Theoretical Investigations of Unimolecular Reaction Dynamics in the Gas Phase

A Thesis submitted by
Anchal Gahlaut

in partial fulfillment of the requirements for the award of the degree of
Doctor of Philosophy

॥ त्वं ज्ञानमयो विज्ञानमयोऽसि ॥

Indian Institute of Technology Jodhpur
Department of Chemistry
October 2020

Declaration

I hereby declare that the work presented in this thesis titled *Theoretical Investigations of Unimolecular Reaction Dynamics in the Gas Phase* submitted to the Indian Institute of Technology Jodhpur in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Manikandan Paranjothy. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.

Anchal Gahlaut
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Certificate

This is to certify that the thesis titled *Theoretical Investigations of Unimolecular Reaction Dynamics in the Gas Phase*, submitted by *Anchal Gahlaut (P15CY004)* to the Indian Institute of Technology Jodhpur for the award of the degree of *Doctor of Philosophy*, is a bonafide record of the research work done by her under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

P. M

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Acknowledgments

This Ph.D. thesis is the output of the support and guidance of many people to whom I am profoundly grateful.

Foremost, I would like to express my sincerest appreciation to my research advisor, *Dr. Manikandan Paranjothy* for giving me an amazing opportunity to work under his guidance and introducing me to chemical reaction dynamics. I appreciate his unflinching support and motivation he offered me through each stage of my Ph.D. life. His immense knowledge, enthusiasm, and passion has given me more power and enriched my scientific interests. His infectious style of giving talks and classroom lectures has influenced me. He always created a motivational and inspirational environment, which helped me in doing my work enthusiastically. It has been a privilege to work with him. I will always be deeply indebted to him.

Sincere thanks to the members of my Doctoral Committee: *Dr. Atul Kumar*, *Dr. Samanwita Pal*, and *Dr. Satyajit Sahu* for their valuable suggestions and insightful comments, which incented me to broaden my research from various perspectives. They all have played a major role in polishing my research skills.

I am highly thankful to *Yogeshwaran Krishnan* for teaching me the basic computer skills during the early stages of my Ph.D. and helping me on several occasions.

I thank my fellow labmates *Erum Gull Naz*, *Pooja*, *Aarti*, and *Himani*, for providing a nice environment to work and have fun.

I am fortunate to have a circle of friends whose support and encouragement I shall cherish through life. I would like to thank *Sumitra Godara* for all scientific help and tremendous support throughout this study, *Bhawna Chaubey* for warm and supportive company and *Vivek Raghuwanshi* for extensive help and always giving me words of encouragement. Also, I thank my friends: *Arpita Jaitawat*, *Divya Gupta*, and *Shubham Vaishnav* for all their care and affection. I am indebted to all of you for making my stay at IITJ a memorable one.

I sincerely acknowledge the financial assistance received towards my Ph.D. from IIT Jodhpur, without which this journey would not have been possible.

Finally, I owe my my heartfelt gratitude towards my parents *Mr. Bhupendra Pal Singh Gahlaut* and *Mrs. Indu Gahlaut* for their infallible love, blessings, and eternal support. A big thank you to my buddies *Swati*, *Shashank*, and *Utkarsh* for always believing and encouraging me to follow my dreams. I consider myself nothing without my family. They have cherished with me each incredible moment and upheld me whenever I needed it. I dedicate this thesis to them.

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List of Symbols

Symbol	*Description*
Å	Angstrom
fs	femstosecond
ps	picosecond
$kcal/mol$	kilo calorie per mole
eV	electronvolt
ρ	Electron probability density
ψ	Molecular wave function
ψ_{el}	Electronic wavefunction
ψ_N	Nuclear wavefunction
$\vec{r}$	Electronic coordinates
$\vec{R}$	Nuclear coordinates
Z	Atomic number of nucleus
$\hat{H}$	Hamiltonian operator
V	Potential energy of the system
T	Kinetic energy of the system
q	Position of a particle
p	Momenta of a particle
rc	Reaction coordinate
ν	Normal mode vibrational frequency
k	Force constant
m	Mass
μ	Reduced mass of the molecule
t	Time
Δt	Integration timestep
$k(E)$	RRKM rate constant
E_{tot}	Total energy
f_t	Fractions of trajectories
h	Planck Constant
H	Hydrogen
Ar	Ar
O	Oxygen
C	Carbon
N	Nitrogen
X	Halogen atoms
F	Fluorine
Cl	Chlorine
Br	Bromine
I	Iodine

List of Abbreviations

Abbreviation	*Full form*
B3LYP	Becke, 3-parameter, Lee–Yang–Parr
BOA	Born Oppenheimer Approximation
CBS	Complete Basis Set
CCSD(T)	Coupled Cluster Single-Double and perturbative Triple
CID	Collision Induced Dissociation
DFT	Density Functional Theory
ECP	Effective Core Potential
FM	Formamide
GA	Glycolaldehyde
HF	Hartree-Fock
HFC	Hydrofluorocarbon
IRC	Intrinsic Reaction Coordinate
IVR	Intramolecular Vibrational energy Redistribution
LANL2DZ	Los Alamos National Laboratory 2-double-zeta
MM	Molecular Mechanics
MP2	Møller-Plesset Perturbation theory of second-order
NWChem	NorthWest Chemistry
PE	Potential Energy
PES	Potential Energy Surface
QM	Quantum Mechanics
RRKM	Rice-Ramsperger-Kassel-Marcus
TS	Transition State
VMD	Visual Molecular Dynamics
ZPE	Zero Point Energy