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International Journal of Mass Spectrometry 223–224 (2003) 253–261

International Journal of Mass Spectrometry

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Calculations of partial electron-impact cross sections for the multiple ionization of fullerenes using a semi-empirical method

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

[a] *Institut für Physik, Ernst-Moritz-Arndt Universität, D-17487 Greifswald, Germany*
[b] *Institut für Ionenphysik, Leopold-Franzens Universität, Technikerstr. 25, A-6020 Innsbruck, Austria*
[c] *Department of Physics, Stevens Institute of Technology, Hoboken, NJ 07030, USA*

Received 15 March 2002; accepted 12 April 2002

Abstract

We extended and generalized our previously developed semi-empirical method for the calculation of cross section functions (absolute value and energy dependence) for the single electron-impact ionization of the neutral and ionized fullerenes C_{60}^{q+} ($q = 0$–3) to the calculation of multiple ionization processes of the neutral fullerenes C_{60} and C_{70}. Systematic trends and tendencies are highlighted and a detailed comparison with available experimental data is made. An attempt is also made to predict how the calculated cross sections scale with the size of the cluster/fullerene. (Int J Mass Spectrom 223–224 (2003) 253–261)

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

1. Introduction

Reliable calculations of total and partial electron-impact ionization cross section functions for clusters and fullerenes that are in reasonably good agreement with experimentally determined cross sections remain a challenging task even though calculations of absolute total single ionization cross sections for many molecules and their energy dependence using semi-rigorous methods such as the BEB method of Kim and coworkers [1,2] and the DM formalism [3] reveal reasonably good agreement (to within 20%) with measured data for a large number of simple as well as complex molecules [1–3]. Various theoretical models have been applied to the quantitative characterization of the ionization properties of clusters and fullerenes, i.e., to the calculation of their absolute ionization cross sections (see e.g., [4–8] and references therein). However, none of the methods appear to succeed in reproducing the experimental data that are available for the few targets studied so far (see the references given in [8]). In this context, we will not distinguish between “clusters” and “fullerenes”. Both will be considered “ensembles of monomers” encompassing a large number of constituents and geometrical structures ranging from a hard sphere packing arrangement to a hollow cage structure.

In a previous paper [9], we introduced a semi-empirical approach to the calculation of cross section functions (absolute value and energy dependence) for

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

1387-3806/02/$ – see front matter
PII S1387-3806(02)00861-8

the *single* electron-impact ionization of several neutral and ionized fullerenes C_{60}^{f+} ($q = 0$–3), for which reliable experimental data have been reported. In particular, our approach modified the simplistic assumption that the ionization cross section of a cluster/fullerene is given as the product of the monomer ionization cross section and a factor m^a, where "m" is the number of monomers in the ensemble and "a" is a constant. A comparison between our calculations and the available experimental data revealed good agreement for $q = 0$, 1 and 3, but only poor agreement in the case of the single ionization of C_{60}^{2+} ($q = 2$) where additional indirect ionization processes are present.

In the present paper, we report the extension and generalization of our previous approach to the calculation of *multiple* electron-impact ionization cross sections of the neutral fullerenes C_{60} and C_{70}. Comparisons are made with available experimental data, systematic trends are highlighted, and an attempt is made to develop predictive capabilities that allow us to calculate absolute cross section functions for multiple ionization processes and for other fullerenes (e.g., C_{84}) for which no experimental data are available as yet.

2. Background

In our previous paper [9] we introduced a partial ionization cross section formula $\sigma(X_m, E)$ for the single ionization of a cluster/fullerene X_m consisting of m monomers as a function of the impact energy E of the form

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

where $\sigma_{\mathrm{tot}}(X, E^*)$ refers to the total ionization cross section of the monomer, the exponent "a" results from a relationship between the radius of the cluster R_{cluster} and the radius of the monomer R_{monomer} of the form

$$R_{\mathrm{cluster}} = m^a R_{\mathrm{monomer}} \qquad (1b)$$

see [10], and the quantities e^{-b}, $F_{\mathrm{cage}}(E)$, and E^* have the following meaning:

(i) The factor e^{-b} ($b > 0$) reflects a reduction in the maximum fullerene ionization cross section compared to the value m^{2a} predicted by the simple "cluster" formula [10]. 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" is a function of the cluster size "m" and of the charge state "z". The feasibility of the application of such a function of the charge state was demonstrated successfully earlier in the case of the single electron-impact ionization of the neutral and ionized fullerenes C_{60}^{f+} ($q = 0$–3) [9]. It was already noted in that paper [9] that it may be advantageous to express the constant "b" as the sum of two constants $b = b_1 + b_2$ and that the factor "e^{-b_1}" can be interpreted as a "structure factor".

(ii) The energy dependence $F_{\mathrm{cage}}(E)$ describes the deviation of the cross section shape of the cluster/fullerene X_m from the cross section shape of the monomer X. The function $F_{\mathrm{cage}}(E)$ has a similar shape for both clusters (see [11,12]) and fullerenes (see [13–15]; for more details regarding the function $F_{\mathrm{cage}}(E)$, see [9]).

(iii) The energy shift E^* was introduced as a way to properly describe the low energy dependence of the cross sections; E^* was defined as

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

where E is the kinetic energy of the primary electron, and E_0 describes the energy loss due to inelastic scattering. The appropriate values for the ionization energies (IPs) can be found in [16,17]. It should be noted that in Eq. (2) the difference of the ionization energies "$\mathrm{IP}_{\mathrm{cluster\text{-}ion}} - \mathrm{IP}_{\mathrm{monomer}}$" is applicable for ionic targets and for the multiple ionization of neutral clusters/fullerenes. Eq. (2) reduces to the simple form $E^* = E - E_0$ in the case of the single ionization of neutral targets.

The combined effect of the function $F_{\mathrm{cage}}(E)$ and 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).

We now want to extend and generalize Eq. (1a) for the case of the multiple ionization of neutral C_{60} and other fullerenes and derive a method that will allow us to describe the different energy dependences of the partial cross sections which have been measured for various fullerene targets and multiple ionization processes ([13,16,18] and references therein). We will, in particular, attempt to describe the influence of the number of monomers, m, on the structure factor "e^{-b_1}".

3. Theoretical method

We start by writing formula (1) in a slightly different way as

$$\sigma(X_m{}^{z+}, E) = m^{2a}\, e^{-b_1}\, e^{-b_2}\, \sigma_{tot}(X, E^*) F_{cage}(E) \quad (3)$$

with

$$E^* = E - [E_0 + (IP_{cluster\text{-}ion} - IP_{monomer})]$$
for multiple ionization of neutral fullerenes (4a)

$$E^* = E - E_0$$
for single ionization of neutral fullerenes (4b)

Here the target can be an arbitrary neutral fullerene X_m consisting of m monomers and the (final) charge state z can be 1, 2, 3, . . . , denoting single, double, triple, etc. . . . ionization processes. The exponent "$2a$" is taken from [6]. The exponent "b_1" for $C_{60}{}^{z+}$ is taken from our previous paper [9] and was determined from the single ionization cross section data of C_{60}. Similarly, the exponent "b_1" for the case of $C_{70}{}^{z+}$ is determined from the experimental data of [13] for the single ionization cross section of C_{70}. Fig. 1 shows the structure factor "e^{-b_1}" for $m = 60$ and 70 as the two circles. If we extrapolate the straight line that connects these two points to lower values of m, it intersects the line defined by $e^{-b_1} = 1$ (or $b_1 = 0$, i.e., no effect of the structure factor on the calculated cross section!) around $m = 20$. This would indicate that the fullerene

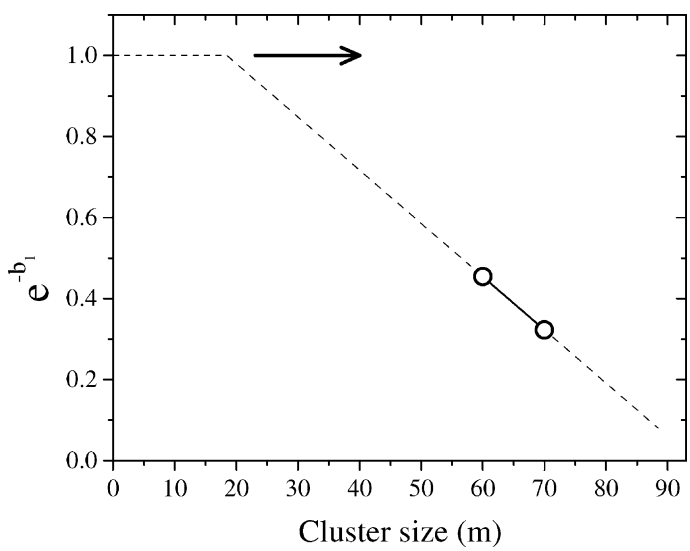

Fig. 1. Structure factor "e^{-b_1}" as a function of cluster/fullerene size m. The two data points correspond to C_{60} and C_{70}. The linear extrapolation of the straight line through these data points to smaller values of m intersects the line corresponding to $e^{-b_1} = 1$ or $b_1 = 0$ (i.e., no influence of the structure factor on the calculated cross section!) around $m = 20$.

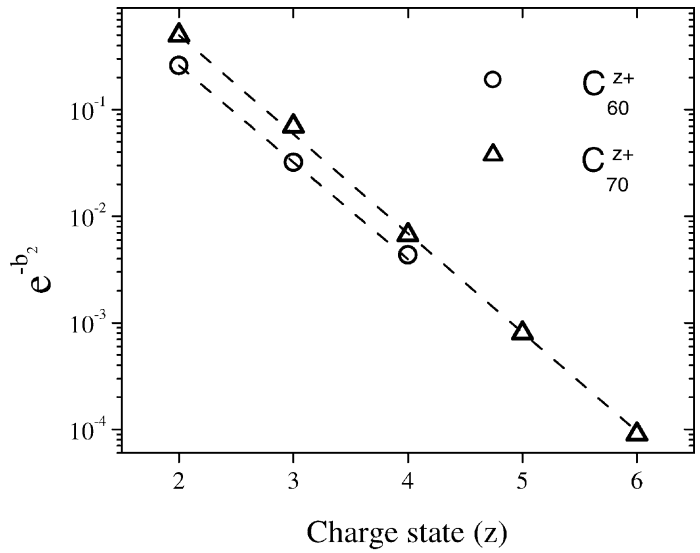

Fig. 2. Ionization factor "e^{-b_2}" as a function of the charge state z for C_{60} and C_{70} in the range $z = 2$–6.

cage structure begins to impact the ionization cross section around C_{20}. It is interesting to note that Jensen and Koch [19] raise the question of "ring structure" vs. "fullerene structure" for C_m compounds for the C_{24} compound. Thus, our extrapolation to $m = 20$ seems to support the notion that the transition from ring structure to fullerene cage structure of carbon clusters may occur around $m = 20$–25. Lastly, the quantity $\sigma_{tot}(X, E^*)$ refers to the total ionization cross section of the monomer X as a function of the "shifted" energy E^*.

The factor "e^{-b_2}" is determined from the experimental data of [13,16]. As can be seen in Fig. 2, the factor "e^{-b_2}", which may be referred to as "ionization factor", declines exponentially for $z > 1$ for both C_{60} and C_{70}. We note that a similar exponential behavior was also found earlier in the case of the multiple ionization of atoms [20]. The various ionization energies $IP_{cluster\text{-}ion}$ are taken from [16,17] and the atomic cross section $\sigma_{tot}(X, E^*)$ from [21].

Different functions $F_{cage}(E)$ apply to C_{60} and C_{70} and to the various values of z. These functions are summarized in Table 1 and for easy reference also in Fig. 3. In the case of the single ($z = 1$) and double ($z = 2$) ionization of, respectively C_{60} and C_{70} the functions $F_{cage}(E)$ were obtained by a comparison with measured cross section shapes [13,16]. For $z > 2$, $F_{cage}(E)$ is identical to 1 for both C_{60} and C_{70} which

Table 1
Summary of energy dependence $F_{cage}(E)$ for various targets

Electron energy (eV)	$F_{cage}(E)$			
	C_{60}^+	C_{60}^{2+}	C_{70}^+	C_{70}^{2+}
Up to 80	1.00	1.00	1.00	1.00
90	1.02	1.00	1.01	1.03
100	1.10	1.00	1.03	1.05
150	1.30	1.05	1.15	1.14
200	1.45	1.08	1.26	1.22
300	1.73	1.11	1.48	1.31
400	1.89	1.14	1.65	1.35
500	2.05	1.15	1.82	1.35
600	2.20	1.15	1.95	1.35
700	2.34	1.15	2.03	1.35
800	2.42	1.15	2.08	1.35
900	2.50	1.15	2.10	1.35
1000	2.56	1.15	2.10	1.35

Even though the function $F_{cage}(E)$ for C_{60}^+ is not being used in the present calculations, it has been included here for reasons of comparison.

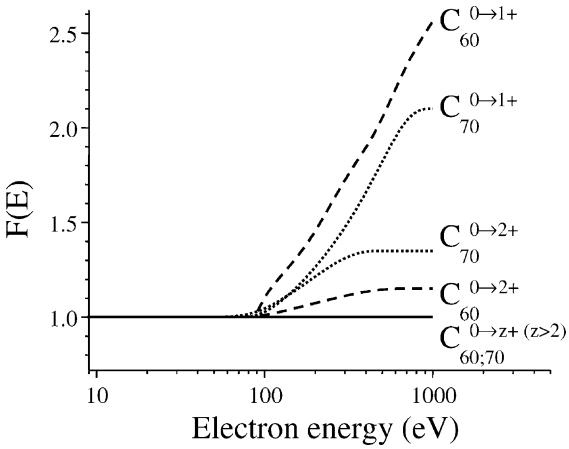

Fig. 3. Function $F_{cage}(E)$ as a function of E for the various fullerenes and charge states (see also Table 1).

was also verified on the basis of measured cross section shapes [13,16].

4. Results and discussion

In this section, we use the explicit functional forms of Eq. (3) that allow us to calculate the absolute ionization cross sections for a variety of single and multiple ionization processes of the fullerenes C_{60} and C_{70} and compare the calculated cross sections with measured data from [13,16]. The various parameters that appear in Eq. (3) for the different cases are summarized in Table 2. The energy dependences $F_{cage}(E)$ for the various cases are listed in Table 1 and are also shown in Fig. 3.

4.1. $e^- + C_{70} \rightarrow C_{70}^+ + 2e^-$

It is illustrative to compare our present calculation for the single ionization of C_{70} with our previous formula for the single ionization of C_{60} [9]

$$\sigma_{60^+}(E) = 60^{0.786}\, e^{-1.045}\, \sigma_C(E^*) F_{cage}(E, C_{60}) \quad (5)$$

Here we also included the specific target—C_{60} in this case—as a label in the energy dependence term $F_{cage}(E)$. Our present formula for C_{70} has the explicit form (see Table 2).

$$\sigma_{70^+}(E) = 70^{0.786}\, e^{-1.132}\, \sigma_C(E^*) F_{cage}(E, C_{70}) \quad (6)$$

The factor m^{2a} increases the C_{70} cross section by about 13%. However, this increase is reduced somewhat by the slightly smaller structure factor for C_{70}. The slight difference in the structure factor is the result of the m-dependence of this quantity (Fig. 1). This results in an overall increase of the maximum in the C_{70} single ionization cross section of about 3.5% over the C_{60} cross section. In addition, there is a slight difference in the energy dependence of the two cross section functions. As can be seen in Fig. 4, the agreement between the calculated single C_{70} ionization cross section according to formula (6) and the measured data [13] is excellent from threshold to 1000 eV.

4.2. $e^- + C_{70} \rightarrow C_{70}^{z+} + (z+1)e^-$; $z = 2$–6

The results for the cross sections for the formation of C_{70}^{z+} ions ($z = 2$–6) following electron impact on C_{70} are summarized in Figs. 5–9. As can be seen, our

Table 2
Summary of relevant quantities for the calculation of ionization cross sections

Number of monomers "m"	Charge state "$z+$"	Exponent "$2a$"	Structure factor "b_1"	Exponent "b_2"	Energy "E_0" (eV)	Ionization energy "$IP_{cluster\text{-}ion}$" (eV)	Ionization energy "$IP_{monomer}$" (eV)
60	2	0.786	0.790	1.347	5	34	11.26
60	3	0.786	0.790	3.442	5	60	11.26
60	4	0.786	0.790	5.438	5	84	11.26
70	1	0.786	1.132	0	5	–	–
70	2	0.786	1.132	0.693	5	35	11.26
70	3	0.786	1.132	2.659	5	65	11.26
70	4	0.786	1.132	5.006	5	90	11.26
70	5	0.786	1.132	7.131	5	120	11.26
70	6	0.786	1.132	9.316	5	150	11.26

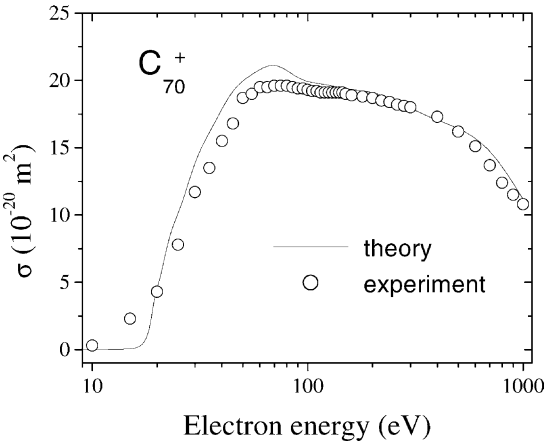

Fig. 4. Calculated cross section for the formation of C_{70}^{+} ions following electron impact on C_{70} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13].

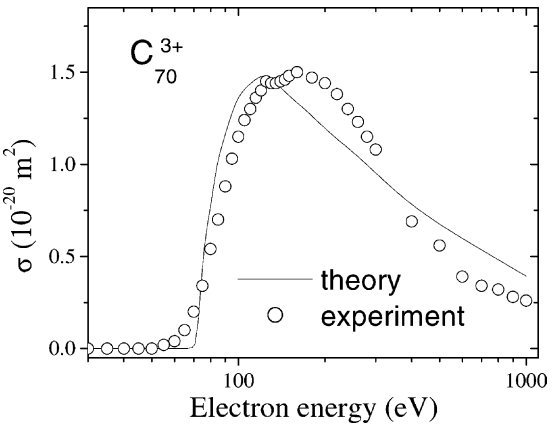

Fig. 6. Calculated cross section for the formation of C_{70}^{3+} ions following electron impact on C_{70} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13].

calculations based on formula (3) in conjunction with the parameters summarized in Tables 1 and 2 provide a very good description of the absolute values of the measured cross sections for these processes [13,16] for $z = 2$–5. However, there is an increasing discrepancy between the calculated and measured cross section shapes with increasing z. At higher z-values, the calculated cross sections peak increasingly at a lower impact energy compared to the measured cross sections. In the case of $z = 4$, it is also apparent that the calculated cross section declines more gradually than the measured cross section.

The case of $z = 6$ (Fig. 9) is noteworthy, as there is a dramatic discrepancy between our calculation and the measured data [16]. The experimental data are smaller than the calculated data by a factor of 20 (!). This is difficult to explain and may suggest that ei-

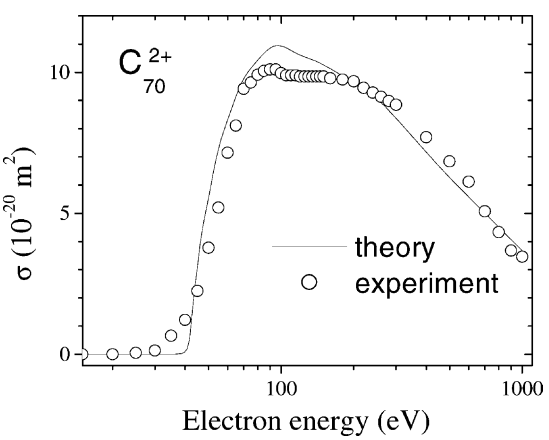

Fig. 5. Calculated cross section for the formation of C_{70}^{2+} ions following electron impact on C_{70} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13].

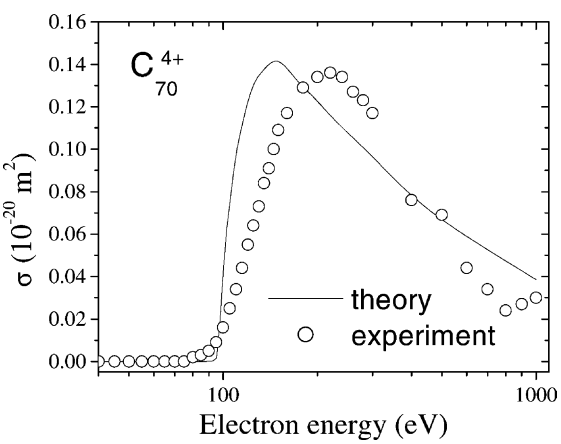

Fig. 7. Calculated cross section for the formation of C_{70}^{4+} ions following electron impact on C_{70} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13].

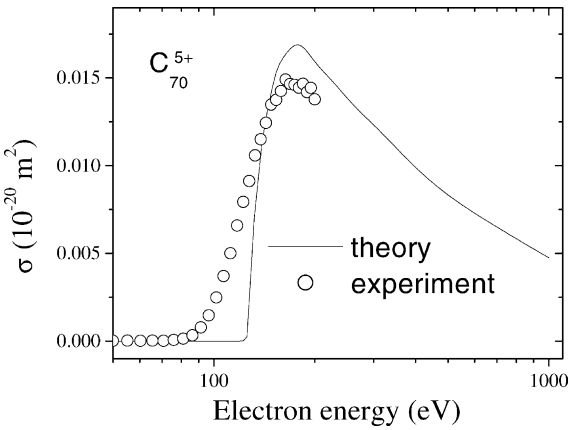

Fig. 8. Calculated cross section for the formation of C_{70}^{5+} ions following electron impact on C_{70} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [16].

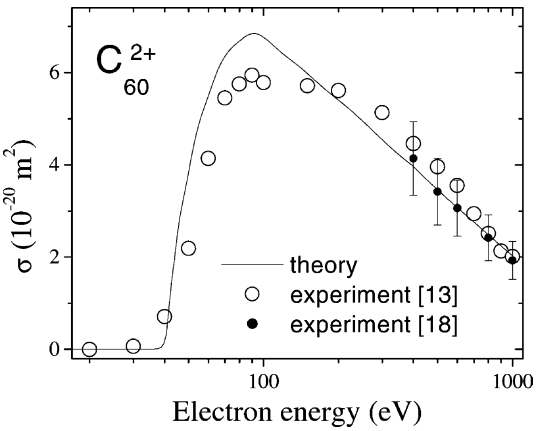

Fig. 10. Calculated cross section for the formation of C_{60}^{2+} ions following electron impact on C_{60} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13] (open circles) and [18] (filled circles).

ther there were some problems with the experimental data or there is a new effect that dominates this particular ionization process that is not included in our description.

4.3. $e^- + C_{60} \rightarrow C_{60}^{z+} + (z+1)e^-$; $z = 2$–4

The single ionization of C_{60} was already discussed in detail in our earlier paper [9] and will not be reiterated here. The results of our calculations of the cross sections for the formation of C_{60}^{z+} ions (z = 2–4) following electron impact on C_{60} are summarized in Figs. 10–12. As can be seen, the same trend that was obvious in the case of C_{70} for z = 2–4 is also found here. The calculations reproduce the absolute values of the measured cross sections quite well in all cases, but the same systematic discrepancies in the cross section shapes for higher values of z that were

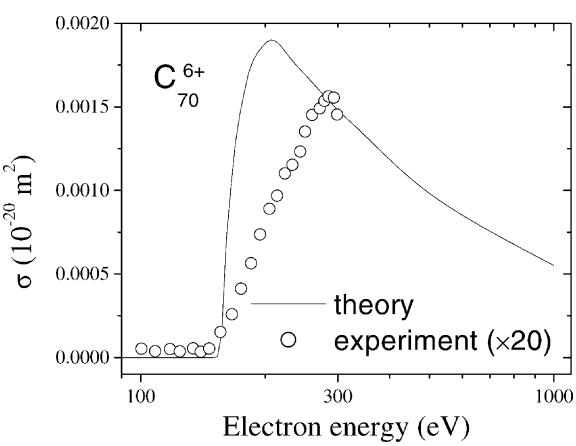

Fig. 9. Calculated cross section for the formation of C_{70}^{6+} ions following electron impact on C_{70} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [16].

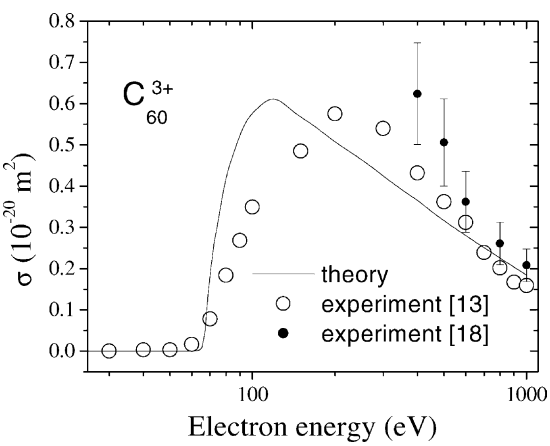

Fig. 11. Calculated cross section for the formation of C_{60}^{3+} ions following electron impact on C_{60} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13] (open circles) and [18] (filled circles).

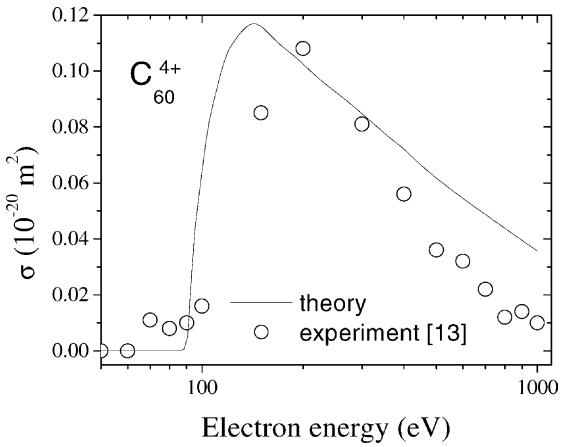

Fig. 12. Calculated cross section for the formation of C_{60}^{4+} ions following electron impact on C_{60} as a function of electron energy. The calculated cross section is shown as the solid line, the experimental data are from [13].

observed for C_{70} are also apparent here in the case of C_{60}.

5. Conclusions

We extended and generalized our previous semi-empirical approach to the calculation of cross sections for the single ionization of neutral and ionic C_{60} fullerenes to the calculation of cross sections for the multiple ionization of the neutral fullerenes C_{60} and C_{70}. Comparisons with available experimental data show good agreement between the calculated absolute cross sections and measured data for the formation of C_{60}^{z+} ions ($z = 2$–4) from C_{60} and C_{70}^{z+} ions ($z = 2$–5) from C_{70}. In the case of the formation of C_{70}^{6+} ions we noted a dramatic discrepancy between our calculation and the measured data [16], i.e., the experimental data were smaller than the calculated data by a factor of 20 (!), a fact for which we have no simple explanation. In terms of the calculated cross section shapes, we found a slightly increasing discrepancy between the calculated and measured cross section shapes with increasing z. At higher z-values, the calculated cross sections peak increasing at a lower impact energy compared to the measured cross sections. Our extended formalism also provides the framework to develop predictive capabilities that allow us to calculate absolute cross section functions for multiple ionization processes and for other fullerenes (e.g., C_{84}) for which no experimental data are available as yet, provided reasonable assumptions and/or extrapolations can be made regarding the ionization factor, the structure factor, and the energy function for the target in question.

Acknowledgements

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

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