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International Journal of Mass Spectrometry 223–224 (2003) 703–711

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

A semi-empirical method for the calculation of cross sections for the electron-impact ionization of negatively charged fullerenes

P. Scheier[a,*], H. Deutsch[b], K. Becker[c], T.D. Märk[a,1]

[a] Institut für Ionenphysik, Leopold-Franzens Universität, A-6020 Innsbruck, Austria
[b] Institut für Physik, Ernst-Moritz-Arndt Universität, D-17487 Greifswald, Germany
[c] Department of Physics, Stevens Institute of Technology, Hoboken, NJ 07030, USA

Received 12 June 2002; accepted 26 June 2002

Abstract

We extended our previously developed semi-empirical method for the calculation of cross section functions (absolute value and energy dependence) for the electron-impact ionization of the neutral fullerenes C_{60} and C_{70} and of the ionized fullerenes ${C_{60}}^{q+}$ ($q = 1$–3) to the calculation of multiple ionization processes of the negatively charged fullerenes ${C_m}^-$ ($m = 60$, 70, and 84). Systematic trends and tendencies are highlighted and a detailed comparison with available experimental data is made. Predictions are also made for cross sections for the ionization of the neutral fullerene C_{84} up to charge state $z = 6$. An attempt is made to elucidate the origin of an experimentally observed scaling law that relates the ratio of the measured ionization cross sections of different fullerenes m and m', $\sigma_{-1,z}(m)/\sigma_{-1,z}(m')$, where the subscript "$-1$" refers to the fact that the initial target is negatively charged and "z" denotes the charge state of the final ion, to the corresponding ratio of the geometric cross sections $\sigma_{\mathrm{geom}}(m)/\sigma_{\mathrm{geom}}(m')$ to the power "z". (Int J Mass Spectrom 223–224 (2003) 703–711)

Keywords: Fullerenes; Ionization cross sections; Cluster; Electron impact

1. Introduction

Recently, we introduced a semi-empirical method for the calculation of absolute cross section functions for the electron-impact ionization of the neutral and positively charged fullerenes C_{60} and C_{70} [1,2] which yielded results that were in good agreement with available experimental data [3–5]. Our method was initially developed for the calculation of partial cross section functions (absolute value and energy dependence) for the single electron-impact ionization of several neutral and ionized fullerenes ${C_{60}}^{q+}$ ($q = 0$–3) [1]. Subsequently, we successfully extended this approach to the calculation of multiple electron-impact ionization cross sections of the neutral fullerenes C_{60} and C_{70} [2]. The necessity to rely on a semi-empirical approach to the calculation of electron-impact ionization cross section functions for fullerenes that are in reasonably good agreement with experimentally determined cross sections comes from the fact that more rigorous calculation methods [6–9], which yield reasonably good agreement (to within 20%) with measured data for a large number of simple as well as complex molecules, yield very poor results

* Corresponding author. E-mail: paul.scheier@uibk.ac.at
1 Present address: Department of Plasma Physics, Comenius University, SK-84248 Bratislava, Slovakia.

PII S1387-3806(02)00943-0

in the case of fullerenes. Specifically, none of the more rigorous methods [6–9] is capable of reproducing the experimental data that are available for fullerenes.

In the present paper, we report the extension of our previously developed approach to the calculation of multiple electron-impact ionization cross sections of the negatively charged fullerenes C_m^- ($m = 60$, 70, 84) for which reliable experimental data have also been reported recently [10]. Predictions are also made for cross sections for the ionization of the neutral fullerene C_{84} up to a charge state $z = 6$ of the product ion. An attempt is made to provide an explanation for a scaling law found by the authors of [10] that relates measured cross section ratios to ratios of the geometrical cross sections of the targets.

2. Background

In our previous paper [2], we introduced a formula for the calculation of the partial ionization cross section $\sigma(X_m{}^{z+}, E)$ for the ionization of a fullerene X_m consisting of m monomers ($m = 60$, 70) to a final charge state z ($z = 1$–6) as a function of the impact energy E of the form

$$\sigma(X_m{}^{z+}, E) = m^{2a} \cdot \mathrm{e}^{-b_1} \cdot \mathrm{e}^{-b_2} \cdot \sigma_{\mathrm{tot}}(X, E^*) \cdot F_{\mathrm{cage}}(E) \qquad (1)$$

with

$$E^* = E - [E_0 + (\mathrm{IP}_{\text{cluster–ion}} - \mathrm{IP}_{\mathrm{monomer}})] \qquad (2a)$$

for ionic targets and multiple ionization of neutral fullerenes.

$$E^* = E - E_0 \qquad (2b)$$

for single ionization of neutral fullerenes.

The exponent "a" (taken from [11]) results from a relationship between the radius of the cluster R_{cluster} and the radius of the monomer r_{monomer} of the form

$$R_{\mathrm{cluster}} = m^a \cdot r_{\mathrm{monomer}} \quad \text{(see [12])}, \qquad (3)$$

and the other quantities in Eq. (1) have the following meaning:

(i) The exponent "b_1" determines the so-called "structure factor", $\exp(-b_1)$. The structure factor leads to a reduction in the maximum fullerene ionization cross section compared to the value m^{2a} predicted by the simple "cluster" formula [12]. The reduction arises from the fact that multiple single ionization processes can occur when a fullerene is ionized by an incident electron which will reduce the cross section for the particular channel under consideration. The exponent "b_1" was found to be a function of the cluster size "m" [2].

(ii) The exponent "b_2" determines the so-called "ionization factor", $\exp(-b_2)$. The ionization factor was found to decline exponentially for $z > 1$ for both C_{60} and C_{70} [2] and is different for fullerenes of different size m. We note that a similar exponential behavior was also found earlier in the case of the multiple ionization of atoms [13].

(iii) The energy dependence $F_{\mathrm{cage}}(E)$ describes the deviation of the cross section shape of the fullerene X_m from the cross section shape of the monomer X. Different functions $F_{\mathrm{cage}}(E)$ apply to C_{60} and C_{70} and to the various values of the final charge state z (see [2] for details).

(iv) The energy shift E^* as defined in Eqs. (2a) and (2b) was introduced as a way to properly describe the low energy dependence of the cross sections. Here E is the kinetic energy of the primary electron, and E_0 describes the energy loss due to inelastic scattering. The values for the ionization energies (IPs) can be found in [5]. The combined effect of the function $F_{\mathrm{cage}}(E)$ and the use of the "shifted" energy E^* in the monomer cross section is a shift of the maximum in the fullerene ionization cross section to higher energies in conjunction with a broadening of the region of the cross section maximum compared to the monomer ionization cross section and a more gradual decline of the fullerene cross section with increasing impact energy at higher impact energies (above about 100 eV).

(v) The quantity $\sigma_{\mathrm{tot}}(X, E^*)$ refers to the total ionization cross section of the monomer X as a function of the "shifted" energy E^*. The ionization cross section of atomic carbon is taken from the paper of Brook et al. [14].

The application of Eq. (1) to the cases discussed in the previous papers [1,2] required the empirical determination of the various parameters (structure factor, ionization factor, function $F_{\text{cage}}(E)$, and shifted energy E^*) from a sub-set of the measured experimental data [3–5] followed by the subsequent application of Eq. (1) to all cases for which experimental data are available. In all but two cases, good agreement was found between the prediction of our semi-empirical formula and the measured data. In one case, the single ionization of C_{60}^{2+}, the discrepancy was attributed to the presence of indirect ionization processes [2] and in the second case, the production of C_{70}^{6+} ions following electron impact on C_{70}, the disagreement was attributed to extremely low signal rates in the experiment [2].

3. Extension to negatively charged fullerenes C_m^- (m = 60, 70, 84)

The application of Eq. (1) to the multiple ionization of the negatively charged fullerenes C_{60}^-, C_{70}^-, and C_{84}^- requires the extension of the structure factor $\exp(-b_1)$, the ionization factor $\exp(-b_2)$, and the energy shape $F_{\text{cage}}(E)$ to these targets and processes.

Since the structure factor depends only on the size of the targets, the structure factors for C_{60}^- and C_{70}^- are the same as those derived in [2]. The structure factor for C_{84} is obtained from the double ionization process $C_{84}^- \rightarrow C_{84}^+$ as there are no experimental data available for the single ionization of neutral C_{84}. Previously, in the case of C_{60} and C_{70} [1,2] the structure factor was obtained from the measured single ionization cross section data of the neutral fullerene target. The structure factor as a function of target size is shown in Fig. 1. The line drawn through the three points is a single-exponential fit and serves only as a guide to the eye. We note that in [2], where we only dealt with two structure factors for $m = 60$ and 70, respectively, we connected the two factors by a straight line and extrapolated this line to lower values of m. This extrapolation intersected the line representing the maximum structure factor of unity around $m = 20$ and we speculated that it is around this cluster size that the fullerene cage structure of carbon clusters as opposed to a simple ring structure begins to play a role. This speculation was supported by the arguments of Jensen and Koch [15] who suggested that the fullerene cage structures become possible around $m = 24$. It is obvious from Fig. 1 that this linear extrapolation to lower values of m cannot be extended in the same fashion to $m = 84$ and larger values of m. The linear extrapolation of the structure factor to larger m values would reach a value of zero around $m = 90$ (dashed line in Fig. 1) which, in turn, would correspond to a physically unrealistic vanishing cross section. Clearly, additional experimental studies of the single ionization of C_{84} and other fullerenes would be desirable to determine the structure factor as a function of fullerene size over a wider range of m values.

The ionization factors were derived from the experimental data for the double and quadruple ionization of the C_m^- species, i.e., from the cross sections for the formation of C_m^+ and C_m^{3+} ions, respectively [10] and extrapolated to the formation of C_m^{2+} and C_m^{4+} (for which no experimental data have been reported

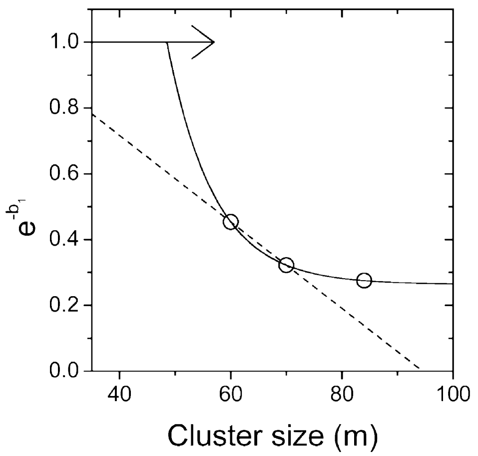

Fig. 1. Structure factor "$\exp(-b_1)$" as a function of fullerene size m. The three data points correspond to C_{60}, C_{70}, and C_{84}. (See text for details of the extrapolation.)

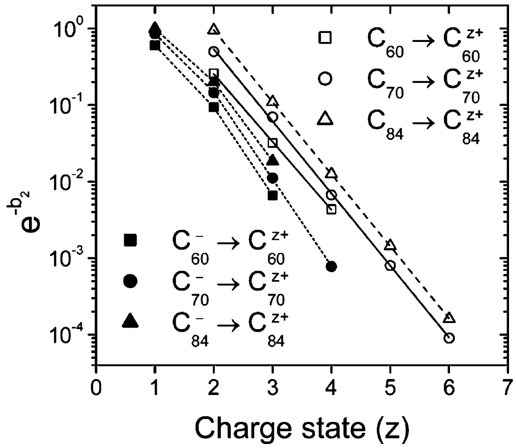

Fig. 2. Ionization factor "exp($-b_2$)" for C_{60}^-, C_{70}^-, and C_{84}^- as a function of the charge state z of the ion produced. Also shown are the previously determined ionization factors for C_{60} and C_{70} and the interpolated ionization factors for C_{84} (see text for details).

yet). The ionization factors derived from this procedure are shown in Fig. 2 together with the ionization factors for the ionization of the neutral fullerenes C_{60} and C_{70}. We note that the ionization factors for the negatively charged fullerenes C_m^- (m = 60, 70, and 84) follow a straight line above $q = 2$, but display a change in the slope towards $q = 1$ which one can attribute to the fact that negatively charged fullerenes represent targets that are less stable than the neutral fullerenes. Also included in Fig. 2 are ionization factors for the neutral C_{84} fullerene. Since no experimental data are available for C_{84}, the ionization factors were determined by interpolation, i.e., a straight line, parallel to the lines for C_{60} and C_{70} was assumed for C_{84} with an appropriate off-set inferred here from the data for the negatively charged fullerenes.

The energy shape function $F_{\mathrm{cage}}(E)$ for the double ionization was obtained from the measured data for C_{84}^- for this process [10] and then used without further modification for the other two fullerenes as well. The numerical values of the function $F_{\mathrm{cage}}(E)$ for the double ionization of the C_m^- species are summarized in Table 1. For all other cases discussed here, i.e., for the three- and four-fold ionization of all C_m^- species, the function $F_{\mathrm{cage}}(E)$ is identical to unity for all impact energies up to 1000 eV (see also [1,2] for higher values of z).

Table 1
Function $F_{\mathrm{cage}}(E)$ for the double ionization of C_m^- (m = 60, 70, 84)

Electron energy (eV)	$F_{\mathrm{cage}}(E)$
>100	1.000
200	1.064
300	1.100
400	1.130
500	1.160
600	1.190
700	1.230
800	1.290
900	1.400
1000	1.570

4. Results and discussion

In this section, we use the explicit functional forms of Eq. (1) applicable to the calculation of the absolute cross sections for the multiple ionization of the negatively charged fullerenes C_m^- (m = 60, 70, 84) and compare the calculated cross sections with measured data from [10].

4.1. $e^- + C_m^- \rightarrow C_m^+ + 3e^-$; m = 60,70,84

Eq. (1) in conjunction with the data derived in Section 3 above yields the following formulas for the double ionization of C_m^- ($m = 60, 70, 84$), i.e., the formation of C_m^+ ions ($z = 1$):

$$\sigma_{60^-}(E, z = 1) = 60^{0.786} \cdot \mathrm{e}^{-0.790} \cdot \mathrm{e}^{-0.4997} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{4a}$$

$$\sigma_{70^-}(E, z = 1) = 70^{0.786} \cdot \mathrm{e}^{-1.132} \cdot \mathrm{e}^{-0.1577} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{4b}$$

$$\sigma_{84^-}(E, z = 1) = 84^{0.786} \cdot \mathrm{e}^{-1.2897} \cdot \mathrm{e}^{-0.0} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{4c}$$

Here $E^* = E - 24$ eV and the explicit form of the function $F_{\mathrm{cage}}(E)$ is given in Table 1. As expected

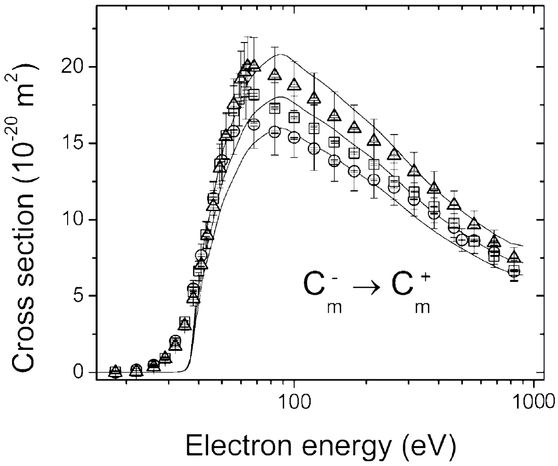

Fig. 3. Calculated cross section for the formation of C_m^+ ($m = 60$, 70, 84) ions following electron impact on C_m^- as a function of electron energy. The calculated cross sections are shown as the solid lines, the experimental data are from [10]. The triangles, squares, and circles denote C_{84}^-, C_{70}^-, and C_{60}^-, respectively.

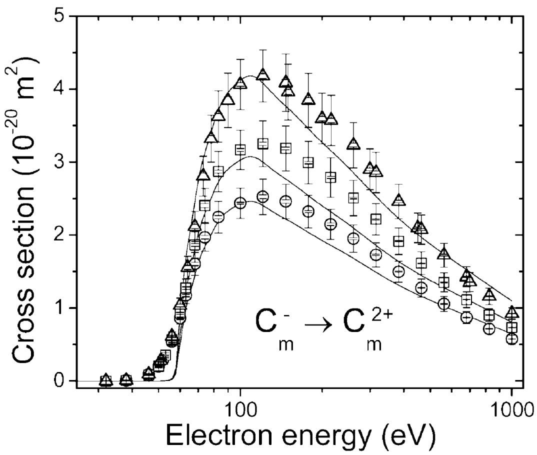

Fig. 4. Calculated cross section for the formation of C_m^{2+} ($m = 60$, 70, 84) ions following electron impact on C_m^- as a function of electron energy. The calculated cross sections are shown as the solid lines, the experimental data are from [10]. The triangles, squares, and circles denote C_{84}^-, C_{70}^-, and C_{60}^-, respectively.

from the discussion in the previous section, the structure factor decreases from C_{60} to C_{70} to C_{84}, whereas the ionization factor increases as one goes to the larger fullerenes. We note that the product of structure factor and ionization factor has the same value of $e^{-1.2897}$ for all three fullerenes. Fig. 3 shows the comparison between the calculated ionization cross sections and the experimental data of [10] for the three fullerenes from threshold to 1000 eV. As can be seen, the agreement is excellent for C_{60}^- and very good for C_{70}^- and C_{84}^- in view of the error bars of the experimental data except for the energy regime very close to threshold.

4.2. $e^- + C_m^- \rightarrow C_m^{2+} + 4e^-$; $m = 60,70,84$

Eq. (1) in conjunction with the data derived in Section 3 above yields the following formulas for the triple ionization of C_m^- ($m = 60$, 70, 84), i.e., the formation of C_m^{2+} ions ($z = 2$):

$$\sigma_{60^-}(E, z = 2) = 60^{0.786} \cdot \mathrm{e}^{-0.790} \cdot \mathrm{e}^{-2.3697} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{5a}$$

$$\sigma_{70^-}(E, z = 2) = 70^{0.786} \cdot \mathrm{e}^{-1.132} \cdot \mathrm{e}^{-1.9278} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{5b}$$

$$\sigma_{84^-}(E, z = 2) = 84^{0.786} \cdot \mathrm{e}^{-1.2897} \cdot \mathrm{e}^{-1.605} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{5c}$$

Here $E^* = E - 45$ eV and the function $F_{\mathrm{cage}}(E)$ is identical to unity for all impact energies. Fig. 4 shows the comparison between the calculated ionization cross sections and the experimental data of [10] for the three fullerenes from threshold to 1000 eV. As can be seen, the agreement is good for all three fullerenes in view of the error bars of the experimental data except for the energy regime very close to threshold. We note that the calculated cross sections tend to lie consistently slightly below the measured data.

4.3. $e^- + C_m^- \rightarrow C_m^{3+} + 5e^-$; $m = 60,70,84$

Eq. (1) in conjunction with the data derived in Section 3 above yields the following formulas for the four-fold ionization of C_m^- ($m = 60$, 70, 84), i.e., the formation of C_m^{3+} ions ($z = 3$):

$$\sigma_{60^-}(E, z = 3) = 60^{0.786} \cdot \mathrm{e}^{-0.790} \cdot \mathrm{e}^{-5.0197} \cdot \sigma_C(E^*) \cdot F_{\mathrm{cage}}(E) \tag{6a}$$

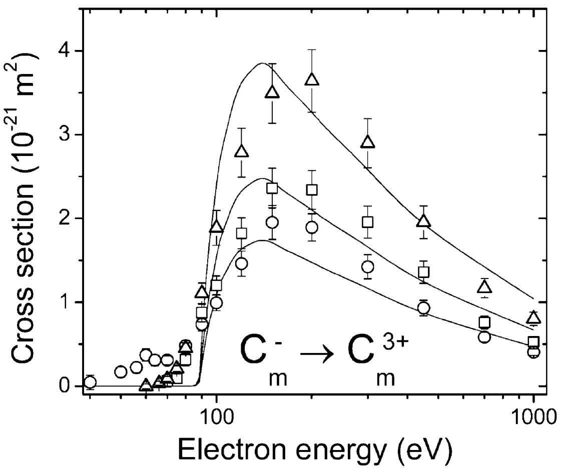

Fig. 5. Calculated cross section for the formation of $C_m{}^{3+}$ ($m = 60$, 70, 84) ions following electron impact on $C_m{}^-$ as a function of electron energy. The calculated cross sections are shown as the solid lines, the experimental data are from [10]. The triangles, squares, and circles denote $C_{84}{}^-$, $C_{70}{}^-$, and $C_{60}{}^-$, respectively.

$$\sigma_{70^-}(E, z = 3) = 70^{0.786} \cdot e^{-1.132} \cdot e^{-4.4457} \cdot \sigma_C(E^*) \cdot F_{\text{cage}}(E) \quad (6b)$$

$$\sigma_{84^-}(E, z = 3) = 84^{0.786} \cdot e^{-1.2897} \cdot e^{-3.9900} \cdot \sigma_C(E^*) \cdot F_{\text{cage}}(E) \quad (6c)$$

Here $E^* = E - 76$ eV and the function $F_{\text{cage}}(E)$ is identical to unity for all impact energies. Fig. 5 shows the comparison between the calculated ionization cross sections and the experimental data of [10] for the three fullerenes from threshold to 1000 eV. As can be seen, the agreement is reasonably good for all three fullerenes in view of the error bars and the scatter of the experimental data.

4.4. $e^- + C_{70}{}^- \rightarrow C_{70}{}^{4+} + 6e^-$

In the case of $C_{70}{}^-$, Hathiramani et al. [10] also reported cross sections for the five-fold ionization of $C_{70}{}^-$, i.e., the formation of $C_{70}{}^{4+}$ ions. If we apply our formalism to this particular case, we obtain the following expression

$$\sigma_{70^-}(E, z = 3) = 70^{0.786} \cdot e^{-1.132} \cdot e^{-7.16} \cdot \sigma_C(E^*) \cdot F_{\text{cage}}(E) \quad (7)$$

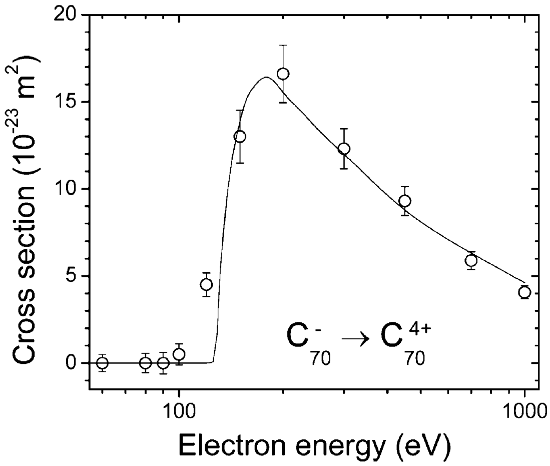

Fig. 6. Calculated cross section for the formation of $C_{70}{}^{4+}$ ions following electron impact on $C_{70}{}^-$ as a function of electron energy. The calculated cross section is the shown as the solid line and the circles denote the experimental data from [10].

Here $E^* = E - 115$ eV and the function $F_{\text{cage}}(E)$ is identical to unity for all impact energies. Fig. 6 shows the comparison between the calculated ionization cross section and the experimental data of [10] from threshold to 1000 eV. As can be seen, the agreement is excellent over the entire range of impact energies.

4.5. Ionization of neutral C_{84} fullerenes up to charge state $z = 6$

Using the basic data for the structure factors and the ionization factors from Figs. 1 and 2, we are now in a position to predict absolute ionization cross sections for the single and multiple ionization of the neutral fullerene C_{84} up to charge state $z = 6$. The calculation follows the procedure outlined in [1,2]. No experimental data have been reported for these processes up to now. The results are shown in Fig. 7. In these calculations, we used the same function $F_{\text{cage}}(E)$ that was used earlier for C_{70} [2].

4.6. Scaling law considerations

Hathiramani et al. [10] found that their measured ionization cross sections of the negatively charged

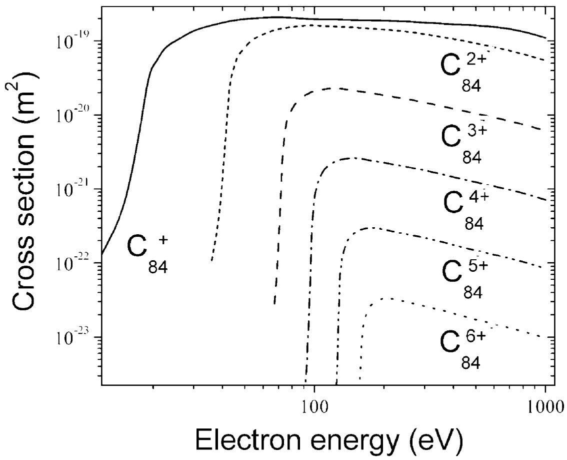

Fig. 7. Calculated cross sections for the formation of singly and multiply charged $C_{84}{}^{z+}$ ions up to charge state $z = 6$ following electron impact on neutral C_{84} fullerenes from threshold to 1000 eV. No experimental data are available for comparison. Further details are given in the text.

fullerenes $C_{60}{}^{-}$, $C_{70}{}^{-}$, and $C_{84}{}^{-}$ could be described by a scaling law of the form

$$\frac{\sigma_{-1,z}(m)}{\sigma_{-1,z}(m')} = \left[\frac{\sigma_{\text{geom.}}(m)}{\sigma_{\text{geom.}}(m')}\right]^{z} \tag{8}$$

where $\sigma_{-1,z}(m)$ and $\sigma_{-1,z}(m')$ denote the ionization cross sections of the negatively charged ("−1") fullerenes m and m' (m, $m' = 60, 70, 84$) to the final charge state "z" and $\sigma_{\text{geom.}}(m)$ and $\sigma_{\text{geom.}}(m')$ refer to the geometric cross sections of the fullerenes m and m'.

In an attempt to understand the origin of this scaling law, we take, for instance, the ratio of the calculated cross sections for the four-fold ionization of $C_{60}{}^{-}$ and $C_{84}{}^{-}$ (see Eqs. (6a) and (6c)) which yields

$$\frac{\sigma_{84^-}(z=3)}{\sigma_{60^-}(z=3)} = \left(\frac{84}{60}\right)^{0.786} e^{+0.53} \tag{9}$$

Using the relation $a^x = \exp(x \ln(a))$ this can be re-written as

$$\frac{\sigma_{84^-}(z=3)}{\sigma_{60^-}(z=3)} = \left(\frac{84}{60}\right)^{0.786} \left(\frac{84}{60}\right)^{1.5752} \tag{10}$$

which takes the approximate form

$$\frac{\sigma_{84^-}(z=3)}{\sigma_{60^-}(z=3)} = \left[\left(\frac{84}{60}\right)^{0.786}\right]^{3} \tag{11}$$

Analyzing the other ratios such as $\sigma_{84^-}(z = 3)/\sigma_{70^-}(z = 3)$ and $\sigma_{70^-}(z = 3)/\sigma_{60^-}(z = 3)$ and extending this comparison to other stages of ionization, one finds a generalized relationship of the form

$$\frac{\sigma_{-1,z}(m)}{\sigma_{-1,z}(m')} = \left[\left(\frac{m}{m'}\right)^{0.786}\right]^{z} \tag{12}$$

where z denotes the final charge state of the ion. In order to relate the ratio of fullerene sizes m and m' in Eq. (12) to the geometric cross section of the respective fullerene, we start from Eq. (3) from which we define the geometric cross section of a fullerene m as

$$\sigma_{\text{geom.}}(m) = \pi(R_{\text{cluster}})^2 = \pi m^{2a}(r_{\text{monomer}})^2 \tag{13}$$

and obtain a cross section ratio for fullerenes of sizes m and m' of the form

$$\frac{\sigma_{\text{geom.}}(m)}{\sigma_{\text{geom.}}(m')} = \frac{[\pi(R_{\text{cluster,m}})^2]}{[\pi(R_{\text{cluster,m'}})^2]} = \left(\frac{m}{m'}\right)^{2a}. \tag{14}$$

In other words, the ratio of the geometric cross sections is given by the ratio of the fullerene sizes m and m' to the power '$2a$'. Thus, it is justified to interpret the ratio $(m/m')^{0.786}$ in Eq. (12) as being proportional to the ratio of the respective geometric cross sections and we have, in fact, derived from the present theoretical considerations a relationship of the form

$$\frac{\sigma_{-1,z}(m)}{\sigma_{-1,z}(m')} = \left[\frac{\sigma_{\text{geom.}}(m)}{\sigma_{\text{geom.}}(m')}\right]^{z} \tag{15}$$

which has already been deduced earlier from the experimental data.

Table 2 summarizes the cross section ratios from the experimental data of [10] together with the geometric cross section ratios, and the cross section ratios based on the present calculation. The geometric cross sections used to determine the ratios listed in Table 1 are based on the well-known radius of C_{60} of 0.5 nm [10] from which equivalent radii for C_{70} and C_{84} were

Table 2
Comparison of cross section ratios obtained from the experimental data of [10], the geometric cross sections, and the results of the present calculation

Cross section ratio	Experiment [10]	Geometric cross section	Present calculation
$\sigma_{-1,1}$ (70)/$\sigma_{-1,1}$ (60)	1.09	1.13	1.13
$\sigma_{-1,1}$ (84)/$\sigma_{-1,1}$ (70)	1.12	1.15	1.15
$\sigma_{-1,1}$ (84)/$\sigma_{-1,1}$ (60)	1.22	1.30	1.30
$\sigma_{-1,2}$ (70)/$\sigma_{-1,2}$ (60)	1.28	1.20	1.25
$\sigma_{-1,2}$ (84)/$\sigma_{-1,2}$ (70)	1.27	1.24	1.36
$\sigma_{-1,2}$ (84)/$\sigma_{-1,2}$ (60)	1.64	1.49	1.70
$\sigma_{-1,3}$ (70)/$\sigma_{-1,3}$ (60)	1.44	1.27	1.42
$\sigma_{-1,3}$ (84)/$\sigma_{-1,3}$ (70)	1.50	1.33	1.56
$\sigma_{-1,3}$ (84)/$\sigma_{-1,3}$ (60)	2.15	1.70	2.21

determined using the relation [10]:

$$r_n = \left[0.15 + 0.35\left(\frac{n}{60}\right)^{0.5}\right] \text{ in nm for } n = 70, 84 \tag{16}$$

which yields equivalent radii of 0.531 nm for C_{70} and 0.571 nm for C_{84}. As can be seen, with very few exceptions there is good agreement between the three cross section ratios for the two-, three-, and four-fold ionization of the negatively charged fullerenes $C_m{}^-$ ($m = 60, 70, 84$).

However, we note that the scaling law of the form expressed in Eq. (15) is unique to the ionization cross sections of the negatively charged fullerenes as its derivation relies on the fact that the ratio of the products of the respective ionization factors and structure factors in Eqs. 6(a–c) can be reduced to the expression given in Eq. (12). This is no longer the case for the ionization and structure factors that are applicable to the ionization of neutral and positively charged fullerenes (see [1,2]). Thus, there is no basic physics principle that stipulates the existence of a general scaling law such as the one expressed in Eq. (12) for all fullerenes, but it is a rather fortuitous coincidence that apparently only applies to the ionization of negatively charged fullerenes.

5. Conclusions

We extended our previously developed semi-empirical approach to the calculation of cross sections for the electron-impact ionization of neutral and positively charged fullerenes C_{60} and C_{70} to the calculation of two-, three-, and four-fold ionization cross sections of the negatively charged fullerenes $C_m{}^-$ ($m = 60, 70, 84$) for which reliable experimental data have also been reported recently [10]. Very good agreement between measured and calculated cross sections was found in all cases. In the case of $C_{70}{}^-$ measured cross sections for the five-fold ionization were also reported which agree very well with our calculation. Predictions are also made for cross sections for the ionization of the neutral fullerene C_{84} up to a charge state $z = 6$ of the product ion. An attempt was made to provide an explanation for the scaling law found by the authors of [10] that relates measured cross section ratios to ratios of the geometrical cross sections of the targets. It was found that the simple form of the scaling law described in [10] does only hold for the negative fullerenes as targets and cannot readily be generalized for neutral and ionized fullerene targets.

Acknowledgements

This work was partially supported by the Österreichischer Fonds zur Förderung der Wissenschaftlichen Forschung, Wien, Austria and the EU Commission network programme, Brussels. One of us (K.B.) wishes to acknowledge partial financial support from the U.S. National Aeronautics and Space Administration (NASA) through award NAG5-8971.

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