Evaluation of direct ionization cross sections for C$_{60}$ by electron interaction

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Abstract. Partial ionization cross sections corresponding to the production of cations C$_{60}$$^q+$ ($q=1$-$3$) in the electron impact ionization of C$_{60}$ have been calculated using a modified Jain-Khare semiempirical formalism. The cross sections calculated in the energy range varying from ionization thresholds to 1000 eV revealed a reasonable good agreement with the available experimental and the theoretical data.

1. Introduction
The study of C$_{60}$ has attracted an enormous amount of interest in recent years, both from the experimental and the theoretical viewpoints because of its characteristic electronic structure reflecting its unique geometry. The exceptional stability, very high symmetry and several other molecular properties may provide the basis for important applications of this novel, natural state of carbon [1-2]. From this point of view of studying the electron ionization of this molecule, it offers a good opportunity for observing a very large molecule thus providing interesting tests of our understanding of ionization.

In the present work, we have extended and generalized the modified Jain-Khare semiempirical formalism for the evaluation of the partial ionization cross sections corresponding to the formation of the cations in the electron impact ionization of molecules [3-4] to the electron impact ionization of C$_{60}$. In the electron impact ionization of C$_{60}$, we have considered the C$_{60}$$^q+$ ($q=1$-$3$) ions produced in the direct single ionization processes for which the reliable theoretical and the experimental data have been reported in the literature. The recent experimental studies on the total single and partial ionization cross sections for C$_{60}$ include those of Baba et al. [5], Vostrikov et al. [6], Märk and co-workers [7-10] and Itoh et al. [11]. From a theoretical standpoint, calculations for C$_{60}$ are particularly challenging. The rigorous quantum mechanical approach for the calculations for molecules is limited to the application of simple molecules. Recently, Deutsch et al. [12] extended their DM formalism and the semiempirical concept based on the modified additive rule (MAR) [13] for the calculations for the ionic, fragment and total cross sections for fullerenes like C$_{60}$ and C$_{70}$. The present calculations for the ionization cross sections leading to the formation of singly, doubly, and triply charged ions in direct ionization of C$_{60}$ reveal a reasonable good agreement with the established experimental [8-11] and the theoretical data [12-13] in the energy range varying from the ionization threshold to 1000 eV.

2. Theoretical
The present calculations are carried out using the modified semi-empirical formalism developed by Khare and co-workers (see the discussion in Refs. 3-4). In brief, the ionization cross sections
corresponding to the formation of the $i^{th}$ type of ion in the ionization of a molecule by the incident electron of energy $E$ is given by

$$Q_i(E) = \frac{4\pi^2 e^2 R}{E} \left[ \frac{E}{(E-I_i)} \left( M_i^2(E) + R \frac{R}{E} S_i(E) \right) \ln \left( 1 + C_i(E-I_i) \right) + \frac{R(E-I_i)}{E} S_i \left( \begin{array}{c} (E-I_i) \\ 0 \end{array} \right) \int_0^{\frac{1}{E}} \frac{e^{-\frac{e^2}{(E-e)^2}}}{(e^2 + e_0^2)^2} de \right] \right] \right)$$

(1)

$M_i^2(E)$ and $S_i(E)$ are the integrals over the oscillator strengths, defined elsewhere [3]. $W (= e + I_i)$, $I_i$, $a_0$, $e_0$, $C_i$, $S_i$ and $R$ are energy loss suffered by the incident electron, the ionization threshold for the production of $i^{th}$ type of ion, the Bohr radius, energy parameter, collision parameter, number of ionisable electrons and Rydberg constant, respectively.

The present formulation requires the dipole oscillator strengths $df_i/dW$, as a major input, that is directly proportional to the photoionization cross section. In the present study, we have used the photoionization cross section data for the different cations in the energy range from ionization threshold to 25 eV from the measurement of Jaensch and Kamke [14]. In the energy range 26 to 130eV, the same were taken from the established data of Reinkoster et al. [15]. Above 130 to 280 eV, we have employed the total valance-shell photoionization cross section data measured by Berkowitz [16] and above 280 eV the same was extrapolated by Thomas-Reiche-Kuhn sum rule [16]. In their measurements, they estimated the total experimental uncertainty by $\pm 20%$. The total photo-absorption cross sections have been distributed into ionic fragments using the constant ionization efficiency above dipole breakdown limit. The collision parameter $C_i$ and energy parameter $e_0$ were evaluated as for other polyatomic molecules [3-4]. The vertical onsets or the ionization potentials corresponding to the various cations are given elsewhere [14-16]. In the present evaluations of cross sections, the estimated error is expected as same as for the measurement of the photoionization cross sections.

2. Results and Discussion

Figure 1 shows the comparison of our partial ionization cross section profiles with the experimental [8-11] and the theoretical data [13]. It is interesting to note that the cross sections corresponding to singly charged ion is much higher than the doubly charged ions. Similarly the cross sections for triply charged ions are much smaller in comparison to singly and doubly charged ions. Although this is in contrast to the situation known for ordinary larger polyatomic molecules, where the parent ion is usually almost nonexistent, with the exception for the case of some hydrocarbons, it is nevertheless in accordance with our studies of ionization and fragmentation of the polyatomic molecules [4]. The reason for the larger cross section lies, on the one hand, in the fact that the production of doubly and triply charged ions is energetically more favourable. In addition to shear size of $C_{60}$ and the fact that the secondary electrons from an initial single ionization process may be ejected into the empty centre of the case and subsequently interact anew with the electron cloud of the $C_{60}$ enhances the chance for the occurrence of inelastic-multiple electron collisions within the quantum system, thereby increasing the possibility for the production of highly charged states.

Formation of $C_{60}^{+}$ is particularly interesting case where the experimental and theoretical data provided by Mark and co-workers revealed a very unusual shape of cross sections. In the energy range from the ionization threshold to 200 eV, our calculated results are in good agreement with the corrected absolute experimental data of Matt et al. [8] (after Foltin et al. [9]), Tarnoviski et al. [10] and the theoretical data [13]. Above 200 eV, a slightly deviation has been noticed. On the other hand our results show a satisfactory agreement with the experimental data of Itoh et al. [11] available in the asymptotic region (400 - 1000 eV). For the sake of brevity, the experimental data of Baba et al. [5] and Vostrikov et al [6] are not shown in the comparison with our results for $C_{60}^{+}$. These data-sets exhibit much larger cross sections and quite different cross section shapes, strongly suggest that these data suffered by the unreliable vapour pressure data used for calibration, and in addition by discrimination effects leading to artefacts in the measured cross section curves.
The results of our calculations of the cross sections for the formation of doubly charged ions following electron impact on C$_{60}$ compare quite well with the experimental data sets [9-11]. However, our results in the energy range 100-300 eV, underestimate the theoretical data of Deutsch et al. [13] but generally lie within the described uncertainties. In low energy region i.e. from the ionization threshold to 100 eV, our results corresponding to the formation of triply charged ions are in good agreement with the experimental and theoretical data sets [9,11,13]. In intermediate and the asymptotic regions, our results are just double to the calculations of Deutsch et al. [13] as well as the experimental data [9,11]. However, a qualitative agreement of the evaluated cross sections with these experimental and the theoretical data has been noticed. In case of the quantitatively dominating molecular ions C$_{60}^+$ and C$_{60}^{2+}$, our results are in satisfactory agreement with the recent measurements [9-11] and the theoretical calculations [13] within certain error bars (~20%). In case of triply charged ion, a large disagreement has been noticed. Nevertheless, considering that this is a comparison with the absolute data where error bars of these sets of data are easily in the 5% to 20% regime (in particular taking into account that the calculations are depending on the accuracy of the experimental input parameters) the agreement is reasonably good.

![Graphs showing partial and total ionization cross sections](image)

**Fig.1:** Partial and total ionization cross section profiles (in the units of 10^-16 cm^2) for the electron impact ionization on C$_{60}$ (designated with solid lines) in comparison with the experimental data designated by: X– Foltin et al. [9], ◊- Tarnovski et al. [10] and ○- Itoh et al. [11] and the theoretical data designated by: ∆- Deutsch et al. [13].

On the other hand, the partial cross sections when added up to a total ionization cross section is in good agreement with the experimental data [11]. Our results underestimate the total cross sections measured by Foltin et al. [9] but lie within the experimental uncertainties. Note that the DM formalism calculations [12] and additive calculations [13] for total ionization cross sections (not shown) are much higher than our calculations and other data-sets [9,11]. Conceptually, the DM calculation relies on the additive rule, which builds the total ionization cross section by adding up contributions from the different C$_{60}$ orbitals. This approach might not be applicable to a case-like structure such as C$_{60}$. It could be argued, for instance, that for the incoming projectile only about half of the 60 carbon atoms that constitute the C$_{60}$ case are contributing to the cross sectional area as seen by the projectile (see for instance Ref. 9 for detailed discussion). As already discussed above, there is a poor agreement between our results and the two earlier experimental data sets [5-6] both in terms of the cross section values and in terms of cross section shapes. However, the Jain-Khare formalism has limitations in applications to the cross section calculations and it depends on the accuracy of required input data. The present calculations for the partial and the total ionization cross sections satisfy the necessary consistency checks to access their consistency and reliability. The consistency checks derived from the fact that the
total electron impact ionization cross section is equal to the sum of the partial ionization cross sections. This condition is used in the summation method for calibration purposes. In low energy limits, close to the onset of ionization, the shapes of the partial and total electron impact ionization cross section curves are governed by the certain threshold law [17]. The precise shape of the cross section in this region is especially important in determination of respective ionization thresholds, to compare with those derived by other means. The most surprising result in the present study is that the relative magnitude of the partial ionization cross sections is quite different from those of ordinary polyatomic molecules [4].

In conclusion, the modified Jain-Khare semiempirical formulation for the calculations for the partial ionization cross sections of molecules by electron impact has been extended and generalized to the calculations of the cross sections for the single and multiple ionization of fullerene C_{60}. Comparison of the calculated partial ionization cross sections for the production of singly and doubly charged ions following the electron impact on C_{60}, with the experimental and the theoretical data show a satisfactory agreement (within the composite error bars) in the complete energy range covered in the calculations. For triply charged ion, a considerable disagreement with the established experimental and theoretical data, except low energy region, has been noticed. The present extended approach also provides the framework to develop predictive capabilities that allow us to evaluate the partial differential and partial integral cross sections for fullerenes.

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