Kinematical Analysis of Ionization and Fragmentation of Molecules

A Thesis

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MOHANLAL SUKHADIA UNIVERSITY

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by

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DEPARTMENT OF PHYSICS

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UDAIPUR

Year of submission: 2013

To

my parents

DECLARATION

I, **Mr. Koushik Saha**, S/O Mr. Naba Kumar Saha, resident of Room No:104, PRL Thaltej Hostel, Thaltej, Ahmedabad-380054, hereby declare that the work incorporated in the present thesis entitled, **"Kinematical Analysis of Ionization and Fragmentation of Molecules"** is my own and original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

Date : December 6, 2013

(Koushik Saha)

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled, **"Kinematical Analysis of Ionization and Fragmentation of Molecules"** embodies a record of the results of investigations carried out by Mr. Koushik Saha under my guidance. He has completed the following requirements as per Ph.D. regulations of the University.

(a) Course work as per the university rules.

(b) Residential requirements of the university.

(c) Regularly submitted six monthly progress reports.

(c) Presented his work in the departmental committee.

(d) Published minimum of one research papers in a refereed research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn. I recommend the submission of thesis.

Date : December 6, 2013

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Acknowledgments

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Abstract

This thesis is concerned with the study of molecular fragmentation due to various electron loss and decay mechanisms. Molecules are quantum mechanical systems in which the electrons and nuclei are in a dynamic equilibrium. Loss of electrons through ionization due to perturbation such as charged particle impact or photoabsorption, disturbs the equilibrium of the molecular system. The perturbation may excite the molecule electronically, vibrationally, rotationally or a combination of these. The excited state attained by the molecule depends on the energy gained from the perturbation. The configuration of the electrons and nuclei in the excited molecular ion is completely different from that of the molecule in the ground state, hence the ground state equilibrium of the molecule may not be maintained. De-excitation inevitably follows, often leading to dissociation of the molecule.

The energy supplied to a molecule upon projectile impact is shared among its electronic and nuclear degrees of freedom. Since there is a priori no fixed pattern in which the energy transferred to the molecule is shared between the electrons and nuclei, the question that immediately arise is, will this energy sharing affect the kinematics of dissociation? And if so, how? What kind of kinematical differences are induced due to various energy sharing mechanisms? To address these questions, the fragmentation of molecules is studied in the light of the kinematical differences between various electron loss and decay processes. Systematic analysis of the electron decay mechanisms and their subsequent effect on the kinematics of molecular dissociation, has been carried out and presented in this thesis. Manifestations of the kinematical differences may be changes in

fragmentation pathways, kinetic energy release upon dissociation and the conformation of the transient molecular ion, corresponding to different energy sharings.

The studies are limited to simple di- and tri-atomic molecules such as CO, OCS and CS_2. Analysis of the fragmentation processes for valence and core ionized molecules is carried out.

Keywords : Shell selective excitation, Auger decay, Molecular fragmentation, Electron spectroscopy, Ion momentum spectroscopy.

List of Publications

1. Ion-induced triple fragmentation of CO_2^{3+} into $C^+ + O^+ + O^+$,
   M. R. Jana, P. N. Ghosh, B. Bapat, R. K. Kushawaha, **K. Saha**, I. A. Prajapati, and C. P. Safvan, Phys. Rev. A, **84**, 062715, (2011).

2. A combined electron-ion spectrometer for studying complete kinematics of molecular dissociation upon shell selective ionization,
   K. Saha, S. B. Banerjee, and B. Bapat, Rev. Sci. Instrum., **84**, 073101 (2013).

3. Three body dissociation of CS_2^{2+} subsequent to various S($2p$) Auger transitions,
   K. Saha, S. B. Banerjee, and B. Bapat, J. Chem. Phys., **139**, 164309 (2013).

4. Dissociation of OCS upon various S($2p$) Auger decay transitions,
   K. Saha, S. B. Banerjee, and B. Bapat, J. Phys. Conf. Ser., (in press).

5. State selective fragmentation kinematics of OCS^{2+} following S($2p$) Auger decay,
   K. Saha, S. B. Banerjee, and B. Bapat, (under preparation).

Acronyms and Abbreviations

CCD	Charged Couple Device
CEM	Channel Electron Multiplier
CFD	Constant Fraction Discriminator
CMA	Cylindrical Mirror Analyzer
COLTRIMS	Cold Target Recoil Ion Momentum Spectroscopy
DLD	Delay Line Detector
FWHM	Full Width Half Maximum
KER	Kinetic Energy Release
LCAO	Linear Combination of Atomic Orbitals
MCP	Micro Channel Plate
MCS	Multi Channel Scalar
PEC	Potential Energy Curve
PES	Potential Energy Surface
RIMS	Recoil Ion Momentum Spectroscopy
TDC	Time to Digital Convertor
TGM	Toroidal Grating Monochromator
ToF	Time of Flight
VMI	Velocity Map Imaging

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