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## MODELLING ELECTRON INTERACTIONS: A SEMI-RIGOROUS METHOD

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We report total electron scattering cross sections (TCS) for SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub>, and CF<sub>3</sub>I, molecules of interest to the plasma industry over the energy range from threshold to 2000 eV. We also report the total scattering cross sections for e-formaldehyde for which there are currently no theoretical or experimental results reported. The ionization cross sections for these targets are also estimated using the Deutsch and Maerk formalism and are compared with Binary Encounter Bethe (BEB) data of Kim.

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## 1 Introduction

Total electron scattering cross sections for molecules are essential for the study of electron transport properties in gases. They define the mean free path of electrons in the medium and, since they are the sum of all the possible collision processes, they constitute a valuable set of reference data. In recent years considerable effort has been made to obtain accurate values for such cross sections due to their use in many physico-chemical models of both natural and industrial processes (e.g. atmospheric auroral emissions and plasma discharges). The development of the next generation of micro- and nano-systems technologies (MST) remains essential to the commercial success of the global information technology industry. MST devices are silicon based and incorporate features that cover a range of scales from fractions of a millimetre down to a few nanometers, the latter being one of the first examples of exploitation of nanotechnology by modern industry. Tailoring processes for plasma etching of silicon is therefore of particular importance for a wide variety of MST demands. Key developments include the production and control of reactive intermediates, and the robust and reliable control of atomic-order surface adsorption, surface diffusion and surface reactions in plasma etching processes.

Development of plasma processing methodology can only occur through a thorough understanding of the properties of such plasmas. However many plasma processes are currently used by

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industry without a complete understanding of the chemical and physical properties of the plasma involved, thus they are non predictive and hence it is not possible to alter the manufacturing process without the risk of considerable product loss. A clear research imperative in the next decade will therefore be to increase our knowledge of the chemical and physical properties in such plasmas. A comprehensive understanding of such processes will allow models of such plasmas to be constructed that may be used to design the next generation of plasma reactors, i.e. reactors that will: (i) allow site specific control of surface reactivity and (ii) be more efficient in the use of materials.

The most fundamental interaction in any plasma is the interaction of electrons with the feed gases since this determines the ion density and reactivity of the plasma. Signing of the Kyoto protocol [1, 2] on gas emissions requires the phasing out of many current feed gases being used by the semiconductor industry e.g.  $\text{SF}_6$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{CHF}_3$ , and  $\text{c-C}_4\text{F}_8$  since these species have high global warming potentials (GWP). The need to provide a database for plausible alternative feed gases e.g.  $\text{CF}_3\text{I}$  and  $\text{C}_2\text{F}_4$  and the need to model electron interactions with reactive species produced in the plasma has therefore been highlighted by the industry. Since it is not feasible to measure all the relevant cross sections within a timescale compatible with industrial reactor development much of the data must be compiled by theoretical models of electron molecule interactions. Once again traditional theoretical methods are not only time consuming but limited to simple targets. Hence the desire to develop simpler semi-rigorous methods capable of providing estimates of TCS/reaction rates with an accuracy acceptable for the industrial plasma models. We are developing a simple hybrid theory Modified Single Centre Additivity Rule MSCAR [3, 4] to calculate electron impact scattering cross sections from different atomic and molecular species. Our calculation is carried out using a complex optical potential comprising of model potential terms to derive TCS [3, 4]. In this paper we illustrate the results of our semi-rigorous method with four targets  $\text{SF}_6$ ,  $\text{SF}_5\text{CF}_3$ ,  $\text{CF}_3\text{I}$  and  $\text{H}_2\text{CO}$ .

Fluorine containing species have been extensively studied in recent years because of their use as feed gases in plasma etching reactors for silicon treatment and their role in the photochemistry of the atmosphere, mainly as ozone depleting molecules.  $\text{SF}_6$  is of particular technical interest because of its insulating properties, being commonly used in high voltage lines and particle accelerators.  $\text{SF}_5\text{CF}_3$  has only recently been detected in the terrestrial atmosphere [5] and was swiftly identified as a potent greenhouse gas with an annual growth rate of 6% per annum. It has the highest radiative forcing on a per molecule basis of any atmospheric pollutant [5, 6]. However its origins are still unclear but it is believed to be purely anthropogenic in origin, probably being related to the plasma technology industry and gas dielectrics being linked to the  $\text{SF}_6$  cycle, a relationship which is sustained by its annual growth rate tending to follow very closely that of  $\text{SF}_6$ .

$\text{CF}_3\text{I}$  has been suggested as a replacement for  $\text{SF}_6$  and  $\text{CF}_4$  in plasma reactors. Formaldehyde ( $\text{H}_2\text{CO}$ ) is commonly used as an industrial fungicide, germicide and disinfectant. As its use has increased it has become a common atmospheric pollutant. However since it is a suspected carcinogen linked to nasal and lung cancer it must be destroyed after the use in the industrial process. Plasma discharges are commonly used to destroy formaldehyde in flu gas.

In this work we have calculated the electron impact total cross sections  $Q_T$  and total inelastic cross sections  $Q_{inel}$  for  $\text{SF}_6$ ,  $\text{SF}_5\text{CF}_3$ ,  $\text{CF}_3\text{I}$  and  $\text{H}_2\text{CO}$  at incident energies  $E_i$  from close to the threshold of electronic excitation to 2000 eV. Excitations to discrete states and to the continuum

include both direct and dissociative processes induced by electrons. Usually measurements of total cross sections (TCS) for individual processes or for the total transmission are carried out in different energy ranges by different groups/laboratories in their own experimental set-ups. The sum-total of the different experimental TCSs does not always agree well with the observed total cross section of a target [7]. One needs therefore, a suitable theory to examine the relative contributions of different TCSs to total (complete) cross section  $Q_T$  and to see their trends with respect to impact energy. Thus our aim in this paper is to calculate various TCSs of electron collisions and to investigate their relative contributions to the total cross sections for the chosen targets.

## 2 Theoretical Methodology

The usual complex potential calculation for electron scattering can provide the total elastic cross section  $Q_{el}$  and total inelastic cross section  $Q_{inel}$ , such that,

$$Q_T(E_i) = Q_{el}(E_i) + Q_{inel}(E_i). \quad (1)$$

In eq. (1), the total inelastic cross section  $Q_{inel}$  can be partitioned into two main contributions viz.,

$$Q_{inel}(E_i) = \sum Q_{exc}(E_i) + Q_{ion}(E_i), \quad (2)$$

where the first term  $\sum Q_{exc}$  is the sum over total excitation cross sections for all accessible electronic transitions. The second term  $Q_{ion}$  is the total cross section of all allowed ionization processes induced by the incident electrons. The first term arises mainly from the low-lying dipole allowed transitions for which the cross section decreases rapidly at higher energies. Our calculation of all these TCSs is based on a complex scattering potential, generated from spherically averaged charge densities of the target molecules [8–14]. The single-centre molecular charge density is obtained by a linear combination of constituent atomic charge densities, renormalized to account for covalent molecular bonding, as discussed in our earlier calculations [8]. Briefly, the charge density  $\rho(r)$  of a molecule  $XY_6$  is expressed in terms of the atomic charge densities  $\rho_x$  and  $\rho_y$  as a function of distance  $r$  from the molecular centre of mass, as follows,

$$\rho(r; R) = f_x \cdot \rho_x(r) + 6 \cdot f_y \cdot \rho_y(r; R). \quad (3)$$

Here,  $\rho_x$  is the charge density of the central atom X, and  $\rho_y$  is that of the atom Y expressed as a function of distance from the centre of atom  $r$  and the bond length  $R$ . The modulating factors  $f_x$  and  $f_y$  arise from the partial charge migration in the covalent bonding as explained in [8]. The molecular charge density  $\rho(r)$  is employed to construct a complex potential  $V_{opt} = V_R + iV_I$ , that contains a real part  $V_R$  comprising static ( $V_{st}$ ), exchange ( $V_{ex}$ ) and polarization ( $V_p$ ) terms, as follows,

$$V_R = V_{st} + V_{ex}(r; E_i) + V_p(r; E_i). \quad (4)$$

The imaginary part  $V_I$ , also called the absorption potential  $V_{abs}$ , accounts for the total loss of scattered flux into all the allowed channels of electronic excitation and ionization. A currently

popular model form for  $V_{abs}$  is that of Staszewska et al [15], who had developed a quasi-free, Pauli-blocking, dynamic absorption potential given in au, as

$$V_{abs} = -1/2 \cdot \rho(r) \cdot v_{loc} \cdot \sigma_{ee} \quad (5)$$

$$= -\rho(r) \left[ \sqrt{\frac{T_{loc}}{2}} \left( \frac{8\pi}{10k_F^3 E_i} \right) \theta(p^2 - k_F^2 - 2\Delta) \cdot (A_1 + A_2 + A_3) \right]. \quad (6)$$

In these expressions,  $v_{loc}$  is the local speed of the external electron, and denotes the average total cross section of the binary collision of the external electron with a target electron. The local kinetic energy of the incident electron is obtained from

$$T_{loc} = E_i - V_R = E_i - (V_{st} + V_{ex} + V_p). \quad (7)$$

For a given energy, the dominant term in eq. (7) is  $V_{st}$ . Further  $p^2 = 2E_i$  in atomic units, au,  $k_F = [3\pi^2 \rho(r)]^{\frac{1}{3}}$  is the Fermi wave vector and  $\Delta$  is an energy parameter. In eq. (5),  $\theta(x)$  is the Heaviside unit step-function, such that  $\theta(x) = 1$  for  $x > 0$  and is zero otherwise. The dynamic functions  $A_1$ ,  $A_2$  and  $A_3$  as defined in [15] depend differently on the molecular properties  $\rho$ ,  $\Delta$  and  $E_i$ . The absorption potential is further modified by incorporating the screening of the inner electrons by the outer ones, and consequently correcting the absorption potential [16]. This method is termed as Modified Single Centre - Additivity Rule (MSC-AR) [17]. The Schrodinger equation when solved numerically for  $V_{abs}$ , yields the imaginary part of the phase shifts  $\text{Im } \delta_l(k)$  for various partial waves  $l$ . We omit here the standard formulae used [18] to generate  $Q_{inel}$  as well as the  $Q_{el}$  by employing the real and the imaginary parts of total phase shift  $\delta_l(k)$ . The total (complete) cross section  $Q_T$  is obtained from eq.(1). The DM formalism was introduced by Deustch and Maerk [19] originally for the calculation of atomic ionization cross sections and subsequently was modified for the molecules. The semi - classical formula used for the atoms is given by [19],

$$\sigma = \sum_{n,l} 4\pi [\gamma_{nl}]^2 \xi_n \left[ \frac{R}{E_{nl}} \right]^2 f(U), \quad (8)$$

where  $\xi_n$  is the number of electrons in the  $n^{th}$  atomic subshell,  $\gamma_{nl}$  is the mean square radius of the (n,l) subshell and  $E_{nl}$  refers to the ionization energy in the  $n^{th}$  subshell, and  $f(U)$  is the energy-dependent function, where  $U$  is the reduced energy given by  $U = \frac{E_i}{E_{nl}}$  where  $E_i$  is the energy of the incident electron. The straightforward extension of the DM formula of eq.(7) to molecular target [20] results in an equation of the form

$$\sigma = \sum_j g_j \pi [\gamma_j]^2 \xi_j f^*(U), \quad (9)$$

where summation is now carried out over the molecular orbitals 'j',  $g_j$  are the new set of weighing factors for the molecules,  $r_j$  is the mean square radius for different molecular orbitals and  $f^*(U)$  is the new energy dependent function for molecules depending on the characters of the molecular electrons.

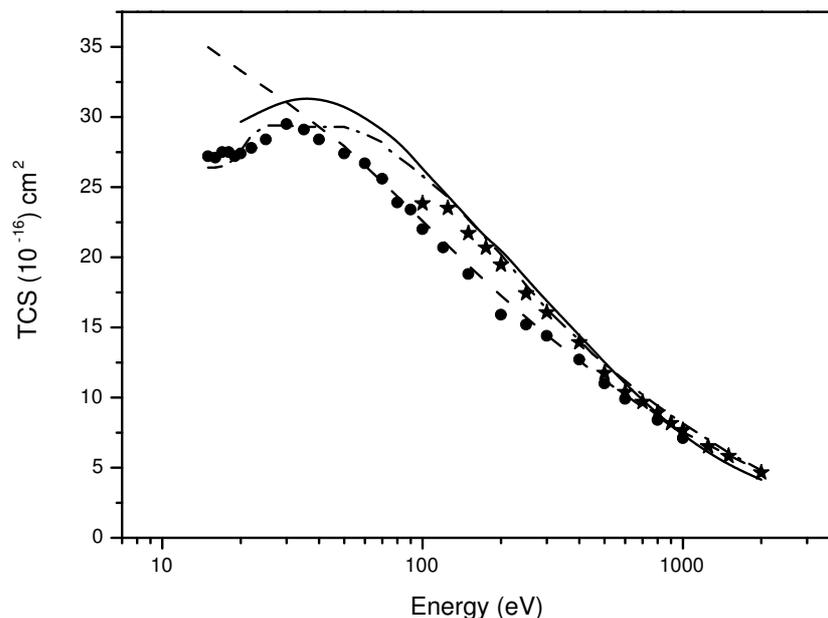


Fig. 1. Total Scattering cross sections for e-SF<sub>6</sub> scattering.  $Q_T \rightarrow$  solid curve (present work), star (in Ref. [17]), dash (in Ref. [17]), filled circle (in Ref. [21]), dash-dot (in Ref. [22]).

### 3 Results, discussions and Conclusions

The calculated total electron scattering cross sections for SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub> CF<sub>3</sub>I are plotted in Figs. 1, 2 and 3 respectively while Fig. 4 shows the total and ionization cross sections for formaldehyde.

Figure 1 for SF<sub>6</sub> shows the comparison of the present data (MSCAR) with the experimental results of Garcia et al. [17] and Sueoka et al. [21] and also with the theoretical values of Garcia Independent Atom Model (IAM) and the recommended data of Christophorou [22]. It is assumed that if the electron energy is high enough the independent-atom model is valid, hence the two calculations are in excellent agreement with experiments [17] at higher energies. For energies below 100 eV the IAM calculation tends to overestimate the experimental cross section data reaching discrepancies of the order of 20% around 20 eV. Our MSCAR model fit the experimental results well even at an energy as low as 20 eV. The MSCAR calculation, using a more refined screening correction, is in good agreement with the recommended data Christophorou et al. [22] below 100 eV while, in contrast the simpler IAM model is lower than the experimental data and does not predict the 'turn over' in the cross section around 50 eV. The discrepancies in the two

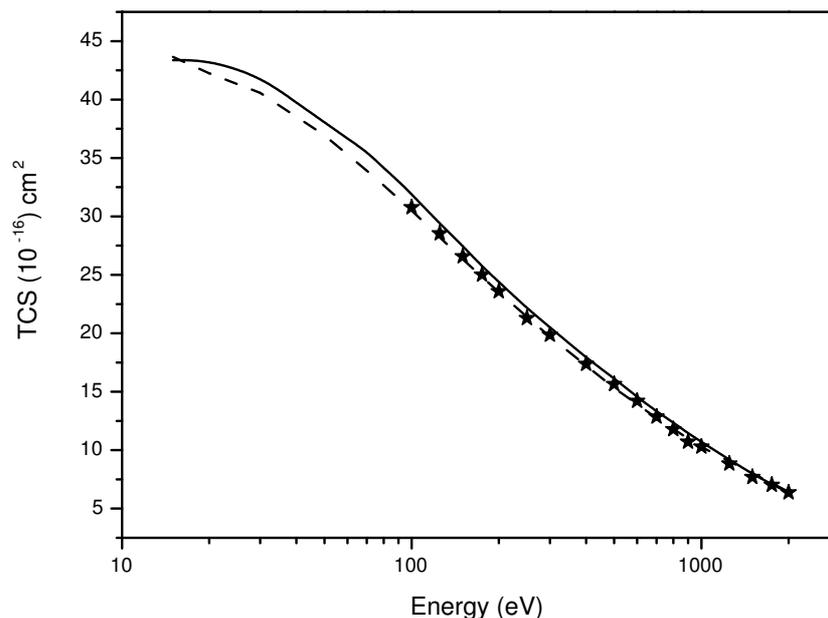


Fig. 2. Total Scattering cross sections for e-SF<sub>5</sub>CF<sub>3</sub> scattering.  $Q_T$  → solid curve (present work); star (in Ref. [17]), dash (in Ref. [17]).

calculations may be attributed to the different ways in which of screening is taken into account and also the basic input parameters. In the IAM model, atomic properties are used as the basic input parameters while in the MSCAR model molecular properties of the target are used instead. The difference in the two calculations may then be attributed to basic input such as the ionization potential to which the total cross sections are very sensitive.

In the case of SF<sub>5</sub>CF<sub>3</sub>, (Fig. 2) the only experimental data is that of Garcia et al. [17]. Both MSCAR and IAM models predict the same cross sectional values which are in excellent agreement with experiment

In Fig. 3, we have plotted  $Q_T$  for CF<sub>3</sub>I molecule considering two scattering centres one being the centre of mass of the CF<sub>3</sub> group and other at the iodine atom. We also applied the screening correction as discussed earlier and used the MSCAR method to calculate the total cross section. Comparison is made in Fig. 3 with the recommended data of Christophorou and Olthoff [23], the measurements of Kawada et al. [24] and Nishimura [25]. Our results agree well with the results of Kawada in the range of 20 to 300 eV and with Nishimura in the range of 200 to 2000 eV. The recommended data of Christophorou are, however, lower than the values produced by our theory.

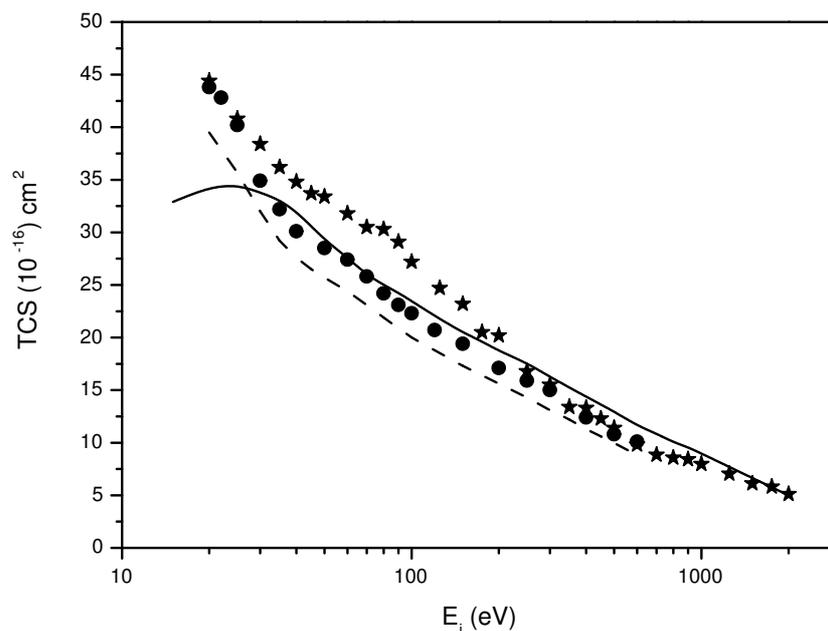


Fig. 3. Total Scattering cross sections for e-CF<sub>3</sub>I scattering.  $Q_T$  → solid curve (present work), filled circle (in Ref. [24]), star (in Ref. [25]), dash-dot (in Ref. [23]).

Figure 4 shows the total and the ionization cross sections for electron scattering from the formaldehyde molecule. The target H<sub>2</sub>CO is treated as having two centres with H<sub>2</sub>C and O. The total cross section is calculated using the MSCAR method and the ionization cross sections was calculated using the DM formalism. The ionization cross sections are compared with the theoretical values of Kim calculated using the BEB method [26]. There is excellent agreement between the two results above 200 eV but present results are higher than those of Kim at lower energies. There appears to be no experimental data with which to compare.

In conclusion the results of our semi-rigorous e-scattering method to predict different total cross sections is shown to be reliable to variety of molecules, SF<sub>6</sub> (symmetrical) and SF<sub>5</sub>CF<sub>3</sub>, CF<sub>3</sub>I and H<sub>2</sub>CO (two center targets). In future this method will be used to estimate  $Q_T$  for larger bio-molecules and by evaluating  $Q_{el}$  and  $Q_{ion}$ , excitation and dissociation cross sections may be estimated.

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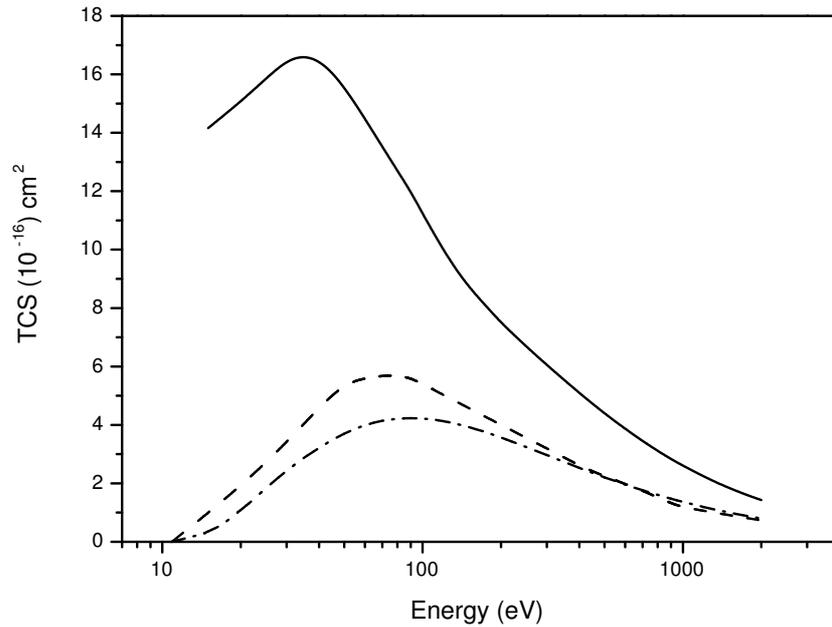


Fig. 4. Total and ionization cross sections for e-H<sub>2</sub>CO scattering.  $Q_T$  → solid curve (present work); dash (present  $Q_{ion}$ ), dash-dot (in Ref. [26]  $Q_{ion}$ ).

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