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Electron-impact ionization of SiCl, $SiCl_2$ and $SiCl_4$ molecules

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Abstract. Total ionization collision cross sections are calculated for silicon chloride compounds namely SiCl, $SiCl_2$ and $SiCl_4$ applying binary -encounter - Bethe (BEB) and modified BEB model for projectile energy from the ionization threshold to 1000 eV. The total ionization cross sections obtained using the binary-encounter-Bethe (BEB) model and the modified BEB model are compared with experimental and theoretical results. This model has been found to be successful for a wide range of molecules but for silicon chloride molecules the results are not in good agreement with experimental data.

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Key words: electron impact ionization, ionization cross sections, BEB model

1 Introduction

The ionization of an atom or molecule by electron impact is one of the most fundamental electron collision processes. The study of electron impact ionization of molecule play a key role in many applications such as radiation and environmental chemistry, gas discharges and gas lasers, fusion edge plasmas and plasma processing of materials [1-3], light-stimulated chemical vapor deposition in the microelectronic industry [4].

Nanocrystalline silicon and polycrystalline silicon films have successful applications in various optoelectronic devices, such as thin film solar cells, thin film transistors, switching devices and so on [5,6]. For depositing poly Silicon films, $SiCl_4/H_2$ mixture gas is used by plasma enhanced chemical vapor deposition. $SiCl_4$ is also used as an admixture in processing plasma feed gas mixtures which are used for selective reactive ion etching of GaAs on AlGaAs [7] and for characterization of polyester fabrics treated in $SiCl_4$ plasma [8,9]. In all these applications, electron impact ionization cross sections with SiCl,

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$SiCl_2$ and $SiCl_4$ are very important quantities for the understanding and modeling of the interaction of silicon -chlorine plasmas with materials.

Mahony *et al.* [10] have measured total ionization cross sections for SiCl and $SiCl_2$ from threshold to 200 eV using the fast-neutral-beam technique. Becker *et al.* [11] have measured electron impact ionization of $SiCl_x$ (x=1-4) using a time-of-flight mass spectrometer (TOF-MS) and a fast-neutral-beam techniques. The energy range covered in the TOF-MS was from the ionization threshold to 900 eV and up to 200 eV in fast-neutral-beam apparatus. Basner *et al.* [12] have measured electron impact ionization of $SiCl_4$ using two different experimental techniques namely, a time-of-flight mass spectrometer (TOF-MS) and a fast-neutral-beam techniques. The energy range covered in the TOF-MS was from the ionization threshold to 900 eV and up to 200 eV in fast-neutral-beam apparatus. The absolute total cross-sections for electron scattering on $SiCl_4$ molecules have been measured by Mozejko *et al.* [13] in two distinct electron-transmission experiments, in Gdansk and in Trento laboratory, for impact energy ranging from 0.3 to 250 eV and from 75 to 4000 eV, respectively. Recently, King and Price [14] have measured relative partial ionization cross sections (PICS) for the formation of fragment ions following electron ionization of $SiCl_4$, in the electron energy range 30-200 eV, using timeof-flight mass spectrometry coupled with an ion coincidence technique.

From theoretical side, the authors [10-12] have calculated the total ionization cross sections using DM formalism. Deutsch *et al.* [15] have calculated the ionization cross sections of $SiCl_x$ (x=1-4) using a modified additivity rule (MAR) in the energy range from 30 to 200 eV. Recently Kothari *et al.* [16] have reported the ionization cross sections of $SiCl_x$ (x=1-4) using their complex scattering potential - ionization contribution (CSP-ic) method.

The binary-encounter-Bethe (BEB) model of Kim and Rudd [17] has produced total ionization cross -sections in good agreement with experimental data for many important gases. It has become a useful tool for supplying cross-section data and also for identifying reliable sets of experimental data. Hwang *et al.* [18] have found that the BEB model was underestimating the cross-section by a significant margin for heavy atoms with the highest principal quantum number $n' \geq 3$, or molecules containing heavy atoms. In order to bring the BEB cross sections into satisfactory accord with experiment, they introduced a scaling factor $1/n_i$ into the expression for the BEB cross-section whenever $n_i' \geq 3$. Here n_i being the principal quantum number of orbital i. For molecules, this scaling was introduced whenever the Muliken population analysis showed that the orbitals were dominated by the high n orbital of the heavy atom. In this article, the total ionization cross sections for SiCl, $SiCl_2$ and $SiCl_4$ molecules are obtained using both, the BEB model and the modified BEB model.

2 Outline of the theory

In electron impact ionization of atoms and molecules, to get an expression of singly differential ionization cross section, Kim and Rudd [17] presented a theoretical model which was free of adjustable or fitted parameters. In this model they combined the dipole part of the Bethe cross sections [19] with a modified form of the Mott cross section[20]. This expression which they call the binary -encounter-dipole cross-section, requires the dipole oscillator strength $f(E)$ for ionization of each target electron. Here E is the photon energy and $f(E)$ can be obtained from the theory or from photo electron spectroscopy. As such data are not available for most molecules, especially over the full range of incident electron energy, Kim and Rudd [17] used a simple approximation for $f(E)$ and obtained the following expression for the BEB cross-section for ionizing an electron out of an orbital i at an incident energy T

$$\sigma_i = \frac{S_i}{t+u_i+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right] \tag{1}$$

where

$$t=\frac{T}{B_i},\ u_i=\frac{U_i}{B_i},\ S=4\pi a_0^2\left(\frac{R^2}{B_i^2}\right) \tag{2}$$

where B_i is the binding energy and U_i is the average kinetic energy of the electron in i^{th} orbital, with a_o and R being the Bohr radius and Rydberg energy constant, respectively. The total ionization cross section in the BEB model is given by

$$\sigma_{BEB}=\sum_i N_i\sigma_i \tag{3}$$

with N_i the electron occupation number of orbital i. Thus the BEB cross-section is determined entirely by the properties of the target and ion state, i.e. bound state properties and hence it provides an efficient means of determining total ionization cross section. This model is applied successfully to many molecules [21-25] and the results agreed well with experimental data over a wide energy range of incident electron-impact energy from the ionization threshold to a few keV.

Hwang *et al.* [18] found that for atomic orbitals with quantum number $n' \geq 3$ or molecular orbitals dominated by an atomic orbital with $n' \geq 3$, the BEB model (eq.1) underestimates the ionization cross section by significant amount. The calculations agreed well with the experimental data when the term u_i+1 in the denominator on the R.H.S. of equation 1 was divided by n_i. The modified BEB expression given by Hwang *et al.* [18] is as follows

$$\sigma_i = \frac{S_i}{t+(u_i+1)/n_i}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right] \tag{4}$$

In the present work all physical quantities occurring in Eq. (1), i.e. B, U and N were calculated for the ground state of the molecules using the Gaussian [26] molecular structure code. The computations are performed using the Restricted Hartree Fock (RHF)

method for closed - shell molecular structure and for open shell molecular structure, Unrestricted Hartree fock (UHF) method is used. The calculations were performed using 6-31G(d) basis set.

3 Results and discussion

Here the BEB model is applied to molecules made of atoms that consisted of M shell electrons which have radial nodes in their atomic orbitals that causes the U values very high. These large U values decrease the contributions to the ionization cross sections from the valence electrons which are dominant ones. To overcome this, the U values of the molecular orbitals identified with 3s and 3p electrons of Si and Cl were divided be their principal quantum number. The BEB cross sections with this modified U values are also plotted in the figures. The curves marked "BEB/3" represent BEB cross sections with the modified U values, while the curves marked " BEB " used the unmodified values.

The dominant part of the ionization cross section comes from valance electrons of 3s and 3p orbitals of Si and Cl atoms. The ionization cross section for a molecule with more chlorine atoms is bigger than the cross section for a molecule with fewer chlorine atoms. This is in support to the logic of additivity rule according to which higher cross sections are obtained for molecules with more atoms of the same kind [27]. This trend is observed here for all three chlorine compounds namely, SiCl, $SiCl_2$ and $SiCl_4$.

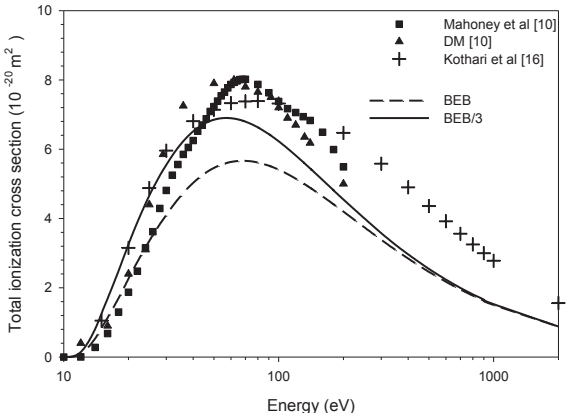

Figure 1: Total ionization cross sections of SiCl by electron impact. Solid line - present BEB Qion; Small dash - modified values of U in BEB; cross hair - data by Kothari *et al.* [16]; triangles - data by DM formalism [10]; squares - data by Mahoney *et al.* [10].

Different theoretical models are compared with the experimental results for SiCl, $SiCl_2$ and $SiCl_4$ in Figs. 1, 2 and 3 respectively. It is observed that for all three molecular targets, the results obtained using the DM formalism agree better with experimental results compared to the results of Kothari *et al.* [16] and the present work.

For SiCl [Fig. 1] the ionization cross sections calculated by Kothari *et al.* [16] using

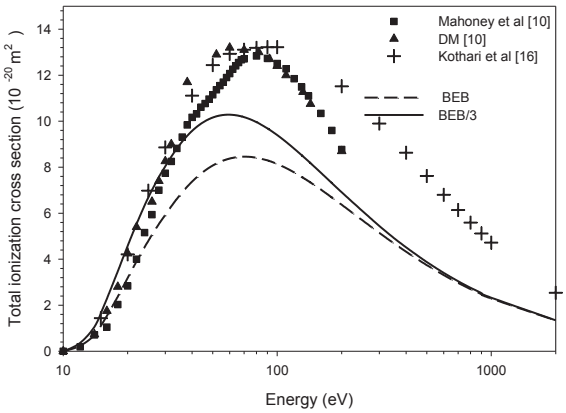

Figure 2: Total ionization cross sections of $SiCl_2$ by electron impact. Solid line - present BEB Qion; Small dash - modified values of U in BEB; cross hair - data by Kothari *et al.* [16]; triangles - data by DM formalism [10] ; squares - data by Mahoney *et al.* [10].

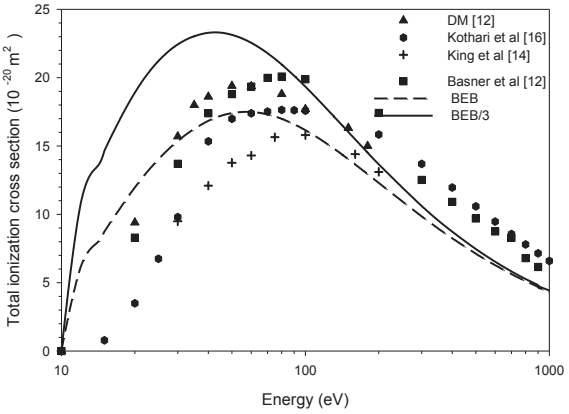

Figure 3: Total ionization cross sections of $SiCl_4$ by electron impact. Solid line - present BEB Qion ; Small dash - modified values of U in BEB; circles - data by Kothari *et al.* [16]; triangles - data by DM formalism [12]; squares - data by Basner *et al.* [12]; crosshair - data by King *et al.* [14].

their CSP-ic model are not satisfactory and underestimate the peak values of experimental measured data of Mahoney *et al.* [10] and for $SiCl_2$ [Fig. 2] the results of Kothari *et al.* [16] are also not satisfactory with the experimental data of Mahoney *et al.*[10]. For $SiCl_4$ [Fig. 3] the ionization cross sections are considerably lower than the experimental results of Basner *et al.* [12] up to 200 eV. Their results for $SiCl_4$ [Fig. 3] overestimates the experimental results of King *et al.* [14]. It is also clear from the above figures that at high T, the results of Kothari *et al.* [16] for SiCl [Fig.1] and $SiCl_2$ [Fig. 2] overestimate the experimental data, the BEB results and the modifie BEB calculations. This indicates that the dipole contribution in their CPS-ic model is not correct which dominates at high T. The total ionization cross sections calculated for Br_2 and I_2 molecules by Joshipura and Limbachiya [28] are also much higher than the BEB calculations of Ali and Kim [29] at

higher T indicating wrong asymptotic behavior of their wave function.

As shown in Figs. 1 to 3 the BEB cross sections are very lower near the peak for all three Silicon chloride molecules. In case of SiCl and $SiCl_2$ the modified BEB results are also very low but in case of $Sicl_4$ the modified BEB results overestimates the experimental data. For SiCl the UHF method is used with average values of α and β orbitals and for $SiCl_2$ and $SiCl_4$ molecules RHF method is used for wave functions. For all orbitals theoretical values of B are considered except the lowest one where the experimental values are taken [30] so that the ionization cross sections switch on at the correct value. It is interpreted that a better wave function is needed for calculating the total ionization cross sections.

4 Conclusions

The total ionization cross sections (Q_{ion}) for SiCl, $SiCl_2$ and $SiCl_4$ are studied here using the BEB model and the modified BEB model. From experimental side a few results are available [10-14] for these molecules. Comparisons are made of present results with experimental results and the theoretical results of DM formalism [10,12] and the CSP-ic model of Kothari *et al.* [16].

It is observed that the DM formalism gives better agreement with experimental data compared to other two theoretical approaches. The DM formalism data are available up to 200 eV only hence its reliability to reproduce reliable Q_{ion} at higher energies can not be judged.

The CSP-ic model of Kothari *et al.* [16] have not satisfactory agreement with the experimental results for all three Silicon chloride molecules. In their calculations by the CSP-ic model they require proper value of Rp which requires a lot of experimental data [31] and as the experimental data for these targets are few, they have carried out the calculations with two approximate inputs of R_p, i.e. $R_p = 0.7$ and $R_p = 0.8$ in their equation (7b) [16] and the second important point to be noted is that the CSP-ic model [31] basically comes from the modified additivity rule proposed by Joshipura and Patel [32] for electron-molecule scattering. In this approach they have separated electron - molecule interactions into short range and long range parts. For short range part , basic atomic properties were used and the molecular average spherical dipole polarizability was used for the long-range part. This model was modified by Joshipura *et al.* [31] to calculate total ionization cross sections for molecules. In this new approach they have calculated total renormalized molecular charge densities in terms of atomic charge densities which were then brought to a single center. This charge density is a basic input in the CSP-ic model to calculate various electron molecule cross sections. In this treatment, the true nature of the molecular charge distribution and potentials are missing. It should be noted that accurate evaluation of the charge density and potentials are very important in such types of calculations and Jain and Baluja [33] have reported electron scattering cross sections for many diatomic and polyatomic molecular targets for which they have employed various

single centre expansion programs to determine the charge density and various potentials for linear and non-linear molecules and for linear molecules the molecular wave functions were obtained from McLean and Yoshmine [34] while for nonlinear cases they have employed the MOLMON computer code.

The BEB model and the modified BEB model used for calculating electron impact ionization cross sections for SiCl, $SiCl_2$ and $SiCl_4$ molecules in the present study also fail to reproduce the experimental results. The BEB cross-sections are determined entirely by the properties of the target and bound state properties and it doesn't depend on any adjusting parameters, fitting parameters or experimental data. The BEB cross sections require only a minimum set of molecular constants for the initial state of a target molecule and such constants can be calculated from the molecular structure codes and hence it provides an efficient means of determining total ionization cross sections. This model has reliably predicted the Q_{ion} of hydrocarbons and other molecules made of light atoms, particularly closed shell molecules. The problems which occur here with Chlorine compounds was expected by Hwang *et al.* [18] as they had same types of problems with fluorine compounds. Other halogen compounds that is bromide and iodide compounds are expected to have similar problems. The BEB model requires further refinements to expand its application to a wider class of molecules.

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