Educational Administration: Theory and Practice
2023, 29(4), 5701-5706
ISSN: 2148-2403
https://kuey.net/ **Research Article**

"Ionization Cross Section Evaluation For Methane And Carbon Tetrafluoride Under Electron Impact Via ICSP-IC Formalism"

Kirti M Korot[1], Harshad S Bhutadia[2], Ashok K Chaudhari[2*], Amitkumar J Patel[3], Tushar K Pathak[4] and Mahesh K Patel[3]

[1]Assistant Professor, Government Engineering College, Palanpur
[2]Assistant Professor, Government Engineering College, Patan
[3]Assistant Professor, Government Engineering College, Godhara
[4]Assistant Professor, Government Engineering College, Rajkot

***Corresponding Author:** Ashok K Chaudhari
*Email: akc12878@gmail.com

Citation: Ashok K Chaudhari, et.al (2023). "Ionization Cross Section Evaluation For Methane And Carbon Tetrafluoride Under Electron Impact Via ICSP-IC Formalism", *Educational Administration: Theory and Practice*, 29(4) 5701-5706
Doi: 10.53555/kuey.v29i4.10611

ARTICLE INFO

ABSTRACT

In this work, we present a theoretical investigation of the total ionization cross sections for methane (CH_4) and carbon tetrafluoride (CF_4) molecules due to electron impact over a wide range of incident energies, employing the Improved Complex Scattering Potential – Ionization Contribution (ICSP-IC) method. The ICSP-IC approach, a refinement of the CSP-ic model, provides a semi-empirical framework to estimate ionization cross sections by incorporating target-specific electronic excitation properties and inelastic scattering parameters.

Methane and CF_4 are important in a variety of scientific and technological contexts, including low-temperature plasma processing, semiconductor etching, atmospheric modeling, andradiation chemistry. Accurate knowledge of their ionization cross sections is crucial for modeling electron-driven processes in these environments. The calculations span from ionization threshold energies up to several keV and are benchmarked against available experimental data and other theoretical models where possible.

The results show consistent physical behavior, with good agreement in peak positions and magnitudes of ionization cross sections. The study demonstrates the utility and reliability of the ICSP-IC method in modeling electron impact ionization of small polyatomic molecules and provides a valuable **contribution to databases needed in** plasma physics, environmental studies, **and** applied molecular collision theory.

Introduction

The study of electron–molecule collisions, particularly electron impact ionization, is fundamental in understanding the microscopic processes that govern various natural and technological environments. Molecules such as methane (CH_4) and carbon tetrafluoride (CF_4) are of significant interest due to their wide-ranging applications in fields such as plasma processing, atmospheric and environmental science, and radiation chemistry.

Methane, being the simplest hydrocarbon, is a major component of natural gas and plays a key role in planetary and interstellar atmospheres [1,2]. It is also extensively used in low-temperature radio-frequency plasmas for material processing and chemical vapor deposition (CVD) [3]. On the other hand, CF_4 is widely used in semiconductor manufacturing, especially in plasma etching of silicon-based devices, as well as in insulating gas applications due to its high electronegativity and stability [4,5]. Both molecules are considered greenhouse gases, and thus, understanding their interaction with energetic electrons is crucial in modeling upper atmospheric chemistry and electron transport in gaseous media [6].

The ionization cross section, defined as the probability of ion formation due to incident electron collisions, is a key parameter in modeling electron-induced processes such as plasma kinetics, atmospheric ionization, and radiation damage. Although experimental measurements for total ionization cross sections of CH_4 and CF_4

have been reported [7–10], they often suffer from energy range limitations, measurement uncertainties, or challenges in generating controlled gas-phase targets, especially for CF_4 due to its reactivity.
To address these limitations and complement experimental efforts, various theoretical models have been developed. Among them, semi-empirical methods like the Binary-Encounter-Bethe (BEB) model [11] and complex potential scattering approaches have proven valuable. A particularly successful approach is the Complex Scattering Potential – Ionization Contribution (CSP-ic) method [12], which estimates total ionization cross sections from the inelastic component of total scattering cross sections. The Improved CSP-IC (ICSP-IC) method enhances this formalism by incorporating a physically motivated estimation of the inelastic-to-ionization ratio (R_P), using target-specific excitation energies and threshold parameters [13,14].
In this work, we apply the ICSP-IC method to compute total ionization cross sections for CH_4 and CF_4 over a wide energy range. The results are compared with available experimental data and other theoretical models for validation. Our study provides new insights into the ionization behavior of these environmentally and technologically relevant molecules and contributes to the growing database of electron impact cross sections needed for plasma modeling, atmospheric transport simulations, and radiation-matter interaction studies.
In this section we report improved calculations of total ionization cross sections, Q_{ion}, for molecules (CH_4, CF_4) on electron impact at energies from circa threshold to 2000 eV using the Improved Complex Spherical Potential – ionization contribution (ICSP-ic) method[15]. It involves the computation of ratio R_P in terms of the first electronic excitation energy (E_1), the ionization threshold (I) and energy at the peak of inelastic cross section (E_P) of the target. The computed R_P values for the present targets are listed in table 1 below.

Table 1: Properties of target along with values of R_P in the ICSP-ic method

Target	E_1 (eV)	I (eV)	E_P (eV)	R_P
CH_4	9.00	12.51	60	0.67
CF_4	12.50	16.19	125	0.75

Theoretical methodology

In the present study, we employ the Improved Complex Scattering Potential – Ionization Contribution (ICSP-IC) method to calculate the total ionization cross sections (Qion) of the O_2 and H_2O molecules due to electron impact over a broad energy range. This semi-empirical approach builds upon the foundational CSP-ic model, introducing refinements that enhance its predictive accuracy and physical grounding, particularly regarding the estimation of the key ratio parameter RP.

Complex Optical Potential Framework

The electron-molecule interaction is described within the fixed-nuclei approximation, and the system is modeled using a spherically symmetric complex optical potential (SCOP):

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

Here, the real part V_R includes:
- Static potential V_{st}, derived at the Hartree-Fock level,
- Exchange potential V_{ex}, and
- Polarization potential V_p, accounting for short-range correlation and long-range polarization effects.

The imaginary part V_I corresponds to the absorption potential V_{abs}, representing the flux loss into all inelastic channels. It is based on the non-empirical, quasi-free model proposed by Staszewska et al., and depends on target charge density, incident energy, and a threshold parameter Δ, which varies with energy to accommodate excitation at low energies and ionization at higher energies.

Calculation of Cross Sections

The Schrödinger equation is solved numerically via partial wave analysis using the Numerov method, yielding complex phase shifts for the SCOP. These are used to calculate:
- Elastic cross section $Q_{el}(E_i)$
- Inelastic cross section $Q_{inel}(E_i)$, from which the total cross section is given by:

$$Q_T(E_i) = Q_{el}(E_i) + Q_{inel}(E_i)$$

Since ionization cross section is not directly extractable, the ICSP-IC method partitions the inelastic component as:

$$Q_{inel}(E_i) = \Sigma Q_{exc}(E_i) + Q_{ion}(E_i)$$

To estimate Q_{ion}, a ratio function is defined:

$R(E_i) = Q_{ion}(Ei) / Q_{inel}(E_i) = 1 - f(U)$

$f(U) = C1 * (C2 / (U + a) + \ln(U)/U)$, where $U = Ei/I$

Parameters C1, C2, a are computed using the following boundary conditions:
- R = 0 for Ei ≤ I
- R = RP at $E_i = E_P$ (peak of Qinel)
- R → 1 as $E_i \rightarrow \infty$

For detail Theoretical Methodology you can refer [15]

Results and discussion

The computed total ionization cross sections for present targets are plotted in figures 1-2 respectively along with other experimental and theoretical results available in the literature as a function of incident energy.

CH_4 and CF_4

Tetrahedral molecules are more stable and they are important targets of great applied interests and hence are widely studied both theoretically as well as experimentally. CH_4 is extremely important prototype of hydrocarbon which finds its importance due to wide applications from chemical vapor deposition for artificial diamond production to recent developments in carbon nanotubes and nanocrystalline diamond films [16]. Moreover CH_4 is highly favored system both for theory as well as experiments due to its nearly spherical structure which attributes stability to it.

The CF_4, molecule plays an important role as a widely used component in feedstock gas mixtures that are used in both the plasma assisted etching of microelectronic structures and in the deposition of thin films. The neutral and ionic fragments of CF_4, generated in the low temperature plasma by low energy electron impact, play an important role in dry plasma etching of silicon and silicon compounds. To understand and model the plasma etching process using CF_4, one needs to know all types of electron impact cross sections [17].

Due to the technological interest of CH_4 and CF_4 molecules and the research on its chemistry in plasmas, they are widely studied experimentally [18,19,20-23]. Kim *et al* [24] have studied total ionization cross sections for both the targets (CH_4 and CF_4) using BEB method. The recommended data of Christophorou and Olthoff [25] are also available in the literature for CF_4 molecule on electron impact ionization. Again the calculated total cross sections on electron impact ionization for CH_4 and CF_4 are the updates of our previous results [26,27]. Electron impact total ionization cross sections for CH_4 and CF_4 molecules using ICSP-ic method are tabulated in table 2and also plotted in figures 1 & 2 with other experimental and theoretical investigations.

Table 2: Total ionization cross sections, Q_{ion} (Å²) for CH_4 and CF_4.

E_i (eV)	CH_4	CF_4
15	0.11	---
20	0.78	0.19
30	2.00	1.20
40	2.85	2.31
50	3.29	3.23
60	3.53	3.93
70	3.63	4.50
80	3.66	4.90
90	3.65	5.18
100	3.61	5.34
200	2.83	5.24
300	2.28	4.49
400	1.91	3.89
500	1.65	3.45
600	1.45	3.08
700	1.29	2.83
800	1.17	2.58
900	1.06	2.38
1000	0.96	2.22
2000	0.43	1.20

In figure 1 we have compared our newly computed total ionization cross sections for e – CH_4, scattering with available data for incident energies ranging from ionization threshold to 2 keV. In case of e - CH_4 scattering the present results are same as earlier results done using CSP-ic method at low and high energies but are lower at peak value compared to earlier data [27]. Due to this lowering of data they compare very well with experimental values of Chatham *et al* [19] and become closer to the theoretical values of Kim *et al* [24]

throughout the energy range. The experimental values of Nishimura and Tawara [21] also compares well except at peak where present results are slightly lower than their data [21]. The peak for all the reported data is around 80 eV.

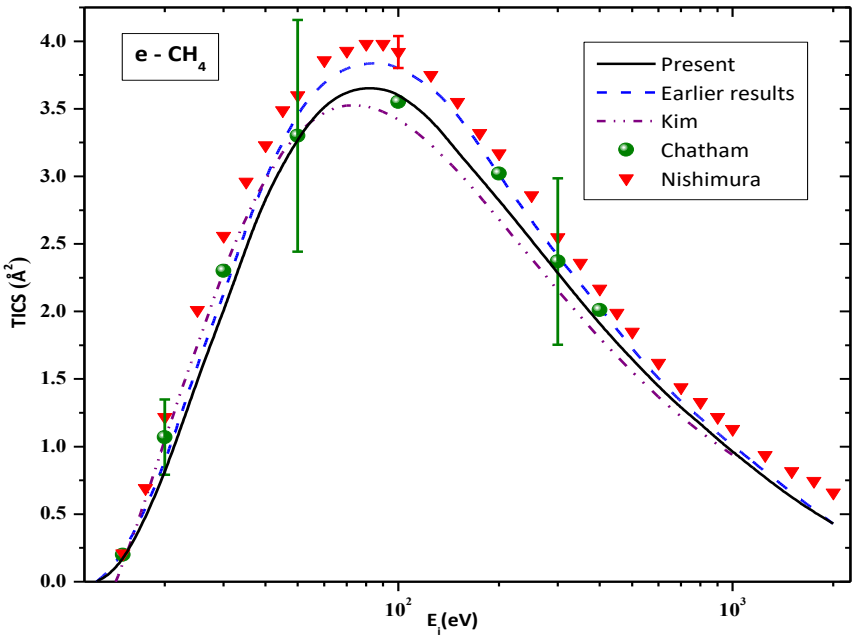

Figure 1 Total ionization cross sections, Q_{ion}, for e – CH_4 scattering in Å².

Solid line → Present results with new CSP-ic method; Dashed line → Earlier results with old CSP – ic method [27]; Dashed dot dot line → Kim *et al* [24]; Filled circles → Chatham *et al* [19]; Filled down triangles → Nishimura and Tawara [21].

In figure 2 we have shown the comparison of ionization cross sections for e – CF_4 scattering and the results have improved and they compare better with experimental data of Nishimura *et al*[18] and theoretical data of Kim *et al*[24] throughout the range. Experimental data of Basner *et al* [22] are in very good agreement at low and high energies but are slightly higher near the peak. The experimental data of Ce Ma *et al*[20] have higher errors of 15% and are lower than all reported values particularly at the peak, but all data are within their experimental uncertainty. However, At lower and higher energies Ce Ma *et al*[20] agree well with all reported values. The experimental data of Poll *et al*[23] are little higher throughout the specified range. Present data matches well with the recommended data of Christophorou and Olthoff [25] at entire energy range.

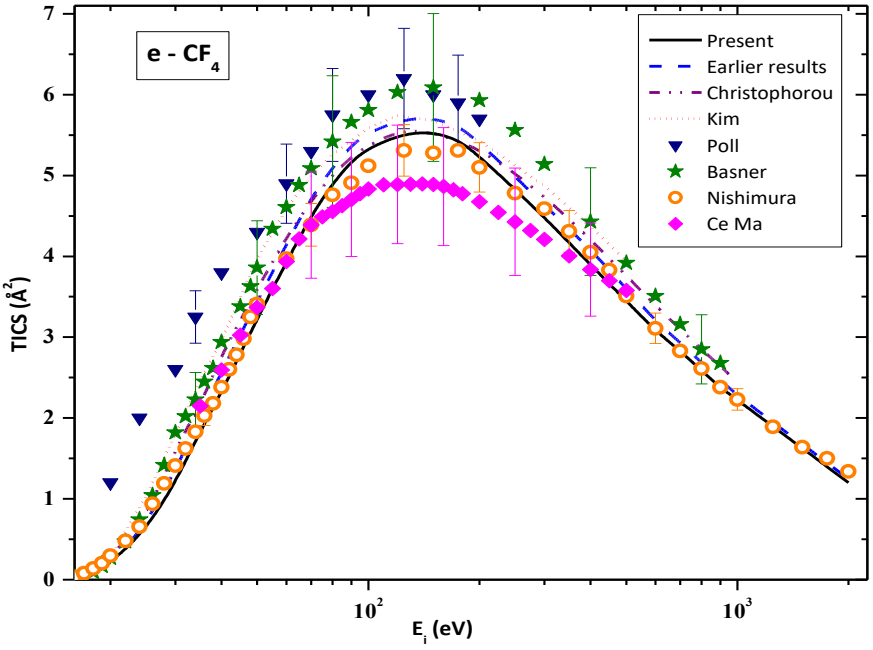

Figure2 Total ionization cross sections, Q_{ion}, for e – CF_4 scattering in Å².

Solid line → present results with new CSP-ic method; Dashed line → Earlier results with old CSP – ic method [26]; Dashed dot dot line → Christophorou and Olthoff [25]; Dotted line → Kim *et al* [24]; Solid down triangles → Poll *et al* [23]; Stars → Basner *et al* [22]; Open circles → Nishimura *et al* [18]; Solid squares → Ce Ma *et al* [20].

Making the general comparison of CH_4 and CF_4 molecules we find that the peak of the ionization cross section drifts to higher energy with increase in ionization threshold of the target. For instance, the peak of the ionization cross section occurs at 80 eV for CH_4 whose ionization threshold is 12.51 eV. And in the case of CF_4, the ionization threshold is 16.99 eV and there is noticeable shift towards right with the peak value around 150 eV. For CF_4 molecule the maximum value of the cross section is around 5.54 $Å^2$ and for CH_4 which is 3.66 $Å^2$ as it is comparatively smaller molecule compared to CF_4 molecule.

Conclusion

In this study, we have employed the Improved Complex Scattering Potential – Ionization Contribution (ICSP-IC) method to compute total ionization cross sections for methane (CH_4) and carbon tetrafluoride (CF_4) under electron impact over a wide energy range. This approach, which refines the conventional CSP-ic method by incorporating target-specific excitation and threshold energies, offers a semi-empirical but physically grounded framework for estimating ionization cross sections.

The ionization cross sections obtained for both CH_4 and CF_4 exhibit expected behavior with respect to incident electron energy, including the onset at ionization threshold, a well-defined peak, and a gradual decrease at higher energies. The results are in good agreement with available experimental data and other theoretical models, validating the applicability and reliability of the ICSP-IC method for small polyatomic molecules.

Given the technological and environmental importance of CH_4 and CF_4—ranging from plasma processing and semiconductor etching to atmospheric modeling and greenhouse gas assessment—the cross section data presented here are valuable for modeling electron-driven processes in various physical and chemical environments.

This work demonstrates the capability of the ICSP-IC method to generate accurate ionization data with minimal computational input and suggests its further use for more complex molecular systems, including fluorinated hydrocarbons, radicals, and biologically relevant molecules. Future extensions of this method may include partial and differential ionization cross sections or integration into plasma and radiation transport simulations.

Acknowledgement

Kirti Korot, Ashok Chaudhari, Harshad bhutadia, Tushar Pathak, Amit Patel and Mahesh patel are thankful to government of Gujarat for motivating and providing facility to carry out research work

References;

1. H. Bethe, “Ionization cross sections by electrons and protons,” *Rev. Mod. Phys.*, **22**, 203 (1950).
2. M.J. Brunger and S.J. Buckman, “Electron-molecule scattering cross sections I: Experimental,” *Phys. Rep.*, **357**, 215–458 (2002).
3. M. Capitelli et al., *Plasma Kinetics in Atmospheric Gases*, Springer (2000).
4. L.J. Overzet et al., “Plasma etching using CF4: A review,” *J. Vac. Sci. Technol. A*, **8**, 3125–3134 (1990).
5. M. Kimura and N. Kobayashi, “Electron impact ionization of fluorinated molecules,” *Int. J. Mass Spectrom.*, **205**, 165–180 (2001).
6. E.C. Zipf, “Ionization of atmospheric constituents by energetic electrons,” *Planet. Space Sci.*, **33**, 1303 (1985).
7. D. Rapp and P. Englander-Golden, “Total cross sections for ionization and attachment in gases by electron impact,” *J. Chem. Phys.*, **43**, 1464 (1965).
8. T.D. Märk et al., “Mass spectrometric determination of partial and total electron impact ionization cross sections,” *Int. J. Mass Spectrom.*, **47**, 161 (1983).
9. M.E. Rudd et al., “Cross sections for ionization of gases by electron impact,” *Phys. Rev. A*, **38**, 6129 (1988).
10. Y.-K. Kim and M.E. Rudd, “Binary-encounter-dipole model for electron-impact ionization,” *Phys. Rev. A*, **50**, 3954 (1994).
11. I. Bray and D.V. Fursa, “Convergent close-coupling calculations of electron scattering on molecules,” *Phys. Rev. A*, **54**, 2991 (1996).
12. M. Vinodkumar et al., “CSP-ic method for calculating total ionization cross sections,” *Eur. Phys. J. D*, **59**, 379–387 (2010).
13. K.N. Joshipura et al., “Theoretical evaluation of ionization cross sections using complex potential methods,” *J. Phys. B*, **35**, 4211 (2002).

14. M. Vinodkumar, C. Limbachiya, K. Korot, "Improved ICSP-IC method for electron impact ionization," *Int. J. Mass Spectrom.*, **273**, 145 (2008).
15. M. Vinodkumar, K. Korot, and P.C. Vinodkumar Eur. Phys. J. D 59, 379–387 (2010)
16. C. Makochekanwa, K. Oguri, R. Suzuki, T. Ishihara, M. Hoshino, M. Kimura and H. Tanaka, Phys. Rev. A **74** (2006) 042704.
17.Ce Ma, M. R. Bruce and R. A. Bonham, Phys. Rev. A **44** (1991) 2921.
18. H. Nishimura, W. M. Huo, M. A. Ali and Y.-K. Kim, J. Chem. Phys. **110** (1999) 3811.
19. H. Chatham, D. Hils, R. Robertson, A. Gallagher, J. Chem. Phys. **81** (1984) 1770.
20.Ce Ma, M. R. Bruce and R. A. Bonham, Phys. Rev. A **44** (1991) 2921.
21. H. Nishimura and H. Tawara, J. Phys. B **27** (1994) 2063.
22. R. Basner, M. Schmidt, E. Denisov, P. Lopata, K. Becker and H. Deutsch, Int. J. Mass Spectrom. **214** (2002) 365.
23. H. U. Poll, C. Winkler, D. Margreiter, V. Grill and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. **112** (1992) 1.
24. Y. –K. Kim:http://physics.nist.gov/PhysRefData/Ionization/EII table.html
25.L. G. Christophorou and J. K. Olthoff, J. Phys. Chem. Ref. Data **28** (1999) 967.
26. K. N. Joshipura, M. Vinodkumar, C. Limbachiya and B. K. Antony, Phys. Rev. A **69** (2004) 022705.
27.M. Vinodkumar, K. N. Joshipura, C. G. Limbachiya and B. K. Antony, Eur. Phys. J. D **37** (2006) 67.