Partial Ionization Cross Sections for SiF_4 by Electron Impact

Satyndra Pal

Abstract— **The present work reports the calculations for differential cross sections as a function of secondary and or ejected electron energy in the ionization of SiF_4 by electron collision corresponding mto the production of various cations viz. singly charged ions SiF_n^+ (n=0-4) and F^+ and doubly charged ions SiF_3^{+2} and SiF_2^{+2} through direct and dissociative ionization processes at a fixed incident electron energy of 200 eV. The modified Jain-Khare semi-empirical formalism based on oscillator strength has been employed for evaluation of cross sections. In absence of the experimental and/ or theoretical data for comparison of the differential cross sections, the corresponding derived partial integral cross sections in terms of the partial ionization cross sections for these cations in the energy range varying from ionization threshold to 1000 eV, revealed a reasonably good agreement with the available data. In addition to the differential and integral ionization cross sections, we have also calculated the ionization rate coefficients using the evaluated partial ionization cross sections and the Maxwell-Boltzmann distribution as a function of electron energy.**

Index Terms— **silicon tetra fluoride, partial cross sections, electron impact, rate coefficients**

I. INTRODUCTION

Silicon tetra fluoride (SiF_4) and free radicals SiF_n (n = 1 – 3) are widely used in plasma, plasma-assisted etching and deposition of silicon layers in the fabrication of microelectronic components and other high technological devices [1]. The highly reactive fluorine atoms and ions present in the etching plasma interact with the surface and produce the volatile products such as SiF_4 and SiF_2 which are further diffused back into the plasma where they are dissociated and ionized by the plasma electrons and the resultant fragments are transported and re-deposited on the silicon surface [2-4]. Along with SF_6, SiF_4 belongs to an important group of popular model compounds useful for studying the so-called ''caged'' effects, particularly, related to the continuum or shape resonances. The valence and Si 2*p* inner-shell electronic structures of SiF_4 have been studied extensively by a variety of techniques including photo absorption and photo ionization studies of Silicon tetra fluoride (SiF_4) and SiF_n (n = 1 – 3) free radicals by Brion et al. [5-6] and Leung et al. [7]. The experimental determination of integral partial and total electron ionization cross sections include those of Poll and Meichsner et al. [8], especially, for SiF_3^+ following the electron impact ionization of SiF_4. Nakano and Sugai [9] used the same results for the calibration of their measured relative ionization curves to give absolute partial ionization cross sections of the SiF_4^+, SiF_2^+, and SiF^+ ions in the energy range from threshold to 60 eV. Basner et al. [10] measured the absolute partial and total electron impact ionization cross sections of SiF_4, including all singly charged positive ions SiF_n^+ (*n*=1–4), Si^+, F^+, and the doubly charged ions SiF_n^{++} (*n*=1 – 3), and Si^{++}. The total ionization cross section was also obtained as the weight sum of the partial ionization cross sections.The transient radicals, due to their high reactivity possess difficulties in the measurement of cross sections, hence some alternative approach through theoretical models are needed besides the experimental results. On the theoretical side, calculations for SiF_4 are particularly challenging. The rigorous quantum mechanical approach for the calculations of molecules is limited to the application of simple molecules. Contrary to it, there exist the binary encounter Bethe formalism by Kim et al. [11], the semi-empirical formalism by Khare et al. [12], DM-formalism by Deutsch et al. [13] and complex potential model calculations by Joshipura et al. [14].

In this brief report, the spectrum of the single differential cross sections with the energy of secondary and/or ejected electron(s) in the ionization of SiF_4 molecule by electron collision at fixed incident electron energy of 200eV, employing a semi-empirical formalism based on Jain-Khare approach [15-16] is presented. At this fixed incident electron energy, the total double differential cross sections as a function of angle and secondary/ ejected electron(s) energy have also been calculated. In absence of data for comparison of our calculated differential cross sections, the corresponding derived integral cross sections (or the partial ionization cross sections) leading to the formation of various singly charged ions SiF_n^+ (n = 0–4) and F^+ and doubly charged ions $SiF_3^{+2}$and SiF_2^{+2} through direct and dissociative ionization of SiF_4 by electron collision are compared with the available experimental and theoretical data.

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II. THEORETICAL

The present calculations are carried out using the modified semi-empirical Jain-Khare formalism [12] (for instant: see our previous publications [15-16] and references therein). In brief, the single differential cross sections in the complete solid angle Ω as a function of secondary electron energy corresponding to the production of i^{th} type of ion in the ionization of a molecule by the incident of electron of energy *E* is given elsewhere [16]. The present formulation is based on the dipole oscillator strength df_i/dW, the key parameter which is directly proportional to the photo ionization cross section [5]. We have used partial photo ionization cross section data set in the energy range from 10 to 100 eV provided by Brion et al. [5] within ±5% uncertainty. In the photon energy range 100–350 eV, we have used their measured total valence photo absorption oscillator strength data [6] and for higher photon energy range *W* >350 eV, the same were extrapolated by Thomas-Reiche-Kuhn (TRK) sum rule (within ±10% error bars) [5-6]. The total photo absorption cross sections have been distributed into ionic fragments considering the constant ionization efficiency to be 1.0 above the dipole breakdown limit of ~20.5eV. However, its evaluation is possible quantum mechanically using the suitable wave functions and transition probabilities corresponding to the production of cations. The collision parameter C_i (=0.0559/eV) and energy parameter ε_0 (=50 eV) are evaluated as for other polyatomic molecules [15,16,19]. The vertical onsets or the ionization potentials corresponding to the various cations are also given along with the photo ionization measurements [5-6]. In the present evaluations of cross sections, the estimated uncertainty is more or less the same as for the measurement of photo ionization cross sections.

The partial ionization cross section is obtained by the integration of the energy dependent single differential cross section over the entire energy loss W (sum of the vertical onsets and the ejected/ secondary electron energy).

III. RESULTS AND DISCUSSIONS

The ground state electronic structure ($^1A_1$) of SiF_4 may be written as:

Core orbitals $\underbrace{(1a_1)^2}_{Si\ 1s}\ \underbrace{(1t_2)^6(2a_1)^2}_{F\ 1s}\ \underbrace{(3a_1)^2}_{Si\ 2s}\ \underbrace{(2t_2)^6}_{Si\ 2p}$

Valence orbitals $\underbrace{(4a_1)^2(3t_2)^6}_{Inner\ Valence}\ \underbrace{(5a_1)^2(4t_2)^6(1e)^4(5t_2)^6(1t_2)^6}_{Outer\ Valence}$

Unoccupied virtual valence orbitals $(6a_1)^0(6t_2)^0(2e)^0(7t_2)^0$

The outer valence ionization energies of SiF_4, 16.4 eV ($1t_1$), 17.5eV ($5t_2$), 18.1 eV (*le*), 19.5eV ($4t_2$) and 21.5eV ($5a_1$) were measured by using synchrotron radiation [20] and these measurements together with measured and calculated photo-electron branching ratio [21] confirm the orbital ordering to be as stated above. The inner-valence region has been studied by electron momentum spectroscopy (EMS) [22] and also by x-ray photoelectron spectroscopy (XPS) [23]. The EMS measurement of momentum distributions and binding energies and also Green's function calculations [23] indicate that the inner valence ionization spectrum is severely splatted by many-body (i.e., electron correlation) effects into numerous intermingled lines belonging to the $4a_1^{-1}$ and $3t_2^{-1}$ manifolds. This prevents any simple molecular orbital description or assignment of the

structure observed in the inner valence binding energy spectrum and thus of any single value for either inner valence ionization energy. The numerous poles or inner valence ionization energies are mainly dispersed into many lines over the energy range 40-49 eV [23].

The differential cross sections as function of energy corresponding to the formation of various cations in electron-SF_4 collision as a function of secondary electron energy in terms of energy loss W at fixed incident electron energy of 200 eV is presented in Fig. 1. More qualitative result is also presented in the Platzman plot of $Y(W)$. The $Y(W)$ parameter is the ratio of the calculated differential cross section and the Rutherford cross section with energy loss W in the dipole energy range. Qualitatively, $Y(W)$ corresponds to the effective number of electrons participating in ionizing collisions [20]. To the best of our knowledge, no experimental data is available to compare the present results for differential cross sections. However, the qualitative behaviour of the cross section is the same as for other molecules investigated [15-16, 19]. The energy dependent cross sections are symmetric at $W/2$ where the energies of primary and the secondary electrons are almost equal. The fig. 1 clearly shows the weight contribution of the molecular and atomic cations. The cross sections for molecular ions are much larger than the atomic ions. The atomic photoionization cross sections include the contribution of the structures and many body states produced near onsets which are speculated in the present calculations for the energy dependent differential cross sections [5-6]. Because of the lack of experimental data for differential cross sections, the corresponding derived partial cross sections and their sum (the total ionization cross sections) from ionization threshold to 1000 eV becomes important.

In Fig. 2, we have presented the comparison of our partial and total ionization cross sections with the experimental data sets [8-10]. It is noted that for the SiF_4^+ ion, our results are in good agreement with the available experimental data [9-10] except the peak value i.e. between 60 to 200 eV. In this energy range, this ion tends to further dissociation into other minor and doubly charged ions. The present calculations are based on the photo ionization cross sections that did not include the auto ionization. Hence our results overestimate to the experimental data. For SiF_3^+ ion, our results are in agreement with the experimental data [8-10] within their composite error bars. The formation of SiF_3^+ ion from SiF_4 is the dominant ionization process which exhibits a maximum around 120 eV and corresponds to about 82% of the total ionization cross section at this incident electron energy. The dominance of SiF_3^+ partial ionization cross section becomes even more dominant in the low energy region, which is of special interest for low-temperature plasma technology. In case of SiF_2^+, SiF^+ and SiF_3^{+2} ions, our results underestimate by almost half to the experimental data which may be due to the excess kinetic energy of these fragment ions that may affect the measurements [10]. Experimentally, it is difficult to collect the minor ions with low kinetic energies For ions such as SiF_2^{+2} , Si^+, SiF^{+2}, F^+ and Si^{+2} ions, our results show a considerable agreement with the only available experimental data of Basner et al. within experimental uncertainty. Nevertheless, considering that this is a comparison with the absolute data where error bars of these sets of data are easily in the range of 15% to 20% [9-10] regime, in particular taking into account that the calculations are depending on the accuracy of the experimental input parameters, the agreement is acceptable. Fig.2 also shows a good agreement of the partial cross sections when added up to a total cross section with the only available experimental data [10] and the theoretical cross section data sets [11,14] in the complete energy range covered in the calculations.

The present calculations for partial and total ionization cross sections satisfy the necessary consistency checks to access their consistency and reliability. The consistency checks are derived from the fact that the total electron impact ionization cross section (i) is equal to the charged-weighted sum of the partial ionization cross sections and (ii) may be obtained by integration of the differential cross sections over secondary electron energies and angles. The former condition is used in the summation method for calibration purposes and the later fact in the use of Platzman plots. Both relationships allow one to check the reliability of the absolute magnitude and the energy dependence of ionization cross sections under consideration. In the low-energy limit close to the onset of ionization, the shapes of the partial and total electron impact ionization cross section curves are governed by a threshold law, which is usually expressed in the form of $Q(E) \sim (E - I_i)^Z$, where Z is the charge state of the ion. The precise shape of the cross section in this region is especially important in determination (by extrapolation) of respective ionization thresholds, to compare with those derived by other means [24-25].

The semi-empirical formalism based on the Jain-Khare approach has been employed in the present calculations for differential cross sections as a function of secondary electron energy and angle at fixed impinging electron energy, corresponding to the formation of various singly and doubly charged ions through direct and dissociative ionization of the SiF_4 molecule. The corresponding derived partial and total ionization cross sections revealed a satisfactory qualitative and quantitative agreement with available experimental and theoretical data sets. The present evaluations for electron ionization cross sections and rate coefficients are indispensable for a microscopic understanding and a detailed modelling of the plasma chemical processes in SiF_4-containing plasmas and in other plasmas containing F-bearing molecules in the feed gas mixtures that are used to etch Si and SiO_2. Undoubtedly the present calculations may fill the void in the experimental and theoretical findings with quantitative ambiguity for such plasma processing molecule.

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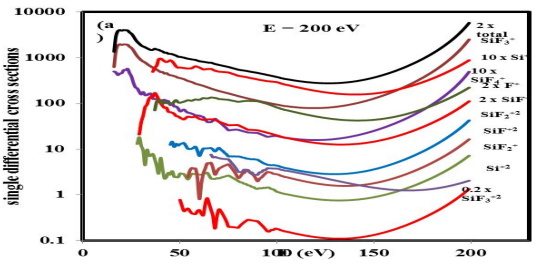


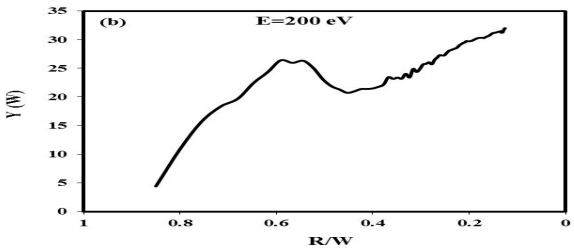
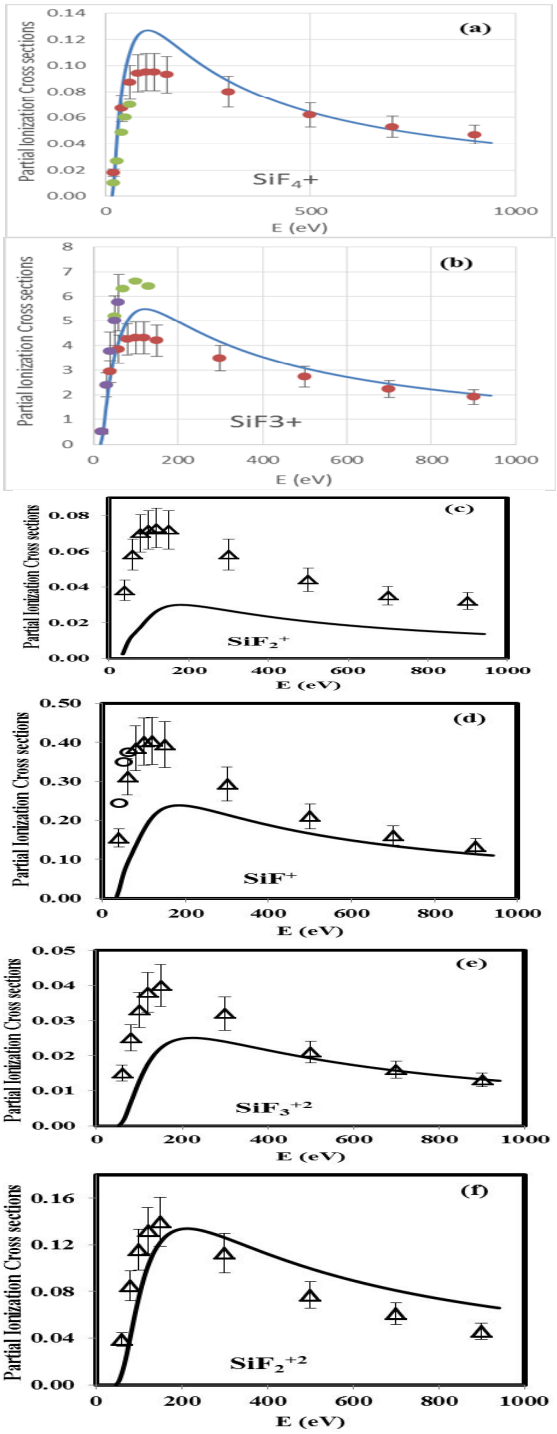


Figure 1 – (a) The single differential cross sections (in the units of 10^{-20} cm^2/eV) as a function of energy loss W for the production of cations from electron impact ionization of SiF_4 at constant electron impact energy of 200 eV (b) The calculated ratio of cross sections in Platzman plot *Y*(*W*) in half energy range at 200 eV which resembles the photoionization cross sections as employed in the input.



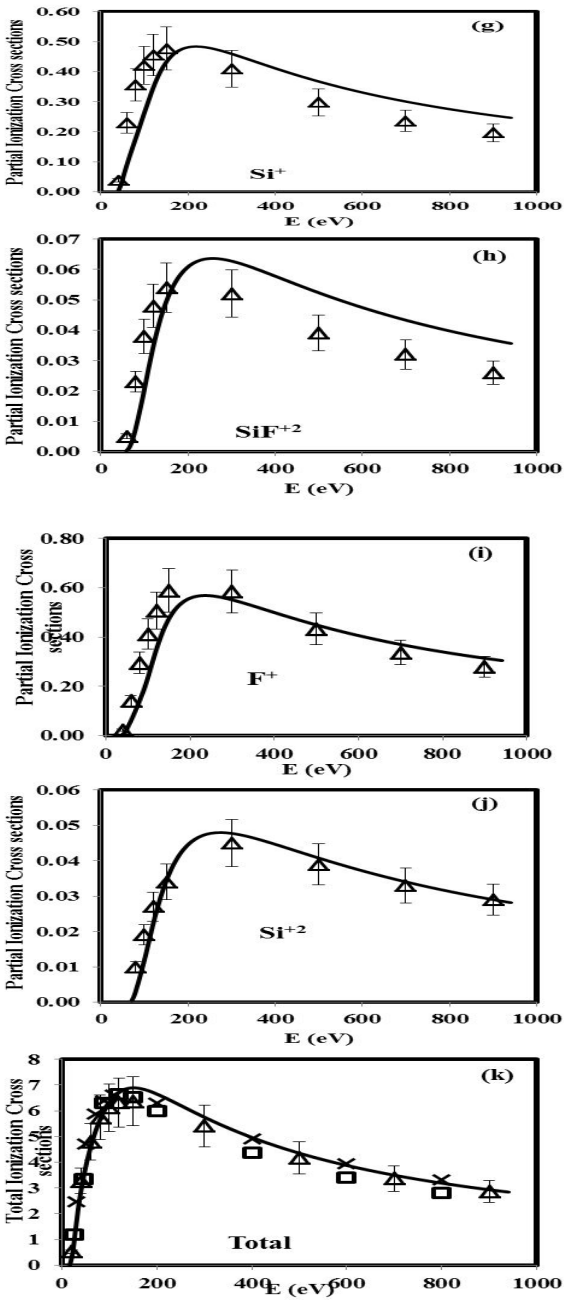


Figure 2 – Partial and total ionization cross sections (in the units of $10^{-16}cm^2$) for electron impact ionization of SiF_4 (designated by solid line) in comparison with the various experimental data sets designated by: + - Poll and Meichsner [8], o - Nakano and Sugai [9] and ⍰- Basner et al.[10] with error bars and theoretical data sets by □ - Kim et al.[11] and ×- Joshipura et al. [14].