

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
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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.



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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.



Manikandan Paranjothy
Ph.D.Thesis Supervisor

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List of Symbols

Symbol	Description
\AA	Angstrom
fs	femtosecond
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_i	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

<i>Abbreviation</i>	<i>Full form</i>
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

