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By

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INTRODUCTION

This study investigates and explains the scattering mechanisms of intermediate to high energy electron collisions with a range of atomic and molecular species. It will include impact energies ranging from the ionisation energy of the majority of atoms and molecules (about 10-15 eV) to energies at or over 5000 eV. The response of an atomic or molecular target to an incident electron depends on a variety of factors, including the energy and angle of the incident electron, the electronic and molecular structure of the target, and the specific interaction mechanisms involved. [1]. Theoretical and experimental groups of molecular physics have examined electron-molecule collisions since the beginning of the 20th century.

The uses of significant cross section data in both pure and applied sciences is what piques our interest in the current collision calculations. The chosen targets have uses in radiation physics, plasma physics, and atmospheric science. In addition to this, Basic understanding of the characteristics of atoms and molecules, as well as the dynamics of electronic structure and molecular interactions, has been made possible through electron molecule interactions. Understanding electrical discharges requires probabilities of basic collision processes expressed in terms of effective collision cross sections. Ion implantation devices, semiconductor etching for device production, chemical vapour deposition on thin films, and air purification devices all use electrical discharges. The interaction of electrons with the feed gases is the most essential interaction in any plasma since it controls the plasma's ion density, dissociation fractions, and reactivity. The industry has called attention to the necessity to describe electron interactions with reactive species created in the plasma and to provide a database of realistic alternative feed gases [2,3].

Other than chemical and surgical treatments, radiation therapy is one of the main cancer treatment modalities. Radiation therapy causes the areas that have been exposed to radiation to produce electrons with a variety of energies. The secondary electrons generated may clash with DNA molecules in human cells, resulting in damage that kills the cancer cells. Accurate information on the electron collision cross sections of pertinent biological molecules is required for simulating such events [4,5].

For a thorough knowledge and accurate identification of particular ions generated by electron collisions, plasmas with complex molecules present in the feed gas are necessary. In order to produce parent molecule ions and the byproducts of dissociative ionisation, cross section measurements are required. The creation of numerical models that may be used to forecast plasma behaviour and associated properties is one of the main objectives of plasma scientists and engineers. Due to the significance of electron-molecule collisions overall, any trustworthy plasma model requires thorough and precise sets of data. Also, understanding the electron cross sections for rare gas elements is essential for optical plasma diagnostics. Many plasma properties can be extracted using knowledge of these cross sections and measurements of plasma emission [6].

Electron scattering experiments with complex molecules e.g. bio-molecules (thymine, adenine, guanine, cytosine, uracil, etc.), plasma relevance molecules (Perfluoroketones, $C_xF_{2x}O$, x=1-6), environmentally important molecules (fluoronitriles) and reactive radicals in the gas phase are challenging because of the practical difficulties involved in the preparation of well-characterized pure gas targets of these molecules and in the subsequent quantitative determination of the target densities. Thus, more thorough theoretical analyses of electron scattering experiments are required to evaluate different quantitative and qualitative cross sections for these compounds and radicals. Because of this, there has been an ever-increasing focus on the development of theoretical methods to deliver data using simpler approximate theories, capable of providing cross sections accurately and quickly over a wide range of energy in order to encompass many significant phenomena, such as the ionisation of the target.

Accurate information on the cross sections of key plasma and biological molecules for electron collisions is required for simulating such events. We executed this investigation for all of the mentioned technological and fundamental reasons. In this work, we examine and analyze the molecular processes that the electrons impact, such as ionisation, excitation, inelastic, elastic, total cross sections, etc. We used the Spherical Complex Optical Potential (SCOP) methodology and the Complex Scattering Potential-ionization Contribution (CSP-ic) method for the computations at intermediate and high energies.

CHAPTERS OF THE THESIS

In the following chapters, the investigation of electron-molecule interactions undertaken for the thesis is presented:

Chapter I	Fundamentals and scope of electron scattering
Chapter II	Theoretical formalism for electron induced molecular processes
Chapter III	Study of molecules relevant to plasma processes

Chapter IV	Electron interaction with hydrated DNA molecules
Chapter V	Electron collision with fluoronitriles
Chapter VI	Summary, Conclusion and future prospects

Chapter I: Fundamentals and scope of electron scattering

Particle scattering reveals a lot of knowledge about the composition of matter. Collision techniques have been successfully utilized to examine the internal structure of atoms and even of their component particles, as well as the nature of interactions. This chapter explains the fundamental scattering events as well as the various electron interaction processes that are seen in everyday life. It also aims to provide a chronology of the history of electron-driven processes in various atoms and molecules. Electron driven processes on atoms/molecules are of great interest due to its possibilities in the investigations of various applied areas like plasma processes, semiconductor industry, micro-electronics, atmospheric sciences and pollution remediation etc. A well-organized database on electron impact collision cross sections is thus desirable due to its wide spread applications. Apart from the importance of the scattering data in various applied fields, they are also of fundamental importance as scattering is one of the most basic electromagnetic processes to study the structure and properties of any target [7].

Chapter II: Theoretical formalism for electron induced molecular processes

In this chapter the details of theoretical formalisms used for the present electron interactions study is given. We have used three different methodologies to study various molecular processes quantitively through the cross-sections.

[1] Spherical Complex Optical Potential (SCOP):

The study of scattering of electrons from the target molecules for the energies from ionization threshold (IE) to 5000 eV is done using the SCOP formalism. The spherically symmetric complex optical potential of the following form is employed for the calculations of inelastic and elastic cross-sections through the partial wave analysis method [8,9].

$$V_{opt}(r, E_i) = V_R(r, E_i) + iV_I(E_i, r)$$

Here, V_R includes the static potential, exchange potential and polarization potential. The imaginary part V_I of the optical potential includes the absorption potential.

[2] Complex Scattering Potential-ionization contribution (CSP-iC):

To bifurcate the continuum (Q_{ion}) and discrete (Q_{exc}) contributions of the inelastic cross-sections, this CSP-ic approach is employed. In this method we compute ionization cross section from inelastic cross sections by defining the dynamic ratio,

$$R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)} = 1 - C_1\left[\frac{C_2}{U+a} + \frac{\ln U}{U}\right]$$

The dimension less parameters C_1, C_2 and a are obtained by applying the boundary conditions of $R(E_i)$, which is given by,

$$R(E_i) = \begin{cases} 0, & for\ E_i \leq IE \\ R_P, & for\ E_i = E_P \\ 1, & for\ E_i \gg IE \end{cases}$$

where, E_p stands for the peak energy at which the Q_{inel} has its maximum value. From the several results of the experiments and theories the value of R_p at the E_p, is found to be around 0.7 - 0.8 [10-12].

[3] Semi-empirical model:

The semi-empirical model is a relatively quick and computationally cheap method for predicting the Total Cross section (TCS) of complex molecules. In this work, TCS for Furfural and Para Benzoquinone are calculated for the energy rang 500 eV to 10,000 eV. Further it might serve to audit both the theoretical approaches commonly used to estimate the TCS and also the experimental data, in the range above several hundreds of eV.

In, reference of [13] following two parameter analytical equation was proposed:

$$\sigma_T = \frac{0.78(Z) + 0.016(\alpha) - 17.9}{E^{0.77}}$$

Where, σ_T= Total cross section in atomic unit (a_0^2), Z= total no. of electrons in the target molecule, α= molecular polarizability in atomic unit (a_0^3) and E is the energy of incident particles in KeV.

Chapter III: Study of molecules relevant to plasma processes

In this chapter, we report the results of calculations of elastic and inelastic (ionization and excitation) cross sections for electron scattering from perfluoroketone (PFK) molecules, $C_xF_{2x}O$

(x = 1-6) over a wide energy range, from ~ the ionization potential (IP) to 5 keV. These molecules have been determined to have extremely low global warming potentials (GWPs) and therefore may have applications in next generation gas discharges and plasma reactors. The results are derived using the Complex Scattering Potential-ionization contribution (CSP-ic) method to investigate ionization cross sections Q_{ION} and are found to be in good agreement with the available data. The Spherical Complex Optical Potential formalism is used to evaluate elastic (Q_{EL}), inelastic (Q_{INEL}) and total cross sections (Q_T). This study is a maiden effort to report summed total excitation cross section ($\sum Q_{EXC}$), Q_{ION} and Q_{INEL} for CF_2O and C_2F_4O, and Q_{EL} and Q_T for $C_xF_{2x}O$ (x=1-6). The study includes various correlation analyses and a prediction of the dipole polarizability.[14]

Chapter IV: Electron interaction with hydrated DNA molecules

In this chapter, we present the theoretical investigations of the electron scattering cross-sections of the important complex biomolecules, viz., Nucleosides (Adenosine, Cytosine, Guanosine, Thymidine and Uridine) for the energy range from molecular ionization energy to 5000 eV. For all of these molecules, the total (Q_T), elastic (Q_{el}), inelastic (Q_{inel}), ionization (Q_{ion}), excitation (ΣQ_{exc}) cross-sections and dielectric constant reported [15]. Since in the human body DNA is always covered by the water molecules, for the present investigations of electron interactions with DNA bases, we have considered the molecules in their aqueous phase.

Chapter V: Electron collision with fluoronitriles

In this Chapter, we present the results of estimates of elastic and inelastic (ionisation and excitation) cross sections for electron scattering from fluoronitrile molecules C_3F_5N and C_4F_7N over a broad energy range, from the ionisation potential (IP) to 5 keV. It has been established that these compounds have exceptionally low global warming potentials (GWPs) and may therefore have applications in gas discharges and plasma reactors of the next generation. Using the Complex Scattering Potential-ionization contribution (CSP-ic) approach, ionisation cross sections Q_{ion} are calculated and found to be in good agreement with the existing data. Utilizing the Spherical Complex Optical Potential formalism, elastic (Q_{el}), inelastic (Q_{inel}), and total cross sections are evaluated (Q_T). This is the first study to present the summed total excitation cross section ($\sum Q_{exc}$), Q_{ion}, and Q_{inel} for C3F5N, as well as Q_{el} and Q_T for C_4F_7N. The study consists of numerous correlation analyses and a prediction of dipole polarizability and dielectric constant [16].

Chapter VII: Summary, Conclusion and future prospects

In this last chapter of the thesis, we summarize the present results and draw important conclusions of the present work. The future prospects of the present work in terms of latest experimental and theoretical status, will be also discussed in this chapter. We believe that the present comprehensive electron scattering studies will help in understanding of the various electron induced molecular processes for different important applied molecules studied here.

References:

[1] Christophorou, Loucas Georgiou, ed. Electron—Molecule Interactions and Their Applications: Volume 2. Vol. 2. Academic Press, 2013.Bates, D. R. (Ed.). (2012). Atomic and molecular processes (Vol. 13). Elsevier.

[2] Bates, David Robert, ed. Atomic and molecular processes. Vol. 13. Elsevier, 2012.

[3] Brode, Robert B. "The absorption coefficient for slow electrons in gases." Physical Review 25, no. 5 (1925): 636.

[4] Christophorou, Loucas G., V. E. Anderson, and J. B. Birks. Atomic and Molecular Radiation Physics. No. ORNL-4720. and others; Oak Ridge National Lab., Tenn., 1971.

[5] Feil, S., K. Gluch, S. Matt-Leubner, P. Scheier, J. Limtrakul, M. Probst, H. Deutsch, K. Becker, A. Stamatovic, and T. D. Märk. "Partial cross sections for positive and negative ion formation following electron impact on uracil." Journal of Physics B: Atomic, Molecular and Optical Physics 37, no. 15 (2004): 3013.

[6] Boffard, John B., Chun C. Lin, and Charles A. DeJoseph Jr. "Application of excitation cross sections to optical plasma diagnostics." Journal of Physics D: Applied Physics 37, no. 12 (2004): R143.

[7] Brunger, Michael J., and Stephen J. Buckman. "Electron–molecule scattering cross-sections. I. Experimental techniques and data for diatomic molecules." Physics reports 357, no. 3-5 (2002): 215-458.

[8] Jain, Ashok. "Total (elastic+ absorption) cross sections for e-CH_4 collisions in a spherical model at 0.10–500 eV." Physical Review A 34, no. 5 (1986): 3707.

[9] Jain, Ashok, and Kasturi L. Baluja. "Total (elastic plus inelastic) cross sections for electron scattering from diatomic and polyatomic molecules at 10–5000 eV: H_2, Li_2, HF, CH_4, N_2, CO, $C_2 H_2$, HCN, O_2, HCl, $H_2 S$, PH_3, SiH_4, and CO_2." Physical review A 45, no. 1 (1992): 202.

[10] Joshipura, K. N., Minaxi Vinodkumar, C. G. Limbachiya, and B. K. Antony. "Calculated total cross sections of electron-impact ionization and excitations in tetrahedral (XY_4) and SF_6 molecules." Physical Review A 69, no. 2 (2004): 022705.

[11] Limbachiya, Chetan, Minaxi Vinodkumar, Mohit Swadia, and Avani Barot. "Electron impact total cross section calculations for CH_3SH (methanethiol) from threshold to 5 keV." Molecular Physics 112, no. 1 (2014): 101-106.

[12] Vinodkumar, Minaxi, Chetan Limbachiya, Hardik Desai, and P. C. Vinodkumar. "Electron-impact total cross sections for phosphorous triflouride." Physical Review A 89, no. 6 (2014): 062715.

[13] Vinodkumar, Minaxi, Chetan Limbachiya, Mayuri Barot, Mohit Swadia, and Avani Barot. "Electron impact total ionization cross sections for all the components of DNA and RNA molecule." International Journal of Mass Spectrometry 339 (2013): 16-23.

[14] **Thakkar, Nirav**, Mohit Swadia, Minaxi Vinodkumar, Nigel Mason, and Chetan Limbachiya. "Electron induced elastic and inelastic processes for perfluoroketone (PFK) molecules." Plasma Sources Science and Technology 30, no. 8 (2021): 085008.

[15] Smruti Parikh, Dhaval Chauhan, **Nirav Thakkar**, Chetan Limbachiya, Electron induced inelastic processes for aqua DNA compounds (to be communicated)

[16] **Thakkar, Nirav**, Dhaval Chauhan, Chetan Limbachiya, Study of electron impact on fluoronitrile molecules (to be communicated)

Publications:

[1] **Thakkar, Nirav**, Mohit Swadia, Minaxi Vinodkumar, Nigel Mason, and Chetan Limbachiya. "Electron induced elastic and inelastic processes for perfluoroketone (PFK) molecules." Plasma Sources Science and Technology 30, no. 8 (2021): 085008.

[2] Smruti Parikh, Dhaval Chauhan, **Nirav Thakkar**, Chetan Limbachiya, Electron induced inelastic processes for aqua DNA compounds (to be communicated)

[3] **Thakkar, Nirav**, Dhaval Chauhan, Chetan Limbachiya, Study of electron impact on fluoronitrile molecules (to be communicated)

Papers presented in the conferences:

[1] Theoretical investigations of electrons impact on perfluoroketone (PFK) molecules $C_XF_{2X}O$ (X=1-5) – inelastic effects
<u>Nirav Thakkar</u>, Chetan Limbachiya
AISAMP-13th (Asian International Seminar on Atomic and Molecular Physics), 3 to 8 December 2018, IIT Bombay and TIFR-mumbai.

[2] Electron assisted elastic and inelastic processes for perfluoroketone (PFK) molecules
<u>Nirav Thakkar</u>, Chetan Limbachiya
National Conference on Atomic and Molecular Physics (NCAMP), 25th to 28th March 2019, IIT Kanpur

[3] Theoretical Study of electron driven elastic and inelastic processes for PFK (PerfluoroKetone) molecules
<u>Nirav Thakkar</u>, Minaxi Vinodkumar, Chetan Limbachiya
International Conference on Photonic, Electronic and Atomic Collisions), which will be held between 23 to 30 July 2019 at DEAUVILLE, FRANCE.

[4] Electron Interaction Processes for chlouroflouromethane and CCl_x (x = 1-4)
<u>Nirav Thakkar</u>, Chetan Limbachiya
International conference on Atomic, Molecular, Optical and Nano Physics with Applications (CAMNP 2019), 18th – 20th December 2019, DTU, Delhi

[5] Electron assisted Processes for Fluoroketone and Fluoronitrile
<u>Nirav Thakkar</u>, Chetan Limbachiya
Topical conference (TC 2020) on Atomic and Molecular collisions for Plasma Applications, 3rd – 5th March 2020, IIT Roorkee, Uttarakhand

[6] e- $C_xF_{2x}O$ (x = 1- 6) Scattering; Qion (Peak) and Polarizability
<u>Nirav Thakkar</u>, Chetan Limbachiya
One Day Seminar on Dynamics of Electron collision processes, Department of Electronics, V.P. & R.P.T.P. Science college, V.V. Nagar, 8 November 2020.

[7] Electron impact ionization processes for Fluoronitrile gases
<u>Nirav Thakkar</u>, Chetan Limbachiya
XXII International Symposium on Electron-Molecule Collisions and Swarms (POSMOL) Conference, 29th - 30th July 2021, University of Norte Dame, USA (online mode)

[8] Electron assisted inelastic processes for Tetramethylsilane (TMS) molecule
<u>Nirav Thakkar</u>, Chetan Limbachiya
One day National Conference on Role of Basic sciences in emerging technologies 6th January 2023.