, 297, 302–308.
- Brünken, S.; Belloche, A.; Martín, S.; Verheyen, L.; Menten, K. M. Astronomy and Astrophysics 2010, 516, A109.
- Brünken, S.; Gottlieb, C. A.; McCarthy, M. C.; Thaddeus, P. *The Astrophysical Journal* **2009**, 697, 880–885.
- Brünken, S.; Gupta, H.; Gottlieb, C. A.; McCarthy, M. C.; Thaddeus, P. *The Astrophysical Journal Letters* **2007**, *664*, L43–L46.
- Buhl, D.; Snyder, L. E. In *Molecules in the Galactic Environment*; Gordon, M. A., Snyder, L. E., Eds.; Wiley: New York, 1973; p 187.
- Cabezas, C.; Cernicharo, J.; Alonso, J. L.; Agúndez, M.; Mata, S.; Guélin, M.; Peña, I. *The Astrophysical Journal* **2013**, 775, 133.
- Callahan, M. P.; Smith, K. E.; Cleaves, H. J.; Ruzicka, J.; Stern, J. C.; Glavin, D. P.; House, C. H.; Dworkin, J. P. *Proceedings of the National Academy of Sciences* **2011**, *108*, 13995–13998.
- Calvin, W. M.; Spencer, J. R. Icarus 1997, 130, 505-516.
- Cami, J.; Bernard-Salas, J.; Peeters, E.; Malek, S. E. Science 2010, 329, 1180.
- Campbell, E. K.; Holz, M.; Gerlich, D.; Maier, J. P. Nature 2015, 523, 322–323.

Carruthers, G. R. The Astrophysical Journal Letters 1970, 161, L81.

Caselli, P.; Hasegawa, T. I.; Herbst, E. The Astrophysical Journal 1998, 495, 309.

- Ceccarelli, C.; Hily-Blant, P.; Montmerle, T.; Dubus, G.; Gallant, Y.; Fiasson, A. *The Astro-physical Journal* **2011**, 740, L4.
- Cernicharo, J.; Bailleux, S.; Alekseev, E.; Fuente, A.; Roueff, E.; Gerin, M.; Tercero, B.; Treviño-Morales, S. P.; Marcelino, N.; Bachiller, R.; Lefloch, B. *The Astrophysical Journal* **2014**, *795*, 40.
- Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Killian, T. C.; Paubert, G.; Thaddeus, P.; Vr-tilek, J. M. *The Astrophysical Journal Letters* **1991**, *368*, L39–L41.
- Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Killian, T. C.; Thaddeus, P.; Vrtilek, J. M. *The Astrophysical Journal Letters* **1991**, *368*, L43–L45.
- Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Thaddeus, P.; Vrtilek, J. M. *The Astrophysical Journal Letters* **1989**, 341, L25–L28.
- Cernicharo, J.; Guelin, M. Astronomy and Astrophysics 1996, 309, L27–L30.
- Cernicharo, J.; Guelin, M. Astronomy and Astrophysics 1987, 183, L10–L12.
- Cernicharo, J.; Guélin, M.; Agúndez, M.; McCarthy, M. C.; Thaddeus, P. *The Astrophysical Journal Letters* **2008**, *688*, L83.
- Cernicharo, J.; Guélin, M.; Agündez, M.; Kawaguchi, K.; McCarthy, M.; Thaddeus, P. Astronomy and Astrophysics 2007, 467, L37–L40.
- Cernicharo, J.; Guélin, M.; Pardo, J. R. The Astrophysical Journal Letters 2004, 615, L145–L148.
- Cernicharo, J.; Kahane, C.; Gomez-Gonzalez, J.; Guelin, M. Astronomy and Astrophysics 1986, 167, L5–L7.
- Cernicharo, J.; Kahane, C.; Gomez-Gonzalez, J.; Guelin, M. Astronomy and Astrophysics 1986, 164, L1–L4.
- Cernicharo, J.; Kahane, C.; Guelin, M.; Gomez-Gonzalez, J. Astronomy and Astrophysics 1988, 189, L1.
- Cernicharo, J.; Kahane, C.; Guelin, M.; Hein, H. *Astronomy and Astrophysics* **1987**, *181*, L9–L12.
- Cernicharo, J.; Kisiel, Z.; Tercero, B.; Kolesniková, L.; Medvedev, I. R.; López, A.; Fortman, S.; Winnewisser, M.; de Lucia, F. C.; Alonso, J. L.; Guillemin, J.-C. Astronomy and Astrophysics **2016**, 587, L4.
- Cernicharo, J.; Lefloch, B.; Agúndez, M.; Bailleux, S.; Margulès, L.; Roueff, E.; Bachiller, R.; Marcelino, N.; Tercero, B.; Vastel, C.; Caux, E. *The Astrophysical Journal Letters* **2018**, *853*, L22.
- Cernicharo, J.; Marcelino, N.; Roueff, E.; Gerin, M.; Jiménez-Escobar, A.; Muñoz Caro, G. M. *The Astrophysical Journal Letters* **2012**, *759*, L43.
- Cernicharo, J. et al. *The Astrophysical Journal Letters* **2015**, 806, L3.
- Cernicharo, J.; Tercero, B.; Fuente, A.; Domenech, J. L.; Cueto, M.; Carrasco, E.; Herrero, V. J.; Tanarro, I.; Marcelino, N.; Roueff, E.; Gerin, M.; Pearson, J. *The Astrophysical Journal Letters* **2013**, 771, L10.
- Cernicharo, J.; Heras, A. M.; Tielens, A. G. G. M.; Pardo, J. R.; Herpin, F.; Guélin, M.; Waters, L. B. F. M. *The Astrophysical Journal Letters* **2001**, *546*, L123–L126.
- Chabot, M.; Tuna, T.; Béroff, K.; Pino, T.; Le Padellec, A.; Désequelles, P.; Martinet, G.; Nguyen-Thi, V. O.; Carpentier, Y.; Le Petit, F.; Roueff, E.; Wakelam, V. *Astronomy & Astrophysics* **2010**, *524*, A39.
- Chang, Q.; Cuppen, H. M.; Herbst, E. Astronomy and Astrophysics 2005, 434, 599–611.
- Chang, Q.; Herbst, E. The Astrophysical Journal 2014, 787, 135.
- Chang, Q.; Herbst, E. The Astrophysical Journal 2016, 819, 145.
- Chang, Q.; Lu, Y.; Quan, D. The Astrophysical Journal 2017, 851, 68.
- Cheung, A. C.; Rank, D. M.; Townes, C. H.; Thornton, D. D.; Welch, W. J. *Physical Review Letters* **1968**, *21*, 1701–1705.
- Cheung, A. C.; Rank, D. M.; Townes, C. H.; Thornton, D. D.; Welch, W. J. *Nature* **1969**, 221, 626–628.
- Chin, Y.-N.; Kaiser, R. I.; Lemme, C.; Henkel, C. Detection of Interstellar Cyanoallene and its Implications for Astrochemistry. 2006; pp 149–153.
- Churchwell, E.; Winnewisser, G. Astronomy and Astrophysics 1975, 45, 229–231.
- Chyba, C. F.; Thomas, P. J.; Brookshaw, L.; Sagan, C. Science 1990, 249, 366–373.
- Combes, F.; Gerin, M.; Wootten, A.; Wlodarczak, G.; Clausset, F.; Encrenaz, P. J. Astronomy and Astrophysics **1987**, 180, L13–L16.
- Combes, F.; Wiklind, T. Astronomy and Astrophysics 1998, 334, L81–L84.
- Cooper, G.; Rios, A. C. Proceedings of the National Academy of Sciences 2016, 113, E3322– E3331.
- Corby, J. F.; Jones, P. A.; Cunningham, M. R.; Menten, K. M.; Belloche, A.; Schwab, F. R.; Walsh, A. J.; Balnozan, E.; Bronfman, L.; Lo, N.; Remijan, A. J. *Monthly Notices of the Royal Astronomical Society* **2015**, 452, 3969–3993.

- Cordiner, M. A.; Charnley, S. B.; Kisiel, Z.; McGuire, B. A.; Kuan, Y.-J. *The Astrophysical Journal* **2017**, *850*, 187.
- Cuppen, H. M. et al. Faraday Discussions 2014, 168, 571–615.
- Cuppen, H. M.; Herbst, E. The Astrophysical Journal 2007, 668, 294.
- Cuppen, H. M.; Walsh, C.; Lamberts, T.; Semenov, D.; Garrod, R. T.; Penteado, E. M.; Ioppolo, S. *Space Science Reviews* 2017,
- Curie, M. Traité de radioactivit; Gauthier-Villars: Paris, 1910.
- D'Hendecourt, L. B.; Jourdain de Muizon, M. Astronomy and Astrophysics 1989, 223, L5-L8.
- Dalgarno, A. In *Atomic and Molecular Processes*; Bates, D. R., Ed.; Academic Press: New York, 1962; pp 623–641.
- Dalgarno, A.; Griffing, G. W. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences **1958**, 248, 415.
- Dartois, E.; Augé, B.; Boduch, P.; Brunetto, R.; Chabot, M.; Domaracka, A.; Ding, J. J.; Kamalou, O.; Lv, X. Y.; Rothard, H.; da Silveira, E. F.; Thomas, J. C. *Astronomy and Astrophysics* **2015**, *576*, A125.
- De Luca, M.; Gupta, H.; Neufeld, D.; Gerin, M.; Teyssier, D.; Drouin, B. J.; Pearson, J. C.; Lis, D. C.; Monje, R.; Phillips, T. G.; Goicoechea, J. R.; Godard, B.; Falgarone, E.; Coutens, A.; Bell, T. A. *The Astrophysical Journal Letters* **2012**, *751*, L37.
- DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C.; Molina, M. J. *JPL Publication* 97-4 **1997**, 1–266.
- Dewhurst, H. A.; Dale, W. M.; Bacq, Z. M.; Swallow, A. J.; Weiss, J.; Magat, M.; Minder, W.; Suttle, J. F.; Schulte, J. W.; Burton, M.; Miller, N. *Discussions of the Faraday Society* **1952**, *12*, 312–318.
- Dickens, J. E.; Irvine, W. M.; Nummelin, A.; Möllendal, H.; Saito, S.; Thorwirth, S.; Hjalmarson, A.; Et. Al., *Spectrochimica Acta* **2001**, *57*, 643–660.
- Dickens, J. E.; Irvine, W. M.; Ohishi, M.; Ikeda, M.; Ishikawa, S.; Nummelin, A.; Hjalmarson, A. *The Astrophysical Journal* **1997**, *489*, 753–757.
- Doménech, J. L.; Cueto, M.; Herrero, V. J.; Tanarro, I.; Tercero, B.; Fuente, A.; Cernicharo, J. *The Astrophysical Journal Letters* **2013**, 771, L11.
- Doroshenko, V.; Kudryavtsev, N.; Smetanin, V. High Energy Chem. 1992, 26, 227–230.

Douglas, A. E.; Herzberg, G. The Astrophysical Journal 1941, 94, 381.

- Draine, B. T. The Astrophysical Journal Supplement Series 1978, 36, 595–619.
- Edgar, B. C.; Miles, W. T.; Green, A. E. S. Journal of Geophysical Research 1973, 78, 6595–6606.
- Edgar, B. C.; Porter, H. S.; Green, A. E. S. Planetary Space Science 1975, 23, 787–804.
- Elkomoss, S. G.; Magee, J. L. The Journal of Chemical Physics 1962, 36, 256–262.
- Engel, M. H.; Macko, S. A.; Silfer, J. A. Nature 1990, 348, 47.
- Engel, M. H.; Nagy, B. Nature 1982, 296, 837.
- Ennis, C.; Kaiser, R. I. *The Astrophysical Journal* **2012**, 745, 103.
- Fano, U. Phys. Rev. 1946, 70, 44–52.
- Fano, U.; Stephens, J. A. *Physical Review B* **1986**, *34*, 438.
- Fayolle, E. C. et al. *Nature Astronomy* **2017**, *1*, 703.
- Feuchtgruber, H.; Helmich, F. P.; van Dishoeck, E. F.; Wright, C. M. *The Astrophysical Journal Letters* **2000**, *535*, L111–L114.
- Fourikis, N.; Takagi, K.; Morimoto, M. The Astrophysical Journal Letters 1974, 191, L139.
- Frerking, M. A.; Linke, R. A.; Thaddeus, P. *The Astrophysical Journal Letters* **1979**, 234, L143–L145.
- Fridman, A. A. *Plasma Chemistry;* Cambridge University Press: Cambridge, New York, 2008.
- Fueki, K.; Magee, J. L. Discuss. Faraday Soc. 1963, 36, 19–34.
- Gardner, F. F.; Winnewisser, G. *The Astrophysical Journal Letters* **1975**, 195, L127–L130.
- Garrod, R. T. Astronomy and Astrophysics 2008, 491, 239–251.
- Garrod, R. T.; Belloche, A.; Müller, H. S. P.; Menten, K. M. Astronomy and Astrophysics 2017, 601, A48.
- Garrod, R. T.; Herbst, E. Astronomy and Astrophysics 2006, 457, 927–936.
- Garrod, R. T.; Wakelam, V.; Herbst, E. Astronomy and Astrophysics 2007, 467, 1103–1115.
- Garrod, R. T. The Astrophysical Journal 2013, 765, 60.
- Garrod, R. T. The Astrophysical Journal 2013, 778, 158.
- Garrod, R. T.; Weaver, S. L. W.; Herbst, E. The Astrophysical Journal 2008, 682, 283.

Geballe, T. R.; Oka, T. Nature 1996, 384, 334–335.

- Gerakines, P. A.; Moore, M. H.; Hudson, R. L. Journal of Geophysical Research 2001, 106, 33381–33386.
- Gerakines, P. A.; Moore, M. H.; Hudson, R. L. Icarus 2004, 170, 202–213.
- Glassgold, A. E.; Langer, W. D. The Astrophysical Journal 1974, 193, 73.
- Godfrey, P. D.; Brown, R. D.; Robinson, B. J.; Sinclair, M. W. Astrophysical Letters **1973**, 13, 119.
- Goldhaber, D. M.; Betz, A. L. The Astrophysical Journal Letters 1984, 279, L55–L58.
- Goldsmith, P. F.; Langer, W. D. The Astrophysical Journal 1978, 222, 881–895.
- Goldsmith, P. F. et al. *The Astrophysical Journal* 2011, 737, 96.
- Goldsmith, P. F.; Melnick, G. J.; Bergin, E. A.; Howe, J. E.; Snell, R. L.; Neufeld, D. A.; Harwit, M.; Ashby, M. L. N.; Patten, B. M.; Kleiner, S. C.; others, *The Astrophysical Journal Letters* **2000**, *539*, L123.
- Gottlieb, C. A.; Ball, J. A.; Gottlieb, E. W.; Lada, C. J.; Penfield, H. *The Astrophysical Journal Letters* **1975**, 200, L147–L149.
- Gottlieb, C. A.; Ball, J. A. *The Astrophysical Journal Letters* **1973**, 184, L59.
- Gottlieb, C. A. Detection of Acetaldehyde in Sagittarius. 1973; p 181.
- Graedel, T. E.; Langer, W. D.; Frerking, M. A. *The Astrophysical Journal Supplement Series* **1982**, *48*, 321–368.
- Gratier, P.; Majumdar, L.; Ohishi, M.; Roueff, E.; Loison, J. C.; Hickson, K. M.; Wakelam, V. *The Astrophysical Journal Supplement Series* **2016**, 225, 25.
- Gredel, R.; Lepp, S.; Dalgarno, A.; Herbst, E. The Astrophysical Journal 1989, 347, 289–293.
- Green, A. E. S.; McNeal, R. J. Journal of Geophysics Research 1971, 76, 133.
- Green, A. E. S.; Stolarski, R. S. Journal of Atmospheric and Terrestrial Physics 1972, 34, 1703–1717.
- Green, S.; Montgomery, J. A., Jr.; Thaddeus, P. *The Astrophysical Journal Letters* **1974**, 193, L89–L91.
- Grenier, I. A.; Black, J. H.; Strong, A. W. Annual Review of Astronomy and Astrophysics 2015, 53, 199–246.
- Guelin, M.; Cernicharo, J. Astronomy and Astrophysics 1991, 244, L21–L24.

- Guelin, M.; Cernicharo, J.; Paubert, G.; Turner, B. E. *Astronomy and Astrophysics* **1990**, 230, L9–L11.
- Guelin, M.; Cernicharo, J.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P.; Ohishi, M.; Saito, S.; Yamamoto, S. *Astronomy and Astrophysics* **1997**, *317*, L1–L4.
- Guelin, M.; Gomez-Gonzalez, J.; Cernicharo, J.; Kahane, C. Astronomy and Astrophysics **1986**, 157, L17–L20.
- Guelin, M.; Green, S.; Thaddeus, P. The Astrophysical Journal Letters 1978, 224, L27–L30.
- Guelin, M.; Langer, W. D.; Snell, R. L.; Wootten, H. A. *The Astrophysical Journal, Letters* **1977**, 217, L165–L168.
- Guelin, M.; Neininger, N.; Cernicharo, J. Astronomy and Astrophysics 1998, 335, L1–L4.
- Guelin, M.; Thaddeus, P. The Astrophysical Journal Letters 1977, 212, L81.
- Gupta, H.; Gottlieb, C. A.; Lattanzi, V.; Pearson, J. C.; McCarthy, M. C. *The Astrophysical Journal Letters* **2013**, 778, L1.
- Guélin, M.; Muller, S.; Cernicharo, J.; Apponi, A. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. Astronomy and Astrophysics **2000**, 363, L9–L12.
- Guélin, M.; Muller, S.; Cernicharo, J.; McCarthy, M. C.; Thaddeus, P. Astronomy and Astrophysics 2004, 426, L49–L52.
- Gärtner, S.; Gundlach, B.; Headen, T. F.; Ratte, J.; Oesert, J.; Gorb, S. N.; Youngs, T. G. A.; Bowron, D. T.; Blum, J.; Fraser, H. J. *The Astrophysical Journal* **2017**, *848*, 96.
- Halfen, D. T.; Clouthier, D. J.; Ziurys, L. M. The Astrophysical Journal Letters 2008, 677, L101.
- Halfen, D. T.; Ilyushin, V. V.; Ziurys, L. M. The Astrophysical Journal Letters 2015, 812, L5.
- Halfen, D. T.; Ziurys, L. M.; Brünken, S.; Gottlieb, C. A.; McCarthy, M. C.; Thaddeus, P. *The Astrophysical Journal Letters* **2009**, 702, L124–L127.
- Harrison, R. L. AIP conference proceedings 2010, 1204, 17–21.
- Hasegawa, T. I.; Herbst, E. Monthly Notices of the Royal Astronomical Society **1993**, 261, 83–102.
- Hasegawa, T. I.; Herbst, E.; Leung, C. M. *The Astrophysical Journal Supplement Series* **1992**, *82*, 167–195.
- Hayakawa, S.; Nishimura, S.; Takayanagi, T. *Publications of the Astronomical Society of Japan* **1961**, *13*, 184.
- Heidner, R. F. The Journal of Chemical Physics 1981, 74, 5618.

Herbst, E. The Astrophysical Journal 1978, 222, 508–516.

- Herbst, E.; van Dishoeck, E. F. *Annual Review of Astronomy and Astrophysics* **2009**, *47*, 427–480.
- Herbst, E. Phys. Chem. Chem. Phys. 2014, 16, 3344–3359.
- Herbst, E.; Klemperer, W. The Astrophysical Journal 1973, 185, 505.
- Herbst, E.; Millar, T. J. In *Low Temperatures and Cold Molecules*; Smith, I. W. M., Ed.; Imperial College Press: London, 2008.
- Hess, V. F. Physikalische Zeitschrift 1912, 1084–1091.
- Hincelin, U.; Chang, Q.; Herbst, E. Astronomy & Astrophysics 2015, 574, A24.
- Hincelin, U.; Wakelam, V.; Commerçon, B.; Hersant, F.; Guilloteau, S. *The Astrophysical Journal* **2013**, 775, 44.
- Hincelin, U.; Wakelam, V.; Hersant, F.; Guilloteau, S.; Loison, J. C.; Honvault, P.; Troe, J. *Astronomy & Astrophysics* **2011**, 530, A61.
- Hinkle, K. W.; Keady, J. J.; Bernath, P. F. Science 1988, 241, 1319–1322.
- Hollenbach, D.; Salpeter, E. E. Journal of Chemical Physics 1970, 53, 79-86.
- Hollis, J. M.; Churchwell, E. B.; Herbst, E.; De Lucia, F. C. Nature 1986, 322, 524–526.
- Hollis, J. M.; Jewell, P. R.; Lovas, F. J. The Astrophysical Journal 1989, 346, 794–798.
- Hollis, J. M.; Jewell, P. R.; Lovas, F. J.; Remijan, A.; Møllendal, H. *The Astrophysical Journal Letters* **2004**, *610*, L21–L24.
- Hollis, J. M.; Lovas, F. J.; Jewell, P. R. The Astrophysical Journal Letters 2000, 540, L107–L110.
- Hollis, J. M.; Lovas, F. J.; Jewell, P. R.; Coudert, L. H. *The Astrophysical Journal Letters* **2002**, *571*, L59–L62.
- Hollis, J. M.; Lovas, F. J.; Remijan, A. J.; Jewell, P. R.; Ilyushin, V. V.; Kleiner, I. *The Astro-physical Journal Letters* **2006**, *643*, L25–L28.
- Hollis, J. M.; Remijan, A. J.; Jewell, P. R.; Lovas, F. J. *The Astrophysical Journal* 2006, 642, 933–939.
- Holtom, P. D.; Bennett, C. J.; Osamura, Y.; Mason, N. J.; Kaiser, R. I. *The Astrophysical Journal* **2005**, *626*, 940.

Hovington, P.; Drouin, D.; Gauvin, R. Scanning **1997**, *19*, 1–14.

Hudson, R. L. Physical Chemistry Chemical Physics 2017,

Hudson, R. L.; Moore, M. H. Journal of Geophysical Research 2001, 106, 33275–33284.

Hudson, R. L.; Moore, M. H.; Dworkin, J. P.; Martin, M. P.; Pozun, Z. D. Astrobiology 2008, 8, 771–779.

Husain, D.; Kirsch, L. J. Transactions of the Faraday Society 1971, 67, 2025–2035.

Hörandel, J. R. AIP Conference Proceedings 2013, 1516, 52–60.

- Iglesias-Groth, S.; Manchado, A.; Rebolo, R.; González Hernández, J. I.; García-Hernández, D. A.; Lambert, D. L. *Monthly Notices of the Royal Astronomical Society* **2010**, 407, 2157–2165.
- Ikhsanov, N. R. Astrophysics and Space Science 1991, 184, 297–311.
- Indriolo, N.; Hobbs, L. M.; Hinkle, K. H.; McCall, B. J. *The Astrophysical Journal* **2009**, 703, 2131–2137.
- Indriolo, N.; McCall, B. J. Chemical Society Reviews 2013, 42, 7763–7773.
- Ip, W.-H.; Axford, W. I. Astronomy and Astrophysics 1985, 149, 7.
- Irvine, W. M.; Brown, R. D.; Cragg, D. M.; Friberg, P.; Godfrey, P. D.; Kaifu, N.; Matthews, H. E.; Ohishi, M.; Suzuki, H.; Takeo, H. *The Astrophysical Journal Letters* 1988, 335, L89–L93.
- Irvine, W. M.; Friberg, P.; Hjalmarson, A.; Ishikawa, S.; Kaifu, N.; Kawaguchi, K.; Madden, S. C.; Matthews, H. E.; Ohishi, M.; Saito, S.; Suzuki, H.; Thaddeus, P.; Turner, B. E.; Yamamoto, S.; Ziurys, L. M. *The Astrophysical Journal Letters* **1988**, 334, L107–L111.
- Ivlev, A. V.; Padovani, M.; Galli, D.; Caselli, P. The Astrophysical Journal 2015, 812, 135.
- Ivlev, A. V.; Röcker, T. B.; Vasyunin, A.; Caselli, P. *The Astrophysical Journal* **2015**, 805, 59.
- Jackman, C. H.; Garvey, R. H.; Green, A. E. S. Journal of Geophysics Research 1977, 82, 5081– 5090.
- Jefferts, K. B.; Penzias, A. A.; Wilson, R. W.; Solomon, P. M. *The Astrophysical Journal Letters* **1971**, *168*, L111–L113.
- Jenkins, E. B. The Astrophysical Journal 2009, 700, 1299–1348.
- Johnson, D. R.; Lovas, F. J.; Gottlieb, C. A.; Gottlieb, E. W.; Litvak, M. M.; Thaddeus, P.; Guelin, M. *The Astrophysical Journal* **1977**, *218*, 370–376.
- Johnson, R. E. *Energetic Charged-Particle Interactions with Atmospheres and Surfaces;* Physics and Chemistry in Space 19; Springer-Verlag: Berlin, 1990.

Johnson, R. E. Journal of Geophysical Research: Planets 1991, 96, 17553–17557.

- Johnson, R. *Physics and Chemistry at Low Temperatures*; Pan Stanford Publishing, 2011; pp 297–339.
- Johnson, R. D. NIST Computational Chemistry Comparison and Benchmark Database; 2016.
- Kaifu, N.; Morimoto, M.; Nagane, K.; Akabane, K.; Iguchi, T.; Takagi, K. *The Astrophysical Journal Letters* **1974**, 191, L135–L137.
- Kaifu, N.; Suzuki, H.; Ohishi, M.; Miyaji, T.; Ishikawa, S.-I.; Kasuga, T.; Morimoto, M.; Saito, S. *The Astrophysical Journal Letters* **1987**, *317*, L111–L114.
- Kamiski, T.; Gottlieb, C. A.; Menten, K. M.; Patel, N. A.; Young, K. H.; Brünken, S.; Müller, H. S. P.; McCarthy, M. C.; Winters, J. M.; Decin, L. Astronomy and Astrophysics 2013, 551, A113.
- Kamiski, T.; Mason, E.; Tylenda, R.; Schmidt, M. R. *Astronomy and Astrophysics* **2015**, *580*, A34.
- Kawaguchi, K.; Kasai, Y.; Ishikawa, S.-I.; Ohishi, M.; Kaifu, N.; Amano, T. *The Astrophysical Journal Letters* **1994**, 420, L95–L97.
- Kawaguchi, K.; Ohishi, M.; Ishikawa, S.-I.; Kaifu, N. *The Astrophysical Journal Letters* **1992**, *386*, L51–L53.
- Kawaguchi, K.; Takano, S.; Ohishi, M.; Ishikawa, S.-I.; Miyazawa, K.; Kaifu, N.; Yamashita, K.; Yamamoto, S.; Saito, S.; Ohshima, Y.; Endo, Y. *The Astrophysical Journal Letters* **1992**, *396*, L49–L51.
- Keller-Rudek, H.; Moortgat, G. K.; Sander, R.; Sörensen, R. *Earth System Science Data* **2013**, *5*, 365–373.
- Kinchin, G. H.; Pease, R. S. Reports on Progress in Physics 1955, 18, 1.
- Klopovskiy, K. S.; Lopaev, D. V.; Popov, N. A.; Rakhimov, A. T.; Rakhimova, T. V. *Journal of Physics D: Applied Physics* **1999**, *32*, 3004.
- Knauth, D. C.; Andersson, B.-G.; McCandliss, S. R.; Warren Moos, H. *Nature* 2004, 429, 636–638.
- Kolesniková, L.; Daly, A. M.; Alonso, J. L.; Tercero, B.; Cernicharo, J. Journal of Molecular Spectroscopy **2013**, 289, 13–20.
- Kolesniková, L.; Tercero, B.; Cernicharo, J.; Alonso, J. L.; Daly, A. M.; Gordon, B. P.; Shipman, S. T. *The Astrophysical Journal Letters* **2014**, *784*, L7.

- Kroto, H. W.; Kirby, C.; Walton, D. R. M.; Avery, L. W.; Broten, N. W.; MacLeod, J. M.; Oka, T. *The Astrophysical Journal Letters* **1978**, *219*, L133–L137.
- Kuiper, T. B. H.; Kakar, R. K.; Rodriguez Kuiper, E. N.; Zuckerman, B. The Astrophysical Journal Letters 1975, 200, L151–L153.
- LaVerne, J. A.; Carrasco-Flores, E. A.; Araos, M. S.; Pimblott, S. M. *The Journal of Physical Chemistry A* **2008**, *112*, 3345–3351.
- Lacombe, S.; Cemic, F.; Jacobi, K.; Hedhili, M. N.; Le Coat, Y.; Azria, R.; Tronc, M. *Physical* review letters **1997**, *79*, 1146.
- Lacy, J. H.; Carr, J. S.; Evans, N. J., II; Baas, F.; Achtermann, J. M.; Arens, J. F. *The Astrophysical Journal* **1991**, *376*, 556–560.
- Lafosse, A.; Bertin, M.; Domaracka, A.; Pliszka, D.; Illenberger, E.; Azria, R. *Physical Chemistry Chemical Physics* **2006**, *8*, 5564.
- Landau, L.; Lifshitz, E. *Mechanics*, 3rd ed.; Course of Theoretical Physics; Butterworth-Heinemann: Oxford, 1976; Vol. 1.
- Langer, W. D.; Velusamy, T.; Kuiper, T. B. H.; Peng, R.; McCarthy, M. C.; Travers, M. J.; Kovács, A.; Gottlieb, C. A.; Thaddeus, P. *The Astrophysical Journal Letters* 1997, 480, L63– L66.
- Latter, W. B.; Walker, C. K.; Maloney, P. R. The Astrophysical Journal Letters 1993, 419, L97.
- Lauck, T.; Karssemeijer, L.; Shulenberger, K.; Rajappan, M.; Öberg, K. I.; Cuppen, H. M. *The Astrophysical Journal* **2015**, *801*, 118.
- Lawson, C. L.; Hanson, R. J.; Kincaid, D. R.; Krogh, F. T. ACM Trans. Math. Softw. 1979, 5, 308–323.
- Le Petit, F.; Nehmé, C.; Le Bourlot, J.; Roueff, E. *The Astrophysical Journal Supplement Series* **2006**, *164*, 506.
- Leger, A.; Jura, M.; Omont, A. Astronomy and Astrophysics 1985, 144, 147–160.

Lemaître, G.; Vallarta, M. S. Physical Review 1933, 43, 87–91.

- Li, Q.; Osborne, M. C.; Smith, I. W. M. International Journal of Chemical Kinetics 2000, 32, 85–91.
- Lias, S. G. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2018.

- Lind, S. Radiation Chemistry of Gases; ACS Monograph Series 151; Reinhold: New York, 1961.
- Lindhard, J.; Scharff, M.; Schiøtt, H. E. *Range concepts and heavy ion ranges*; Munksgaard, 1963.
- Linke, R. A.; Frerking, M. A.; Thaddeus, P. *The Astrophysical Journal Letters* **1979**, 234, L139–L142.
- Lis, D. C. et al. Astronomy and Astrophysics 2010, 521, L9.
- Liszt, H. S.; Turner, B. E. The Astrophysical Journal Letters 1978, 224, L73–L76.
- Little, L. T.; MacDonald, G. H.; Riley, P. W.; Matheson, D. N. *Monthly Notices of the Royal Astronomical Society* **1978**, *183*, 45P–50P.
- Loomis, R. A.; Shingledecker, C. N.; Langston, G.; McGuire, B. A.; Dollhopf, N. M.; Burkhardt, A. M.; Corby, J.; Booth, S. T.; Carroll, P. B.; Turner, B.; Remijan, A. J. *Monthly Notices of the Royal Astronomical Society* **2016**, *463*, 4175–4183.
- Loomis, R. A.; Zaleski, D. P.; Steber, A. L.; Neill, J. L.; Muckle, M. T.; Harris, B. J.; Hollis, J. M.; Jewell, P. R.; Lattanzi, V.; Lovas, F. J.; Martinez, O., Jr.; McCarthy, M. C.; Remijan, A. J.; Pate, B. H.; Corby, J. F. *The Astrophysical Journal Letters* **2013**, *765*, L9.
- Loren, R. B.; Wootten, A.; Mundy, L. G. The Astrophysical Journal Letters 1984, 286, L23–L26.
- Lovas, F. J.; Hollis, J. M.; Remijan, A. J.; Jewell, P. R. *The Astrophysical Journal Letters* **2006**, 645, L137–L140.
- Lovas, F. J.; Remijan, A. J.; Hollis, J. M.; Jewell, P. R.; Snyder, L. E. *The Astrophysical Journal Letters* **2006**, *637*, L37–L40.
- MacLeod, J. M.; Avery, L. W.; Broten, N. W. *The Astrophysical Journal Letters* **1984**, *282*, L89–L92.
- Magee, J. L. International journal of radiation applications and instrumentation. Part C, Radiation physics and chemistry **1988**, 32, 1–2.
- Marcelino, N.; Cernicharo, J.; Agúndez, M.; Roueff, E.; Gerin, M.; Martín-Pintado, J.; Mauersberger, R.; Thum, C. *The Astrophysical Journal Letters* **2007**, *665*, L127–L130.
- Marcelino, N.; Cernicharo, J.; Tercero, B.; Roueff, E. *The Astrophysical Journal Letters* **2009**, 690, L27–L30.
- Mason, N. J.; Nair, B.; Jheeta, S.; Szymaska, E. Faraday Discussions 2014, 168, 235.

Matsumi, Y.; Inagaki, Y.; Kawasaki, M. The Journal of Physical Chemistry 1994, 98, 3777–3781.

- Matthews, H. E.; Irvine, W. M.; Friberg, P.; Brown, R. D.; Godfrey, P. D. *Nature* **1984**, *310*, 125.
- Mayer, S. W.; Schieler, L.; Johnston, H. S. *Symposium (International) on Combustion* **1967**, *11*, 837 844.
- McCarthy, M. C.; Gottlieb, C. A.; Gupta, H.; Thaddeus, P. *The Astrophysical Journal Letters* **2006**, 652, L141–L144.
- McCarthy, M. C.; Martinez, O.; McGuire, B. A.; Crabtree, K. N.; Martin-Drumel, M.-A.; Stanton, J. F. *Journal of Chemical Physics* **2016**, *144*, 124304.
- McCrea, W. H.; McNally, D. Monthly Notices of the Royal Astronomical Society 1960, 121, 238.
- McGuire, B. A.; Burkhardt, A. M.; Kalenskii, S.; Shingledecker, C. N.; Remijan, A. J.; Herbst, E.; McCarthy, M. C. *Science* **2018**, *359*, 202–205.
- McGuire, B. A.; Burkhardt, A. M.; Shingledecker, C. N.; Kalenskii, S. V.; Eric Herbst,; Remijan, A. J.; McCarthy, M. C. *The Astrophysical Journal Letters* **2017**, *843*, L28.
- McGuire, B. A.; Carroll, P. B.; Loomis, R. A.; Finneran, I. A.; Jewell, P. R.; Remijan, A. J.; Blake, G. A. *Science* **2016**, *352*, 1449–1452.
- McGuire, B. A.; Loomis, R. A.; Charness, C. M.; Corby, J. F.; Blake, G. A.; Hollis, J. M.; Lovas, F. J.; Jewell, P. R.; Remijan, A. J. *The Astrophysical Journal Letters* **2012**, *758*, L33.
- McGuire, B. A.; Shingledecker, C. N.; Willis, E. R.; Burkhardt, A. M.; El-Abd, S.; Motiyenko, R. A.; Brogan, C. L.; Hunter, T. R.; Margulès, L.; Guillemin, J.-C.; Garrod, R. T.; Herbst, E.; Remijan, A. J. *The Astrophysical Journal Letters* 2017, 851, L46.
- McKellar, A. Publications of the Astronomical Society of the Pacific 1940, 52, 187.
- Mehringer, D. M.; Snyder, L. E.; Miao, Y.; Lovas, F. J. *The Astrophysical Journal Letters* **1997**, 480, L71–L74.
- Menten, K. M.; Wyrowski, F.; Belloche, A.; Güsten, R.; Dedes, L.; Müller, H. S. P. Astronomy and Astrophysics **2011**, 525, A77.
- Merrill, P. W. Publications of the Astronomical Society of the Pacific **1934**, 46, 206–207.
- Metropolis, N.; Ulam, S. Journal of the American Statistical Association 1949, 44, 335–341.
- Meyer, D. M.; Roth, K. C. The Astrophysical Journal Letters 1991, 376, L49–L52.
- Miller, J. H.; Green, A. E. S. Radiation Research 1973, 54, 343.
- Milligan, D. E.; Jacox, M. E. The Journal of Chemical Physics 1971, 54, 927–942.
- Millikan, R. A.; Cameron, G. H. *Physical Review* **1928**, *32*, 533–557.

Montroll, E. W.; Weiss, G. H. Journal of Mathematical Physics 1965, 6, 167.

- Morris, M.; Gilmore, W.; Palmer, P.; Turner, B. E.; Zuckerman, B. *The Astrophysical Journal Letters* **1975**, *199*, L47–L51.
- Mousis, O. et al. The Astrophysical Journal 2016, 823, L41.
- Nath, B. B.; Biermann, P. L. Monthly Notices of the Royal Astronomical Society 1994, 270, L33.
- Neufeld, D. A.; Falgarone, E.; Gerin, M.; Godard, B.; Herbst, E.; Pineau des Forêts, G.; Vasyunin, A. I.; Güsten, R.; Wiesemeyer, H.; Ricken, O. *Astronomy and Astrophysics* **2012**, 542, L6.
- Neufeld, D. A.; Schilke, P.; Menten, K. M.; Wolfire, M. G.; Black, J. H.; Schuller, F.; Müller, H. S. P.; Thorwirth, S.; Güsten, R.; Philipp, S. *Astronomy and Astrophysics* **2006**, 454, L37–L40.
- Neufeld, D. A.; Wolfire, M. G.; Schilke, P. The Astrophysical Journal 2005, 628, 260-274.
- Neufeld, D. A.; Zmuidzinas, J.; Schilke, P.; Phillips, T. G. *The Astrophysical Journal Letters* **1997**, *488*, L141–L144.
- Newson, K. A.; Luc, S. M.; Price, S. D.; Mason, N. J. International Journal of Mass Spectrometry and Ion Processes **1995**, 148, 203 213.
- Nicholson, J. The Chemistry of Polymers; The Royal Society of Chemistry, 2006.
- Norgett, M. J.; Robinson, M. T.; Torrens, I. M. Nuclear Engineering and Design 1975, 33, 50–54.
- Ohishi, M.; Ishikawa, S.-I.; Amano, T.; Oka, H.; Irvine, W. M.; Dickens, J. E.; Ziurys, L. M.; Apponi, A. J. *The Astrophysical Journal Letters* **1996**, *471*, L61.
- Ohishi, M.; Ishikawa, S.-I.; Yamada, C.; Kanamori, H.; Irvine, W. M.; Brown, R. D.; Godfrey, P. D.; Kaifu, N.; Suzuki, H. *The Astrophysical Journal Letters* **1991**, *380*, L39–L42.
- Ohishi, M.; Kaifu, N.; Kawaguchi, K.; Murakami, A.; Saito, S.; Yamamoto, S.; Ishikawa, S.-I.; Fujita, Y.; Shiratori, Y.; Irvine, W. M. *The Astrophysical Journal Letters* **1989**, *345*, L83– L86.
- Ohishi, M.; McGonagle, D.; Irvine, W. M.; Yamamoto, S.; Saito, S. *The Astrophysical Journal Letters* **1994**, 427, L51–L54.
- Oka, T. Faraday Discussions 2011, 150, 9.
- Okabe, H. Photochemistry of small molecules; Wiley, 1978.
- Ossenkopf, V. et al. Astronomy and Astrophysics 2010, 518, L111.
- Padovani, M.; Galli, D.; Glassgold, A. E. Astronomy and Astrophysics 2009, 501, 619–631.

- Pagani, L. et al. Astronomy & Astrophysics 2003, 402, L77–L81.
- Paretzke, H. G. In *Fourth symposium on microdosimetry*; Booz, J., Ebert, H., Eickel, R., Waker, A., Eds.; Commision of European Communities: Luxembourg, 1974.
- Parise, B.; Bergman, P.; Du, F. Astronomy and Astrophysics 2012, 541, L11.
- Parker, E. N. Phys. Rev. 1958, 110, 1445–1449.
- Pelleg, J. *Diffusion in Ceramics;* Solid Mechanics and Its Applications; Springer, Cham, 2016; pp 15–20.
- Penzias, A. A.; Solomon, P. M.; Wilson, R. W.; Jefferts, K. B. *The Astrophysical Journal Letters* **1971**, *168*, L53.
- Peterson, L. R.; Green, A. E. S. Journal of Physics B: Atomic and Molecular Physics 1968, 1, 1131.
- Pety, J.; Gratier, P.; Guzmán, V.; Roueff, E.; Gerin, M.; Goicoechea, J. R.; Bardeau, S.; Sievers, A.; Le Petit, F.; Le Bourlot, J.; Belloche, A.; Talbi, D. *Astronomy and Astrophysics* **2012**, *548*, A68.
- Peverall, R.; Rosén, S.; Peterson, J. R.; Larsson, M.; Al-Khalili, A.; Vikor, L.; Semaniak, J.; Bobbenkamp, R.; Le Padellec, A.; Maurellis, A. N.; van der Zande, W. J. *The Journal of Chemical Physics* 2001, 114, 6679–6689.
- Phelps, A. V. Canadian Journal of Chemistry 1969, 47, 1783–1793.
- Philip, J.; Sprengers, J. P.; Pielage, T.; de Lange, C. A.; Ubachs, W.; Reinhold, E. *Canadian Journal of Chemistry* **2004**, *82*, 713–722.
- Pimblott, S. M.; LaVerne, J. A. The Journal of Physical Chemistry A 2002, 106, 9420–9427.
- Pimblott, S. M.; LaVerne, J. A.; Mozumder, A. *The Journal of Physical Chemistry* **1996**, 100, 8595–8606.
- Platzman, R. L. Radiation Research 1955, 2, 1.
- Poggi, G.; Francisco, J. S. The Journal of Chemical Physics 2004, 120, 5073–5080.
- Porter, H. S. The Journal of Chemical Physics 1976, 65, 154.
- Prasad, S. S.; Tarafdar, S. P. The Astrophysical Journal 1983, 267, 603–609.
- Pshezhetskii, S. Y.; Morozov, N. M.; Kamenetskaya, S. A.; Siryatskaya, V. N.; Gribova, E. I. *Russ. J. Phys. Chem. (Engl. Transl.)* **1959**, 33, 1–20.
- Pulliam, R. L.; Savage, C.; Agúndez, M.; Cernicharo, J.; Guélin, M.; Ziurys, L. M. The Astrophysical Journal Letters 2010, 725, L181–L185.

- Remijan, A. J.; Hollis, J. M.; Lovas, F. J.; Cordiner, M. A.; Millar, T. J.; Markwick-Kemper, A. J.; Jewell, P. R. *The Astrophysical Journal Letters* **2007**, *664*, L47–L50.
- Remijan, A. J.; Hollis, J. M.; Snyder, L. E.; Jewell, P. R.; Lovas, F. J. *The Astrophysical Journal Letters* **2006**, *643*, L37–L40.
- Remijan, A. J.; Snyder, L. E.; McGuire, B. A.; Kuo, H.-L.; Looney, L. W.; Friedel, D. N.; Golubiatnikov, G. Y.; Lovas, F. J.; Ilyushin, V. V.; Alekseev, E. A.; Dyubko, S. F.; McCall, B. J.; Hollis, J. M. *The Astrophysical Journal* **2014**, *783*, 77.
- Ribeiro, F. d. A.; Almeida, G. C.; Garcia-Basabe, Y.; Wolff, W.; Boechat-Roberty, H. M.; Rocco, M. L. M. *Physical Chemistry Chemical Physics (Incorporating Faraday Transactions)* 2015, 17, 27473–27480.
- Ridgway, S. T.; Hall, D. N. B.; Wojslaw, R. S.; Kleinmann, S. G.; Weinberger, D. A. *Nature* **1976**, 264, 345.
- Rimmer, P. B.; Herbst, E.; Morata, O.; Roueff, E. Astronomy & Astrophysics 2012, 537, A7.
- Roberge, W. G.; Jones, D.; Lepp, S.; Dalgarno, A. Astrophysical Journal Supplement Series 1991, 77, 287–297.
- Robinson, M. T.; Torrens, I. M. Physical Review B 1974, 9, 5008–5024.
- Rossi, B. Physical Review 1930, 36, 606–606.
- Rothard, H.; Domaracka, A.; Boduch, P.; Palumbo, M. E.; Strazzulla, G.; da Silveira, E. F.; Dartois, E. *Journal of Physics B: Atomic, Molecular and Optical Physics* **2017**, *50*, 062001.
- Ruaud, M.; Wakelam, V.; Hersant, F. *Monthly Notices of the Royal Astronomical Society* **2016**, 459, 3756–3767.
- Rubin, R. H.; Swenson, G. W., Jr.; Benson, R. C.; Tigelaar, H. L.; Flygare, W. H. *The Astro-physical Journal Letters* **1971**, *169*, L39.
- Saito, S.; Kawaguchi, K.; Yamamoto, S.; Ohishi, M.; Suzuki, H.; Kaifu, N. *The Astrophysical Journal Letters* **1987**, 317, L115–L118.
- Salvat, F.; Fernández-Varea, J. M.; Sempau, J. PENELOPE-2006: A code system for Monte Carlo simulation of electron and photon transport. Workshop proceedings. 2006.
- Schwenn, R. Encyclopedia of Astronomy and Astrophysics (ed. P. Murdin), Institute of Physics and Macmillan Publishing, Bristol **2001**, 1–9.
- Senn, G.; Skalny, J. D.; Stamatovic, A.; Mason, N. J.; Scheier, P.; Märk, T. D. *Phys. Rev. Lett.* **1999**, *82*, 5028–5031.

- Shannon, R. J.; Cossou, C.; Loison, J.-C.; Caubet, P.; Balucani, N.; Seakins, P. W.; Wakelam, V.; Hickson, K. M. RSC Advances 2014, 4, 26342–26353.
- Shingledecker, C. N.; Tennis, J. D.; Le Gal, R. The Astrophysical Journal 2018,
- Shingledecker, C. N.; Bergner, J. B.; Le Gal, R.; Öberg, K. I.; Hincelin, U.; Herbst, E. *The Astrophysical Journal* **2016**, *830*, 151.
- Shingledecker, C. N.; Gal, R. L.; Herbst, E. *Physical Chemistry Chemical Physics* 2017, 19, 11043–11056.
- Shingledecker, C. N.; Herbst, E. Physical Chemistry Chemical Physics 2018, 20, 5359–5367.
- Sigmund, P. Physical Review 1969, 184, 383–416.
- Simon Wedlund, C.; Gronoff, G.; Lilensten, J.; M?nager, H.; Barth?lemy, M. Annales Geophysicae 2011, 29, 187–195.
- Sinclair, M. W.; Fourikis, N.; Ribes, J. C.; Robinson, B. J.; Brown, R. D.; Godfrey, P. D. Australian Journal of Physics 1973, 26, 85.
- Smith, I. W. M.; Zellner, R. Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics **1973**, 69, 1617–1627.
- Snyder, L. E.; Buhl, D.; Schwartz, P. R.; Clark, F. O.; Johnson, D. R.; Lovas, F. J.; Giguere, P. T. *The Astrophysical Journal Letters* **1974**, 191, L79.
- Snyder, L. E.; Hollis, J. M.; Jewell, P. R.; Lovas, F. J.; Remijan, A. *The Astrophysical Journal* **2006**, *647*, 412–417.
- Snyder, L. E.; Hollis, J. M.; Ulich, B. L. The Astrophysical Journal Letters 1976, 208, L91–L94.
- Snyder, L. E.; Hollis, J. M.; Ulich, B. L.; Lovas, F. J.; Johnson, D. R.; Buhl, D. *The Astrophysical Journal Letters* **1975**, *198*, L81–L84.
- Snyder, L. E.; Buhl, D. The Astrophysical Journal 1972, 177, 619.
- Snyder, L. E.; Buhl, D. The Astrophysical Journal Letters 1971, 163, L47.
- Snyder, L. E.; Buhl, D.; Zuckerman, B.; Palmer, P. Physical Review Letters 1969, 22, 679–681.
- Sobral, J. H. A.; Takahashi, H.; Abdu, M. A.; Muralikrishna, P.; Sahai, Y.; Zamlutti, C. J.; de Paula, E. R.; Batista, P. P. *Journal of Geophysical Research: Space Physics* **1993**, *98*, 7791–7798.
- Soifer, B. T.; Puetter, R. C.; Russell, R. W.; Willner, S. P.; Harvey, P. M.; Gillett, F. C. *The Astrophysical Journal Letters* **1979**, 232, L53–L57.

- Solomon, P. M.; Jefferts, K. B.; Penzias, A. A.; Wilson, R. W. *The Astrophysical Journal Letters* **1971**, *168*, L107.
- Souza, S. P.; Lutz, B. L. The Astrophysical Journal Letters 1977, 216, L49–L51.
- Spencer, J. R.; Calvin, W. M.; Person, M. J. Journal of Geophysical Research: Planets 1995, 100, 19049–19056.
- Spinks, J.; Woods, R. An introduction to radiation chemistry; Wiley, 1990.
- Spitzer, L., Jr.; Tomasko, M. G. The Astrophysical Journal 1968, 152, 971.
- Suzuki, H.; Ohishi, M.; Kaifu, N.; Ishikawa, S.-I.; Kasuga, T. *Publications of the Astronomical Society of Japan* **1986**, *38*, 911–917.
- Sweeney, C. J.; Shyn, T. W. Phys. Rev. A 1996, 53, 1576–1580.
- Swings, P.; Rosenfeld, L. The Astrophysical Journal 1937, 86, 483–486.
- Taquet, V.; Furuya, K.; Walsh, C.; van Dishoeck, E. F. Monthly Notices of the Royal Astronomical Society 2016, 462, S99–S115.
- Tenenbaum, E. D.; Woolf, N. J.; Ziurys, L. M. *The Astrophysical Journal Letters* 2007, 666, L29–L32.
- Tenenbaum, E. D.; Ziurys, L. M. The Astrophysical Journal Letters 2008, 680, L121.
- Tenenbaum, E. D.; Ziurys, L. M. The Astrophysical Journal Letters 2010, 712, L93–L97.
- Tenenbaum, E. D.; Ziurys, L. M. The Astrophysical Journal Letters 2009, 694, L59–L63.
- Tercero, B.; Cernicharo, J.; López, A.; Brouillet, N.; Kolesniková, L.; Motiyenko, R. A.; Margulès, L.; Alonso, J. L.; Guillemin, J.-C. *Astronomy and Astrophysics* **2015**, *582*, L1.
- Tercero, B.; Kleiner, I.; Cernicharo, J.; Nguyen, H. V. L.; López, A.; Muñoz Caro, G. M. *The Astrophysical Journal Letters* **2013**, 770, L13.
- Thaddeus, P.; Cummins, S. E.; Linke, R. A. *The Astrophysical Journal Letters* **1984**, 283, L45–L48.
- Thaddeus, P.; Gottlieb, C. A.; Gupta, H.; Brünken, S.; McCarthy, M. C.; Agúndez, M.; Guélin, M.; Cernicharo, J. *The Astrophysical Journal* 2008, 677, 1132–1139.
- Thaddeus, P.; Gottlieb, C. A.; Hjalmarson, A.; Johansson, L. E. B.; Irvine, W. M.; Friberg, P.; Linke, R. A. *The Astrophysical Journal Letters* **1985**, 294, L49–L53.

Thaddeus, P.; Guelin, M.; Linke, R. A. The Astrophysical Journal Letters 1981, 246, L41–L45.

- Thaddeus, P.; Kutner, M. L.; Penzias, A. A.; Wilson, R. W.; Jefferts, K. B. The Astrophysical Journal Letters 1972, 176, L73.
- Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *The Astrophysical Journal Letters* **1985**, 299, L63–L66.
- Tucker, K. D.; Kutner, M. L.; Thaddeus, P. *The Astrophysical Journal Letters* **1974**, *193*, L115–L119.
- Turner, B. E. The Astrophysical Journal Letters 1992, 396, L107–L110.
- Turner, B. E. The Astrophysical Journal Letters 1971, 163, L35.
- Turner, B. E. *The Astrophysical Journal Letters* **1992**, *388*, L35–L38.
- Turner, B. E. *The Astrophysical Journal Letters* **1977**, 213, L75–L79.
- Turner, B. E. The Astrophysical Journal Letters 1974, 193, L83–L87.
- Turner, B. E.; Apponi, A. J. The Astrophysical Journal Letters 2001, 561, L207–L210.
- Turner, B. E.; Bally, J. The Astrophysical Journal Letters **1987**, 321, L75–L79.
- Turner, B. E.; Liszt, H. S.; Kaifu, N.; Kisliakov, A. G. The Astrophysical Journal Letters 1975, 201, L149–L152.
- Turner, B. E.; Steimle, T. C.; Meerts, L. The Astrophysical Journal Letters 1994, 426, 97–100.
- Ulich, B. L.; Hollis, J. M.; Snyder, L. E. The Astrophysical Journal Letters 1977, 217, L105–L108.
- Vasyunin, A. I.; Herbst, E. *The Astrophysical Journal* **2013**, 769, 34.
- Vijh, U. P.; Witt, A. N.; Gordon, K. D. The Astrophysical Journal Letters 2004, 606, L65–L68.
- Wakelam, V.; Herbst, E. *The Astrophysical Journal* **2008**, *680*, 371–383.
- Wakelam, V.; Smith, I. W. M.; Herbst, E.; Troe, J.; Geppert, W.; Linnartz, H.; Öberg, K.; Roueff, E.; Agúndez, M.; Pernot, P.; Cuppen, H. M.; Loison, J. C.; Talbi, D. SSr 2010, 156, 13–72.
- Walmsley, C. M.; Bachiller, R.; Pineau des Forêts, G.; Schilke, P. *The Astrophysical Journal Letters* **2002**, *566*, L109–L112.
- Walmsley, C. M.; Jewell, P. R.; Snyder, L. E.; Winnewisser, G. Astronomy and Astrophysics **1984**, 134, L11–L14.
- Warnatz, J. In *Combustion Chemistry*; Gardiner, W. C., Ed.; Springer US: New York, NY, 1984; pp 197–360.

Weinreb, S.; Barrett, A. H.; Meeks, M. L.; Henry, J. C. Nature 1963, 200, 829-831.

- Willis, E. R.; Garrod, R. T. The Astrophysical Journal 2017, 840, 61.
- Wilson, R. W.; Jefferts, K. B.; Penzias, A. A. The Astrophysical Journal Letters 1970, 161, L43.
- Wilson, R. W.; Penzias, A. A.; Jefferts, K. B.; Kutner, M.; Thaddeus, P. *The Astrophysical Journal Letters* **1971**, *167*, L97.
- Wilson, W. E.; Paretzke, H. G. Radiation Research 1981, 87, 521.
- Windhorst, R. A.; Franklin, B. E.; Neuschaefer, L. W. *Publications of the Astronomical Society of the Pacific* **1994**, *106*, 798–806.
- Winnewisser, G.; Walmsley, C. M. Astronomy and Astrophysics 1978, 70, L37–L39.
- Wishart, J. F. In *Photochemistry and radiation chemistry*; Wishart, J. F., Nocera, D. G., Eds.; Advances in Chemistry Series 254; ACS Publications, 1998; pp 1–4.
- Woods, R. C.; Gudeman, C. S.; Dickman, R. L.; Goldsmith, P. F.; Huguenin, G. R.; Irvine, W. M.; Hjalmarson, A.; Nyman, L.-A.; Olofsson, H. *The Astrophysical Journal* **1983**, 270, 583–588.
- Woon, D. E. The Astrophysical Journal 2011, 728, 44.
- Woon, D. E.; Herbst, E. The Astrophysical Journal Supplement Series 2009, 185, 273–288.
- Wootten, A.; Boulanger, F.; Bogey, M.; Combes, F.; Encrenaz, P. J.; Gerin, M.; Ziurys, L. *Astronomy and Astrophysics* **1986**, *166*, L15–L18.
- Wulf, T. Physikalische Zeitschrift 1910, 10, 152–157.
- Wyrowski, F.; Menten, K. M.; Güsten, R.; Belloche, A. Astronomy and Astrophysics **2010**, 518, A26.
- Yamamoto, S.; Saito, S.; Ohishi, M.; Suzuki, H.; Ishikawa, S.-I.; Kaifu, N.; Murakami, A. *The Astrophysical Journal Letters* **1987**, 322, L55–L58.
- Yu, H.-G.; Francisco, J. S. The Journal of Physical Chemistry A **2009**, 113, 3844–3849.
- Yu, H.-G.; Muckerman, J. T.; Francisco, J. S. *The Journal of Physical Chemistry A* **2005**, 109, 5230–5236.
- Yu, H.-G.; Muckerman, J. T.; Francisco, J. S. *The Journal of Chemical Physics* **2007**, 127, 094302.
- Yusef-Zadeh, F.; Cotton, W.; Viti, S.; Wardle, M.; Royster, M. *The Astrophysical Journal Letters* **2013**, 764, L19.

- Yusef-Zadeh, F.; Hewitt, J. W.; Wardle, M.; Tatischeff, V.; Roberts, D. A.; Cotton, W.; Uchiyama, H.; Nobukawa, M.; Tsuru, T. G.; Heinke, C.; Royster, M. *The Astrophysical Journal* 2013, 762, 33.
- Yldz, U. A. et al. Astronomy & Astrophysics 2013, 558, A58.
- Zack, L. N.; Halfen, D. T.; Ziurys, L. M. The Astrophysical Journal Letters 2011, 733, L36.
- Zaleski, D. P. et al. *The Astrophysical Journal Letters* 2013, 765, L10.
- Zhaunerchyk, V.; Geppert, W. D.; Österdahl, F.; Larsson, M.; Thomas, R. D.; Bahati, E.; Bannister, M. E.; Fogle, M. R.; Vane, C. R. *Physical Review A* **2008**, 77.
- Ziegler, J. F.; Biersack, J. P. In Treatise on Heavy-Ion Science, by Bromley, D. Allan, ISBN 978-1-4615-8105-5. Springer-Verlag US, 1985, p. 93; Bromley, D. A., Ed.; 1985; p 93.
- Ziegler, J. F.; Manoyan, J. M. Nuclear Instruments and Methods in Physics Research B **1988**, 35, 215–228.
- Ziurys, L. M. The Astrophysical Journal Letters 1987, 321, L81–L85.
- Ziurys, L. M.; Apponi, A. J.; Guelin, M.; Cernicharo, J. *The Astrophysical Journal Letters* **1995**, 445, L47–L50.
- Ziurys, L. M.; Apponi, A. J.; Hollis, J. M.; Snyder, L. E. *The Astrophysical Journal Letters* **1994**, 436, L181–L184.
- Ziurys, L. M.; Savage, C.; Highberger, J. L.; Apponi, A. J.; Guélin, M.; Cernicharo, J. *The Astrophysical Journal Letters* **2002**, *564*, L45–L48.
- Ziurys, L. M.; Turner, B. E. *The Astrophysical Journal Letters* **1986**, 302, L31–L36.
- Zuckerman, B.; Ball, J. A.; Gottlieb, C. A. The Astrophysical Journal Letters 1971, 163, L41.
- Zuckerman, B.; Turner, B. E.; Johnson, D. R.; Lovas, F. J.; Fourikis, N.; Palmer, P.; Morris, M.; Lilley, A. E.; Ball, J. A.; Clark, F. O. *The Astrophysical Journal Letters* **1975**, *196*, L99–L102.
- van Dishoeck, E. F. In *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Astrophysics Space Science Library 146; Kluwer Academic Publisher: Dordrecht, 1988; pp 49–73.
- van Dishoeck, E. F.; Jansen, D. J.; Schilke, P.; Phillips, T. G. *The Astrophysical Journal Letters* **1993**, *416*, L83.
- Hart, E.J.,; Platzman, R. L., *Physical Mechanisms in Radiation Biology* 1; Academic: San Diego, 1961; pp 93–120.

Appendices

APPENDIX A

RADIOLYSIS REACTIONS

Number	Process		$f_{\rm br}$	<i>G</i> -value	Туре
		H_2O			
1	$H_2O \rightsquigarrow O^* + H_2^*$		0.500	3.704	Ι
2	$H_2O \rightsquigarrow OH^* + H^*$		0.500	3.704	Ι
3	$H_2O \rightsquigarrow OH + H$		1.000	1.747	II
4	$H_2O \rightsquigarrow H_2O$		1.000	1.747	III
		O_2			
5	$O_2 \rightsquigarrow O^* + O^*$		1.000	3.704	Ι
6	$O_2 \rightsquigarrow O + O$		1.000	2.138	II
7	$O_2 \rightsquigarrow O_2^*$		1.000	2.138	III
		O_3			
8	$O_3 \rightsquigarrow O_2^* + O^*$		1.000	3.704	Ι
9	$O_3 \rightsquigarrow O_2 + O$		1.000	4.059	II
10	$O_3 \rightsquigarrow O_3^*$		1.000	4.059	III
		СО			
11	$\rm CO \rightsquigarrow C^* + O^*$		1.000	3.704	Ι
12	$CO \rightsquigarrow C + O$		1.000	1.269	II
13	$\rm CO \rightsquigarrow \rm CO^*$		1.000	1.269	III
		CO_2			
14	$\mathrm{CO}_2 \rightsquigarrow \mathrm{CO}^* + \mathrm{O}^*$		1.000	3.704	Ι
15	$CO_2 \rightsquigarrow CO + O$		1.000	1.249	II
16	$\mathrm{CO}_2 \rightsquigarrow \mathrm{CO}_2^*$		1.000	1.249	III
		NO			
17	$\mathrm{NO} \rightsquigarrow \mathrm{N}^* + \mathrm{O}^*$		1.000	3.704	Ι
18	$NO \rightsquigarrow N + O$		1.000	1.922	II
19	$\rm NO \rightsquigarrow NO^*$		1.000	1.922	III
		NO_2			
20	$NO \rightsquigarrow NO^* + O^*$		1.000	3.704	Ι
21	$NO \rightsquigarrow NO + O$		1.000	1.207	II
22	$NO \rightsquigarrow NO_2^*$		1.000	1.207	III
		O_2H			
23	$O_2H \rightsquigarrow OH^* + O^*$		1.000	3.704	Ι

Table A.1: New solid-phase radiolysis processes

24	$O_2H \rightsquigarrow OH + O$	1.000	3.714	II
25	$O_2H \rightsquigarrow O_2H^*$	1.000	3.714	III
	H_2O_2			
26	$H_2O_2 \rightsquigarrow OH^* + OH^*$	0.500	3.704	Ι
27	$H_2O_2 \rightsquigarrow O^* + H_2O^*$	0.500	3.704	Ι
28	$H_2O_2 \rightsquigarrow OH + OH^*$	1.000	2.296	II
	NH ₃			
29	$\mathrm{NH}_3 \rightsquigarrow \mathrm{H}^* + \mathrm{NH}_2^*$	0.500	3.704	Ι
30	$\mathrm{NH}_3 \rightsquigarrow \mathrm{H}_2^* + \mathrm{NH}^*$	0.500	3.704	Ι
31	$\mathrm{NH}_3 \rightsquigarrow \mathrm{H} + \mathrm{NH}_2$	1.000	2.721	II
32	$\mathrm{NH}_3 \rightsquigarrow \mathrm{NH}_3^*$	1.000	2.721	III
	CH_4			
33	$\mathrm{CH}_4 \rightsquigarrow \mathrm{H}^* + \mathrm{CH}_3^*$	0.500	3.704	Ι
34	$\mathrm{CH}_4 \rightsquigarrow \mathrm{H}_2 + \mathrm{CH}_2^*$	0.500	3.704	Ι
35	$CH_4 \rightsquigarrow H + CH_3$	1.000	1.505	II
36	$CH_4 \rightsquigarrow CH_4^*$	1.000	1.505	III
	1 4			
	H ₂ CO			
37	$H_2CO \rightsquigarrow H^* + HCO^*$	1.000	3.704	Ι
37 38	$H_2CO \rightarrow H^* + HCO^*$ $H_2CO \rightarrow H + HCO$	$1.000 \\ 1.000$	$3.704 \\ 2.910$	I II
37 38 39	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$	$1.000 \\ 1.000 \\ 1.000$	$3.704 \\ 2.910 \\ 2.910$	I II I
37 38 39	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH$	$1.000 \\ 1.000 \\ 1.000$	3.704 2.910 2.910	I II I
37 38 39 40	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$	$ 1.000 \\ 1.000 \\ 1.000 \\ 0.333 $	3.704 2.910 2.910 3.704	I II I I
37 38 39 40 41	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$	$ \begin{array}{r} 1.000 \\ 1.000 \\ 1.000 \\ 0.333 \\ 0.333 \\ \end{array} $	3.704 2.910 2.910 3.704 3.704	I II I I I
37 38 39 40 41 42	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$ $CH_{3}OH \rightarrow OH^{*} + CH_{3}^{*}$	$ \begin{array}{r} 1.000\\ 1.000\\ 1.000\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ \end{array} $	3.704 2.910 2.910 3.704 3.704 3.704	I II I I I I I
37 38 39 40 41 42 43	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$ $CH_{3}OH \rightarrow OH^{*} + CH_{3}^{*}$ $CH_{3}OH \rightarrow H + CH_{3}^{*}$ $CH_{3}OH \rightarrow H + CH_{3}O$	$\begin{array}{c} 1.000 \\ 1.000 \\ 1.000 \\ \hline 0.333 \\ 0.333 \\ 0.333 \\ 0.333 \\ 0.333 \end{array}$	$3.704 \\ 2.910 \\ 2.910 \\ 3.704 \\ 3.704 \\ 3.704 \\ 1.571 \\ $	I II I I I I II
37 38 39 40 41 42 43 44	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$ $CH_{3}OH \rightarrow OH^{*} + CH_{3}^{*}$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow H + CH_{2}OH$	$\begin{array}{c} 1.000 \\ 1.000 \\ 1.000 \\ \end{array}$ $\begin{array}{c} 0.333 \\ 0.333 \\ 0.333 \\ 0.333 \\ 0.333 \\ 0.333 \end{array}$	$\begin{array}{c} 3.704 \\ 2.910 \\ 2.910 \\ \hline \\ 3.704 \\ 3.704 \\ 3.704 \\ 1.571 \\ 1.571 \\ \hline \end{array}$	I II I I I II II
37 38 39 40 41 42 43 44 45	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$ $CH_{3}OH \rightarrow OH^{*} + CH_{3}^{*}$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow H + CH_{2}OH$ $CH_{3}OH \rightarrow OH + CH_{3}$	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ \hline 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\end{array}$	$\begin{array}{r} 3.704\\ 2.910\\ 2.910\\ \hline 3.704\\ 3.704\\ 3.704\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ \end{array}$	I II I I I II II II
37 38 39 40 41 42 43 44 45 46	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$ $CH_{3}OH \rightarrow OH^{*} + CH_{3}^{*}$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow OH + CH_{3}OH$ $CH_{3}OH \rightarrow OH + CH_{3}OH$	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ \hline 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 1.000\\ \end{array}$	$\begin{array}{c} 3.704\\ 2.910\\ 2.910\\ \hline \\ 3.704\\ 3.704\\ 3.704\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ \end{array}$	I II I I II II II II II
37 38 39 40 41 42 43 44 45 46	$\begin{array}{c} H_{2}CO \\ H_{2}CO \\ \leftrightarrow H^{*} + HCO^{*} \\ H_{2}CO \\ \leftrightarrow H + HCO \\ H_{2}CO \\ \leftrightarrow H_{2}CO^{*} \end{array}$ $\begin{array}{c} CH_{3}OH \\ \leftrightarrow H^{*} + CH_{3}O^{*} \\ CH_{3}OH \\ \leftrightarrow H^{*} + CH_{2}OH^{*} \\ CH_{3}OH \\ \leftrightarrow OH^{*} + CH_{3}^{*} \\ CH_{3}OH \\ \leftrightarrow H + CH_{3}O \\ CH_{3}OH \\ \leftrightarrow H + CH_{2}OH \\ CH_{3}OH \\ \leftrightarrow OH + CH_{3}O \\ CH_{3}OH \\ \leftrightarrow OH + CH_{3} \\ CH_{3}OH \\ \leftrightarrow CH_{3}OH^{*} \end{array}$	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ \hline 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 1.000\\ \end{array}$	$\begin{array}{c} 3.704\\ 2.910\\ 2.910\\ \hline 3.704\\ 3.704\\ 3.704\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ \end{array}$	I II I I II II II II
37 38 39 40 41 42 43 44 45 46 47	$H_{2}CO \rightarrow H^{*} + HCO^{*}$ $H_{2}CO \rightarrow H^{*} + HCO$ $H_{2}CO \rightarrow H_{2}CO^{*}$ $CH_{3}OH$ $CH_{3}OH \rightarrow H^{*} + CH_{3}O^{*}$ $CH_{3}OH \rightarrow H^{*} + CH_{2}OH^{*}$ $CH_{3}OH \rightarrow OH^{*} + CH_{3}^{*}$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow H + CH_{3}O$ $CH_{3}OH \rightarrow OH + CH_{3}$ $CH_{3}OH \rightarrow CH_{3}OH^{*}$ $CH_{3}COCH_{3} \rightarrow CH_{3}^{*} + CH_{3}CO^{*}$	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ \hline 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 1.000\\ \hline 1.000\\ \hline \end{array}$	$\begin{array}{c} 3.704\\ 2.910\\ 2.910\\ \hline \\ 3.704\\ 3.704\\ 3.704\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 3.704\\ \end{array}$	I I I I I I I I I I I I I I I I
37 38 39 40 41 42 43 44 45 46 47 48	$\begin{array}{c} H_{2}CO \\ H_{2}CO \rightsquigarrow H^{*} + HCO^{*} \\ H_{2}CO \rightsquigarrow H + HCO \\ H_{2}CO \rightsquigarrow H_{2}CO^{*} \\ \hline \\ CH_{3}OH \\ \sim H_{2}CO^{*} \\ \hline \\ CH_{3}OH \rightsquigarrow H^{*} + CH_{3}O^{*} \\ CH_{3}OH \rightsquigarrow H^{*} + CH_{2}OH^{*} \\ CH_{3}OH \\ \sim OH^{*} + CH_{3}^{*} \\ CH_{3}OH \\ \rightarrow H + CH_{3}O \\ CH_{3}OH \\ \rightarrow H + CH_{2}OH \\ CH_{3}OH \\ \sim OH + CH_{3}O \\ CH_{3}OH \\ \sim OH + CH_{3}OH \\ CH_{3}OH \\ \rightarrow CH_{3}OH^{*} \\ \hline \\ CH_{3}COCH_{3} \\ \sim CH_{3} + CH_{3}CO^{*} \\ CH_{3}COCH_{3} \\ \sim CH_{3} + CH_{3}CO \\ \end{array}$	$\begin{array}{c} 1.000\\ 1.000\\ 1.000\\ \hline 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 0.333\\ 1.000\\ \hline 1.000\\ 1.000\\ \hline \end{array}$	$\begin{array}{c} 3.704\\ 2.910\\ 2.910\\ \hline \\ 3.704\\ 3.704\\ 3.704\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 1.571\\ 3.704\\ 4.020\\ \end{array}$	I I I I I I I I I I I I I I I I

APPENDIX B CLASS 2 REACTIONS

Number	Reaction	$f_{ m br}$	Source
	C*		
50	$C^* + H_2O \rightarrow CH + OH$	1.0	Mayer et al. (1967)
51	$C^* + CO \rightarrow CCO$	1.0	Husain and Kirsch (1971)
52	$C^* + CH_3OH \rightarrow CH_3CHO$	0.5	Shannon et al. (2014)
53	$C^* + CH_3OH \rightarrow CH_3 + HCO$	0.5	Shannon et al. (2014)
	O*		
54	$O^* + CH_4 \rightarrow CH_3OH$	0.65	Bergner et al. (2017)
55	$O^* + CH_4 \rightarrow H_2CO + H_2$	0.35	Bergner et al. (2017)
56	$O^* + CH_3OH \rightarrow CH_3 + HCO$	1.0	Matsumi et al. (1994)
57	$O^* + NO \rightarrow NO_2$	1.0	Atkinson et al. (2004)
	CH_2^*		
58	$\mathrm{CH}_2^* + \mathrm{CH}_3\mathrm{OH} \to \mathrm{CH}_3\mathrm{CH}_2\mathrm{OH}$	0.5	Bergantini et al. (2018)
59	$CH_2^* + CH_3OH \rightarrow CH_3OCH_3$	0.5	Bergantini et al. (2018)

Table B.1: New Class 2 reactions involving suprathermal species.

APPENDIX C **New Hoco Reactions**

See Text	9.438	1.623×10^{-9}	1.000	$HOCO + C^+ \rightarrow HOCO^+ + C$	69
See Text	9.438	3.609×10^{-9}	1.000	$HOCO + He^+ \rightarrow HOCO^+ + He$	68
See Text	9.438	2.978×10^{-9}	1.000	$HOCO + H_3^+ \rightarrow HOCO^+ + H + H_2$	67
See Text	9.438	5.049×10^{-9}	1.000	$HOCO + H^+ \rightarrow HOCO^+ + H$	66
		$cm^3 s^{-1}$	$f_{ m br}$		
		_	Ion-Neutral		
Yu and Francisco (2009)	0.000	0.000	5.800×10^{-11}	$\rm HOCO + CH_3 \rightarrow H_2O + H2C_2O$	65
Yu et al. (2005)	0.000	0.000	1.030×10^{-11}	$\mathrm{HOCO} + \mathrm{OH} \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{CO}_2$	64
Yu et al. (2007)	0.000	0.000	1.440×10^{-11}	$HOCO + O \rightarrow OH + CO_2$	63
Poggi and Francisco (2004)	0.000	0.000	2.450×10^{-12}	$HOCO + NO \rightarrow HNO + CO_2$	62
Poggi and Francisco (2004)	0.000	0.000	1.900×10^{-12}	$\mathrm{HOCO} + \mathrm{O}_2 \rightarrow \mathrm{O}_2\mathrm{H} + \mathrm{CO}_2$	61
Li et al. (2000)	0.000	0.000	4.800×10^{-11}	$HOCO + Cl \rightarrow HCl + CO_2$	60
		K	s^{-1}		
		ral	Neutral-Neut		
Source	γ	β	α	Reaction	Number
			0 I		

	Table C.1: New
C I	gas-phase HOC
	O destruction reactions

APPENDIX D

TIME-LINE OF INTERSTELLAR MOLECULE DISCOVERY

D.1 The Optical Absorption Era



D.2 The Post-War Science Boom and Efflorescence of Radio Astronomy

1951 -	-	Bates and Spitzer (1951) publish the first quantitative study of the abundance of interstellar molecules.
		The National Radio Astronomy Observatory (NRAO) is estab- lished
		The Lovell 240ft radio telescope at Jodrell Bank Observatory be- gins science operations.
		McCrea and McNally (1960) publish the first study of H_2 formation on dust grains.
		Construction of the Parkes 64m Radio Telescope is completed.
1956		The Green Bank 300ft telescope begins science operations.
1957		The Arecibo 305m radio telescope begins science operations.
		Weinreb et al. (1963) detect OH towards Cas A.
		The Green Bank 140ft radio telescope begins science operations.
1960		Cheung et al. (1968) detect ammonia, NH_3 toward the galactic center.
		Cheung et al. (1969) detect water toward several sources.
1961		Snyder et al. (1969) detect the first organic molecule formaldehyde,
1962		112CO, in several sources.
1963	+ / ///	
1965		
1968	$\downarrow//$	
1969 -	¥	





D.3 The Birth of Astrochemical Models
















D.4 Astrochemistry in the Age of ALMA





