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Electron impact single and double ionization of halogens

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Abstract. The binary encounter approximation has been used for calculations of electron impact single ionization cross-sections for F, Cl, Br and I and double ionization cross-sections for Br and I. Contributions of ionization from inner shells have also been included in the calculations. Hartree-Fock momentum distribution has been used for the bound electron as far as possible. The results have been found to be in satisfactory agreement with experimental observations.

Keywords. Electron impact; single ionization; double ionization; halogen.

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1. Introduction

Cross-sections for electron impact single and multiple (mainly double) ionization of atoms and ions are required in many fields of current interest (Chatterjee and Roy 1984 and references therein). Experimental measurements of these cross-sections are available only for a few systems and over a limited energy range. Hence, experimental and theoretical studies of these processes are of considerable importance. Theoretically, quantum-mechanical investigations of these processes are very complicated. On the other hand, the binary encounter approximation (BEA) was successfully used for theoretical studies of these processes (Shrivastava and Roy 1984; Chatterjee and Roy 1984, 1987). In the present work, electron impact single and double ionization cross-sections for halogen atoms have been calculated in the BEA, for which experimental measurements have been reported in the recent past (Hayes *et al* 1987) over a limited energy range. These cross-sections are of particular importance because of their applications in plasma processing technologies used by the microelectronics industry for etching of semiconductors and metals.

Since the present work is based on the binary encounter approximation it would be worthwhile to present a brief discussion on the physical basis of the approximation.

The basic approximations involved in the binary encounter collision theory are (Vriens 1969):

(i) the incident particle interacts with only one target particle (generally electron) at a time,
(ii) the mutual interaction between the atomic electrons and the nucleus can be disregarded during the collision except that the nucleus provides velocity distribution to the electrons characteristic to the binding forces.

The atomic electrons and the nucleus are thus assumed to be independent scattering

centres. In the BEA, cross-sections are calculated in two steps. In the first step expressions for cross-section for collision between two freely moving structureless charged particles are obtained. This step requires no approximation. In the second step these expressions for Coulomb cross-section are related to specific charged particle-atom collision process and in this step approximation is involved.

The approximations made in the BE calculations are justified when the region of interaction between the primary particles is small compared to the atomic dimensions. In that situation, the momentum and energy transferred to the target are much large as compared to the momentum and binding energy of the target electron, respectively. This condition is expected to be satisfied in ionizing collisions. Hence the BEA has been found suitable for the study of ionization process.

2. Theoretical methods

In the present work, Vriens' (1966) expression for electron impact ionization cross-section of an atomic target, which includes the contributions of exchange and interference, has been used to calculate electron impact single ionization cross-sections of atoms. The expression can be written in a suitable form, convenient for numerical calculations, as (see Roy and Rai 1973a)

$$Q^i_{\text{ion}}(s,t) = \frac{4}{(s^2+t^2+1)}\left[\left(\frac{s^2-1}{s^2U}\right)+\frac{2t^2}{3}\left(\frac{s^4-1}{s^4U^2}\right)-\frac{\phi \ln s^2}{U^2(s^2+1)}\right](\pi a_0^2),$$

where

$$\phi = \cos\left[\left(\frac{1}{s^2U+U}\right)^{1/2}\ln s^2\right]. \tag{1}$$

In the above equation $s^2 = v_1^2/v_0^2$, $t^2 = v_2^2/v_0^2$, where v_1 and v_2 are the velocities of the incident and bound electrons respectively, in atomic units and $v_0^2 = U$ is the relevant ionization potential in rydberg. The above expression for Q_i has been integrated over the Hartree-Fock velocity distribution for the bound electron to obtain the ionization cross-section. Hence, the expression for electron impact single ionization cross-section for the target shell, in final form becomes

$$Q^i_{\text{ion}} = n_e \int_0^\infty Q^i_{\text{ion}}(s,t) f(t) U^4 \, \mathrm{d}t, \tag{2}$$

where n_e is the number of equivalent electrons in the atomic shell under consideration and $f(t)$ is the momentum distribution function for the bound electron.

Here we would like to mention that Hartree-Fock (HF) wave functions do not take proper account for the correlation between the electrons in an atom. In fact the HF method is a form of the central field approximation in which each electron is assumed to move in the potential of the nucleus and a time averaged potential of the other electrons. The motion of an individual electron is therefore independent of the motion of the others, with the exception of the incomplete correlation introduced through the use of antisymmetrized wave function. There are a number of methods by which better account of correlation between electrons can be taken into the wave function e.g. configuration interaction approach based on Slater-Condon theory, multiconfiguration Hartree-Fock approach used by Fischer. Calculations of complex

atomic structure using these approaches give reasonably accurate results leading to improved agreement with experiments (see Griffin and Pindzola 1983). Hence, it is expected that cross-sections calculated using wave functions which take account of configuration interaction would lead to improved agreement between the theoretical and experimental results. However, such calculations are hard to perform as they require extensive computational work. In view of this, we have decided to use HF wave function in the present work.

Inner shell electrons in heavy atoms have high velocity and hence they are relativistic in nature. Hence, relativistic effects become important for these targets, specially at low impact velocities. At low velocities the incident particle has to penetrate deep inside the electronic shell in order to make an ionizing collision. It results in slowing down of the projectile. Consequently, in order to keep momentum conserved in the collision process, the ejection of high momentum electrons is more favoured. As a result the ionization cross-section becomes specially sensitive to the high momentum component of the electron wave function. Due to relativistic increase of mass the relativistic wave functions have more high-momentum components than the non-relativistic ones and hence their use enhances the ionization cross-sections at low impact energies (Jesus and Lopes 1982). However, these features are significant in case ionization occurs from deep inner shells of heavy atoms. In the present work ionization from valence shell and the next inner shell has only been considered. In such cases relativistic effects are expected to make insignificant contribution to the ionization cross-section. Keeping this point in view we have used non-relativistic wave function in the present calculation.

Roy and Rai (1973b) developed a modified binary encounter method, based on the double binary encounter model proposed by Gryzinski (1985) for calculation of double ionization cross-sections of atoms due to impact of charged particles, for calculation of electron impact double ionization cross-section of atomic targets. In Gryzinski's model it is supposed that double ionization of a target may take place by one of the following two independent mechanisms. In one of these processes the incident particle is supposed to knock out two electrons from the target due to two successive binary encounters with it. In the alternative process one electron is supposed to be ejected out from the target by the projectile. The ejected electron knocks out another electron from the residual target. The total double ionization cross-section for the target is taken as the sum of the cross-sections for these two alternative processes. In the case of electron impact, due to indistinguishability of electrons, cross-sections for the above mentioned processes are equal.

Using Vriens' (1966) expression for electron impact ionization cross-sections of atoms, the expression for electron impact double ionization cross-section of an atomic target shell may be written, in final form, as

$$Q_{\text{ion}}^{ii} = 2\frac{n_e(n_e-1)}{4\pi\bar{r}^2}\int_{t=0}^{\infty}\int_{U_i}^{E_q-U_{ii}}\left\{\frac{2}{(s^2+t^2+1)U_i}\left[\left(\frac{1}{\Delta E^2}+\frac{4t^2U_i}{3\Delta E^3}\right)\right.\right.$$
$$+\left(\frac{1}{(s^2U_i+U_i-\Delta E)^2}+\frac{4t^2U_i}{3(s^2U_i+U_i-\Delta E)^3}\right)$$
$$\left.\left.-\frac{\phi}{\Delta E(s^2U_i+U_i-\Delta E)}\right]\alpha f(t)U_i^{1/2}\right\}\mathrm{d}(\Delta E)\,\mathrm{d}t\,8{\cdot}797\times10^{-17}(\pi a_0^2). \tag{3}$$

The meaning of various terms in the above equation has been discussed by Roy and Rai (1973b) (see also Kumar and Roy 1978). In deriving the above equation a quantum-mechanical (Hartree-Fock) velocity distribution $f(t)$ has been assumed for the ejection of the first electron and a hydrogenic velocity distribution for the second ejected electron. In this context, we would like to point out that use of Hartree-Fock velocity distribution for both the ejected electrons would be more appropriate. However, it would give rise to complex numerical integrations making the evaluation of double ionization cross-sections very difficult.

In the present work momentum distribution functions for the bound electrons have been constructed using Hartree-Fock radial functions reported by Clementi and Roetti (1974). For shell radii and binding energies of electrons, quantum-mechanical values of radial distance of maximum probability given by Desclaux (1973) and quantum-mechanical values of orbital energies given by Clementi and Roetti (1974) have, respectively, been used in the calculations. Here we would like to point out that after the ejection of the first electron, in the case of slow collision i.e. close to the threshold, the target will get sufficient time for rearrangement and hence for the ejection of the second electron, binding energy of the target ion would be an appropriate choice. However, at high impact energies the two electrons would be ejected almost simultaneously and hence the target rearrangement after the first process would not be possible. In that situation, while considering the ejection of the second electron binding energy of the neutral atom should be used. In the present work we have used the binding energy of neutral atom in the ejection of both the electrons. This choice is expected to overestimate the cross-section at low impact energies but it would become more and more appropriate with increase in impact energy.

In the present work, contributions from inner shells have been included in the calculations of single as well as double ionization cross-sections. While calculating these contributions to double ionization cross-section it has been assumed that the first electron is always ejected from the valence shell and the second electron from an inner shell. For these calculations the factor $n_e(n_e - 1)/4\pi\bar{r}^2$ has been suitably modified (see Kumar and Roy 1978).

3. Results and discussion

Electron impact single ionization cross-sections for F, Cl, Br and I and double ionization cross-sections for Br and I have been calculated using the method described in § 2. The calculated results along with the experimental observations of Hayes *et al* (1987) have been presented in figures 1 to 6.

Single ionization cross-sections due to electron impact have been calculated from threshold up to 2000 eV impact energy. It is well known that besides direct ionization electron impact, ionization cross-section is contributed by a number of alternative processes e.g. excitation-autoionization. However, in the present case no such evidence has been found in experiments (Hayes *et al* 1987) and hence these channels of ionization have not been considered in the calculations. Experimental observations are available only up to 200 eV impact energy. The uncertainties in the measured cross-sections have been reported to be $\pm 20\%$ for F, $\pm 14\%$ for Cl, $\pm 11\%$ for Br and $\pm 12\%$ for I.

Experimental observations in all cases except F, show a well-resolved cross-section maximum. In F the fall in cross-section with energy, after reaching a maximum is

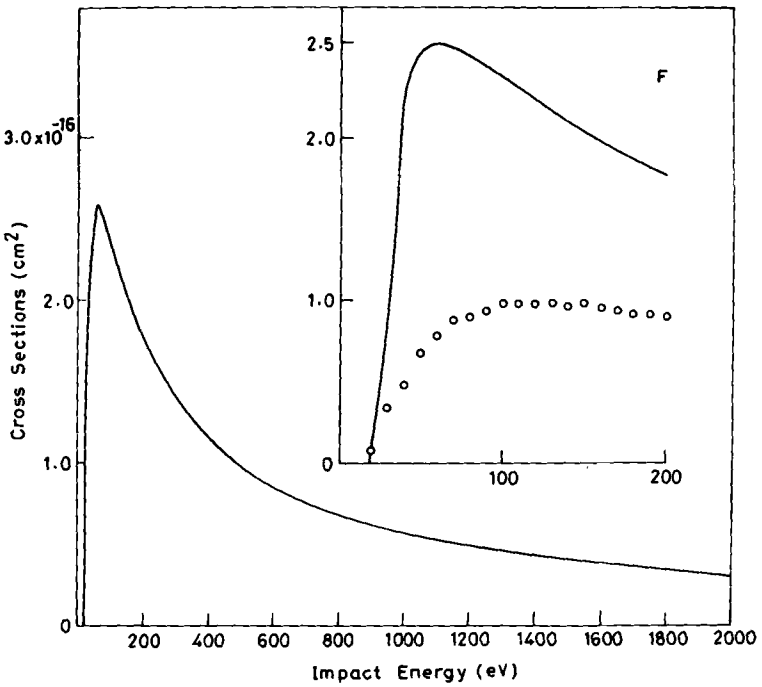

Figure 1. Electron impact single ionization cross-sections of F. Full curve – present calculations, o – Experimental results of Hayes *et al* (1987).

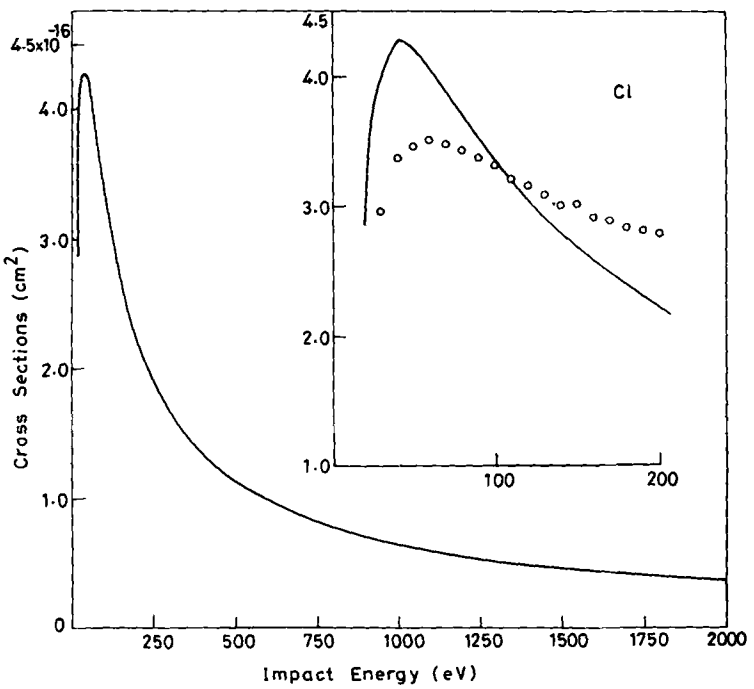

Figure 2. Electron impact single ionization cross-sections of Cl; legends same as in figure 1.

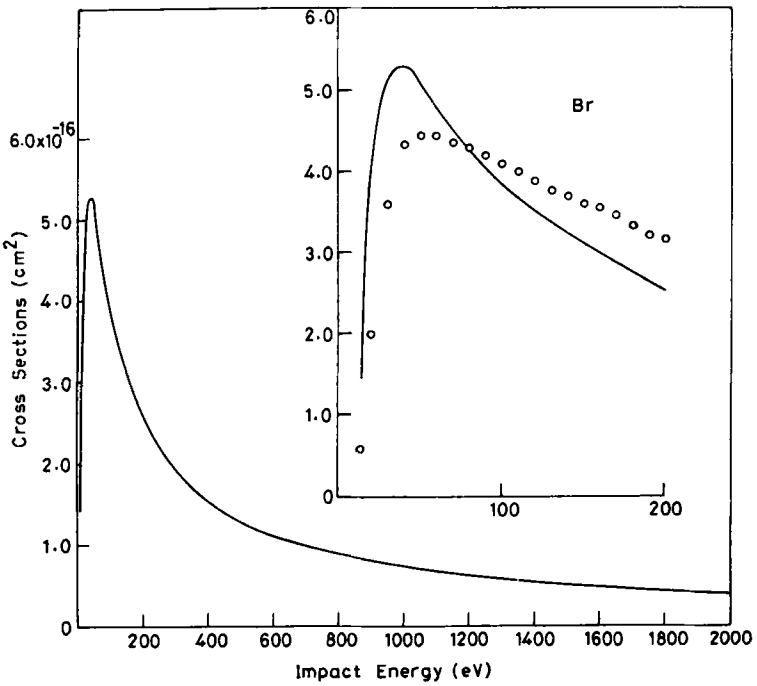

Figure 3. Electron impact single ionization cross-sections of Br; legends same as in figure 1.

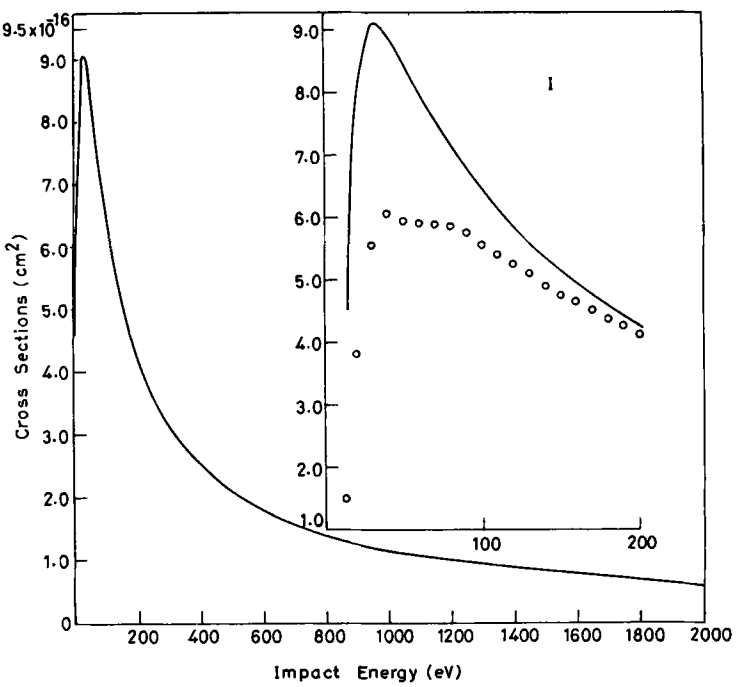

Figure 4. Electron impact single ionization cross-section of I; legends same as in figure 1.

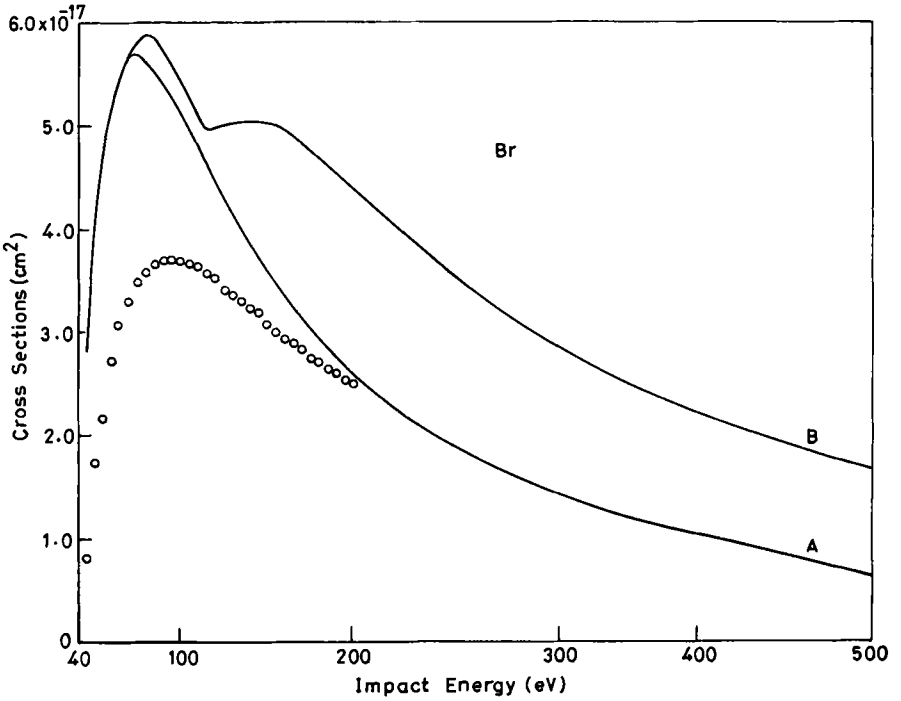

Figure 5. Electron impact double ionization cross-section of Br. A – Present calculations (valence shell contributions). B – Present calculations (including contributions from inner shells). o – experimental results of Hayes *et al* (1987).

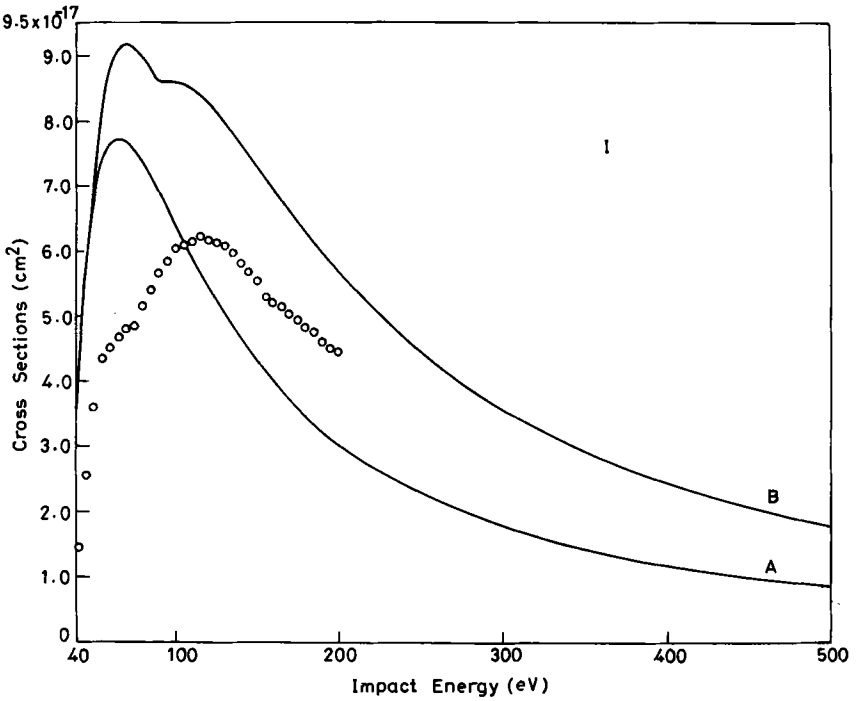

Figure 6. Electron impact double ionization cross-sections of I; legends same as in figure 5.

much slower than that observed in other cases leading to an almost flat peak. The calculated cross-section curves show peaks in all cases. However, in F the maximum of cross-section curve is comparatively broad. As far as the position of the cross-section maximum is concerned, the calculated positions are close to their experimental counterparts (in fact slightly below the experimentally observed positions) in all cases. Close to the peaks the present calculations overestimate the experimental cross-sections. This overestimation has been found to be largest in F but the situation improves with increase in the atomic number of the target. These discrepancies are expected because in the present calculations the binary encounter approximation has been used which is suitable at high impact energies i.e. in fast collisions. From the binding energy considerations, for a specific value of impact energy the condition of fast collision is more appropriately satisfied for heavier targets. Moreover, the overestimation at the peak is a general feature of the binary encounter electron impact ionization cross-sections. In I the experimental cross-sections show a slight structure at the peak and the reason for this is not clear. The present calculations show no such structure. More experimental and theoretical studies are required to resolve this discrepancy. Despite these discrepancies, magnitudes of the present cross-sections are always (except in F) within a factor of 1·5 as compared to the experimental observations, except at impact energies below the peak. In fluorine the trend of variation of the experimental and calculated cross-sections with impact energy indicates that in case the experimental observations were extended beyond 200 eV both the sets of results would have shown a close agreement.

The double ionization cross-sections for Br and I calculated in the present work from threshold to 500 eV impact energy have been presented in figures 5 and 6 respectively along with the recent experimental observations of Hayes *et al* (1987). In this case also experimental observation does not indicate any contribution from alternative channels (e.g. excitation-autoionization, auger emission) to double ionization cross-section and hence these have not been considered in the present work. However, the contributions of ionization from the next two inner shells have been included in the calculations.

In the Br the experimental cross-sections do not show any structure. There is a peak of magnitude $3{\cdot}71 \times 10^{-17}\,\mathrm{cm}^2$, at about 90 eV impact energy. In the present calculations two peaks have been found at about 80 eV and 140 eV impact energies. The magnitudes of the peaks are $5{\cdot}9 \times 10^{-17}\,\mathrm{cm}^2$and $5{\cdot}06 \times 10^{-17}\,\mathrm{cm}^2$, respectively. The first peak observed in the present calculations is sharp whereas the second peak is comparatively flat. The second peak arises due to the contributions of ionization from the 3*d* shell (threshold of ionization is about 116 eV). The position of the first peak in the present calculations is close to that of the maximum of the experimental cross-section. However, the magnitude of the calculated peak is higher than the corresponding experimental value but the two values are within a factor of 2. Except for these discrepancies the present results are in good agreement with the experimental observation and they are always within a factor of 2 (except below 55 eV impact energy). Agreement between the present results and the experimental cross-sections improves with increase in impact energy.

The present double ionization cross-section curve for I shows a peak of magnitude $9{\cdot}17 \times 10^{-17}\,\mathrm{cm}^2$ at about 70 eV impact energy. Corresponding to this, a small break has been found in the experimental cross-section curves at about 80 eV, the magnitude of cross-section at this break being $5{\cdot}14 \times 10^{-17}\,\mathrm{cm}^2$. Apart from this, in the present

calculations, there is a comparatively broad maximum of magnitude $8{\cdot}6 \times 10^{-17}\,cm^2$ in the vicinity of about 100 eV which arises due to contributions of ionization from $4d$ shell (threshold of ionization is about 77 eV). The experimental cross-section curve shows a pronounced peak of magnitude $6{\cdot}24 \times 10^{-17}\,cm^2$ at about 115 eV impact energy. Thus the position of this peak is shifted towards higher energy side as compared to that observed in the present work whereas the magnitude of the peak is lower than the present value. Except these discrepancies the present results are always within a factor of two (above 50 eV impact energy) as compared to the experimental observations. The agreement between the present calculations and the experimental cross-sections is found to improve with increase in impact energy, as observed in Br.

4. Conclusion

From a critical study of the results obtained in the present work it is concluded that the present method gives electron impact single and double ionization cross-sections in reasonably good agreement with experiments at high impact energies. The overestimation of the calculated cross-sections close to the peak (both single and double ionization) is a general feature of the BEA electron impact ionization cross-sections. Good agreement of the present results with the experimental observations at low impact energies (close to the threshold of the process) is not expected because the assumptions underlying the BEA are expected to hold only at impact energies well beyond the threshold. Moreover, in the case of double ionization cross-section calculations, the use of binding energy of the neutral atom while considering the ejection of the second electron might partly be responsible for discrepancies observed at low impact energies. This use is justified at high impact energies which is supported from the observation that the agreement between the present results and the experimental cross-sections gradually improves with increase in impact energy. At this point we would like to mention that the effects of partial rearrangement of the target have been incorporated by Chatterjee and Roy (1985) in case of calculations of double electron capture cross-section by multi-charged ions from atoms. Unfortunately, this type of calculation is not possible in the case of electron impact. Besides, the use of hydrogenic wavefunction for the bound electron while considering the ejection of the second electron might partly explain the discrepancies observed at low energies. Kumar and Roy (1981) have reported a comparative study of HF and hydrogenic velocity distribution functions. They have concluded that use of accurate HF velocity distribution in case of both the ejected electrons would reduce the magnitudes of calculated cross-sections at low impact energies. If it would have been possible to use HF velocity distribution for both the ejected electrons then our cross-sections would have been lowered at low impact energies leading to better agreement with the experiment.

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