Electron Impact Ionization of C_{60}

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Absolute partial and total cross sections for the electron impact ionization of C_{60} have been measured using a novel approach for the absolute calibration. The results obtained reveal not only an anomalous large parent ion cross section (as compared to the other ionization channels), but also anomalies for the production of multiply charged parent and fragment ions. This special behavior has its origin in the specific electronic and geometric structure of C_{60}. Semiclassical calculations for singly charged ions support the measured data.

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Despite numerous measurements of mass spectral cracking patterns of C_{60} and other fullerenes [1], quantitative partial and total ionization cross section functions (cross section σ versus electron energy E) for C_{60} are not yet available, the only exception to this being the cross section data for attachment to C_{60} [2] and a cross section value of 53.5×10^{-20} m^2 for the production of the parent ion at an electron energy of 38 eV [3,4]. This is primarily because C_{60} is solid at room temperature, making it difficult to determine the absolute gas density of the C_{60} introduced into an ion source after sublimation in an oven. A knowledge of this gas density is, however, necessary for the determination of the absolute cross sections from the measured ion currents produced by the interaction of a beam of electrons (of known current and energy) with the C_{60} gas target in an ion source.

In this Letter we report the first measurements of cross section functions for the production of the various parent ions C_{60}^{z+} and the most abundant fragment ions C_{60-2m}^{z+} ($m = 1, \ldots 8$) by single electron collision in the energy range from threshold up to 1000 eV, including ions with charge states up to $z = 4$ and fragment ions down to C_{44}. For these measurements we used a crossed-beams apparatus dedicated to the accurate determination of partial ionization cross sections [6] invoking, however, for the present case a novel technique for the absolute calibration of the cross sections. The experimental results obtained are compared with theoretical predictions (additivity rule, semiclassical collision theories). The most surprising result in the present study is that the relative magnitude of the various partial ionization cross sections is quite different from those for ordinary polyatomic molecules [7]; e.g., the maximum cross section values for the production of doubly and triply charged parent ions are larger than that for any fragment ion.

The measurements were carried out with a double-focusing mass spectrometer of reversed geometry with a maximum resolution of 25 000 and a mass range of 10 000 Dalton at a nominal acceleration voltage of 3000 V. The C_{60} powder of 99.99% purity was evaporated in a temperature-controlled oven (usually set between 700 and 800 K) and introduced as an effusive beam via a small orifice from the oven into a three-electrode open electron impact ion source [6]. Other gases are introduced into the ion source via supplementary gas inlets. After entering the ion source (typical fullerene pressure around 10^{-6} Pa) the C_{60} beam is crossed at right angles by the ionizing electrons (with electron currents below 10 μA) which can have energies varying from close to 0 up to 1000 eV with an energy spread of approximately 0.5 eV FWHM. The resulting ions are extracted out of the ion source at right angles to both beams by a weak electric field. The influence of this field on the electron energy and on the shape of the measured cross sections for anions and cations has been discussed previously [6] and can be accounted for. The extracted and focused ions are then accelerated and analyzed in the high resolution mass spectrometer and after postacceleration detected with an ion counting system. The electron energy scale was calibrated using known cross section curves for the production of SF_6 anions and onsets for partial cross sections for rare gases. The relative partial ionization cross section functions for C_{60} cations have been obtained following the procedures outlined previously [5] to obtain reliable cross section data.

In order to calibrate the measured relative partial ionization cross sections for the various C_{60-2m}^{z+} ions a novel technique has been employed, because the conventional relative flow methods used for ordinary gas targets [7,8] cannot be applied here. The key to the present technique lies in the fact that the interaction of electrons with C_{60} leads to both negative and positive ions and that we have recently been able to measure the absolute attachment cross section function for the production of C_{60}^- using a combination of crossed beams and flowing afterglow and Langmuir probe technique [9]. Therefore, measurement of the C_{60}^- and C_{60}^+ ion yield under identical ion source (and mass spectrometer) conditions (gas pressure, electron currents, ion extraction, and detection efficiency) should allow us to derive the absolute ionization cross section for the production of C_{60}^+. As the ion extraction and detection efficiency is, however, usually different for positive and negative ions (in particular, in the case of different electron energies considered) these efficiencies have

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been determined in the present case using a calibrant gas and corresponding ions for which both the attachment and ionization cross sections are known. Measuring the production of SF_4^+ and SF_4^- via electron interaction with SF_6 under exactly identical experimental conditions as the formation of the respective C_{60} ions we obtain the necessary correction factor from the ratio of the measured ion currents and the known cross sections [10,11]. It turns out that the total detection efficiency for the negative ions is approximately a factor of 10 smaller than that for the positive ions and strongly depends on the experimental conditions used.

The cross section thus derived for the production of C_{60}^+ is $(22 \pm 8) \times 10^{-20}$ m^2 at an electron energy of 100 eV and thus lies way below the previous determination using a Knudsen cell approach [3] (see below). The error bars given correspond only to the statistical uncertainty and do not include errors in the cross sections used in the calibration procedure and other systematic errors (a conservative estimate of these uncertainties leads to a factor of 2 in the overall error). The other partial ionization cross section functions of C_{60} can be derived from the measured relative partial ionization cross sections, and the total counting or total ionization cross sections can be obtained from the ordinary or charge-weighted sum of all of the partial cross sections, respectively. This is the first time that this procedure has been used, but it has obvious value for the quantitative study of electron impact ionization of other normally solid substances such as some polycyclic aromatic hydrocarbons, a topic of current interest in mass spectrometry [12] and astrochemistry [13].

The partial ionization cross section results obtained for the parent ions C_{60}^+ to C_{60}^{4+} are presented in Fig. 1; results for the two strongest fragment ions are illustrated in Fig. 2. For all ions studied here Table I gives the maximum cross section (and the corresponding electron energy) and the cross section at 100 and 200 eV. By far the largest cross section is observed for the parent ion

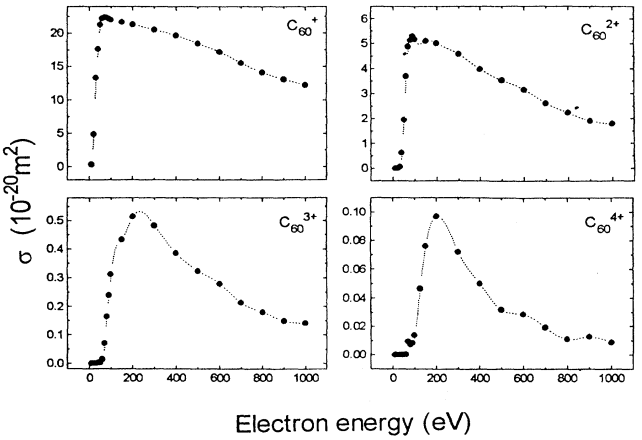

FIG. 1. Absolute ionization cross sections versus electron energy for the formation of singly, doubly, triply, and quadruply charged C_{60} parent ions.

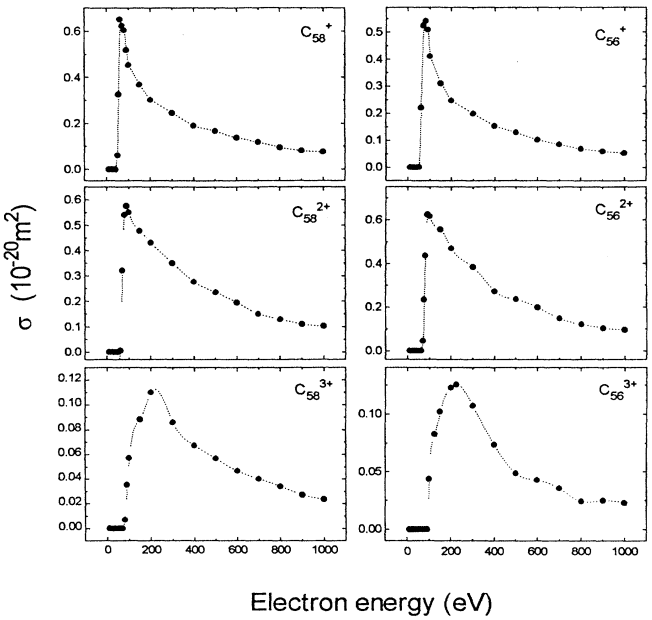

FIG. 2. Absolute ionization cross sections versus electron energy for the formation of the singly, doubly, and triply charged fragment ions C_{58}^{z+} and C_{56}^{z+}.

C_{60}^+. 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 polycyclic aromatic hydrocarbons [14]), it is nevertheless in accordance with previous mass spectrometric studies and theoretical considerations (RRKM calculations) of the ionization and fragmentation of C_{60} [1]. The large binding energy and the large number of degrees of freedom (and the resulting huge kinetic shift of more than 34 eV) render dissociative ionization processes of C_{60} less likely. The maximum value for the process $C_{60} \rightarrow C_{60}^+$ of 22×10^{-20} m^2 is close to the value of 21×10^{-20} m^2 reported previously [15] for the process $C_{60}^+ \rightarrow C_{60}^{2+}$. This is not surprising taking into account that the highest occupied molecular orbital level h_u of the neutral molecule is tenfold degenerate [16] and that the removal of the first two π electrons requires rather similar ionization energies of 7.6 and 11.4 eV [17], respectively. In contrast, the cross section for the process $C_{60}^{3+} \rightarrow C_{60}^{4+}$ which requires a much larger ionization energy of 27.4 eV [16] is according to [15] only 13×10^{-20} m^2. A comparison with the cross sections reported earlier [15] for the process $C_{60}^{2+} \rightarrow C_{60}^{3+}$ appears to be complicated by additional effects (see Salzborn and co-workers [15,18]).

Another interesting anomaly is the rather large magnitude of the cross section for the production of multiply charged *parent* ions relative to that of the singly charged parent ion (see Fig. 1). Whereas here the ratio for doubly to singly charged is more than 20%, for ordinary molecules or atoms this ratio seldom is more than a few percent (the gas with the highest percentage of doubly

TABLE I. Absolute measured electron impact ionization cross sections in 10^{-20} m^2 for the production of parent and fragment ions of C_{60} at electron energies of 100 and 200 eV and at the maximum of the cross section function.

Ion	σ_{max}	(E_{max})	σ 100 eV	σ 200 eV
C_{44}^+	0.0076	(150)	0.0066	0.0073
C_{46}^+	0.0093	(100)	0.0093	0.0085
C_{48}^+	0.023	(100)	0.023	0.018
C_{50}^+	0.06	(90)	0.058	0.05
C_{52}^+	0.064	(100)	0.064	0.057
C_{54}^+	0.188	(90)	0.187	0.095
C_{56}^+	0.54	(80)	0.411	0.248
C_{58}^+	0.652	(60)	0.454	0.303
C_{60}^+	22.4	(70)	22.0	21.3
C_{48}^{2+}	0.109	(150)	0.029	0.093
C_{50}^{2+}	0.227	(150)	0.14	0.206
C_{52}^{2+}	0.235	(125)	0.233	0.2
C_{54}^{2+}	0.277	(100)	0.277	0.254
C_{56}^{2+}	0.625	(90)	0.617	0.47
C_{58}^{2+}	0.576	(90)	0.552	0.433
C_{60}^{2+}	5.31	(90)	5.2	5.0
C_{52}^{3+}	0.062	(175)	0.0056	0.061
C_{54}^{3+}	0.135	(175)	0.0115	0.13
C_{56}^{3+}	0.125	(225)	0.044	0.123
C_{58}^{3+}	0.11	(200)	0.057	0.11
C_{60}^{3+}	0.514	(200)	0.312	0.514
C_{60}^{4+}	0.097	(200)	0.014	0.097

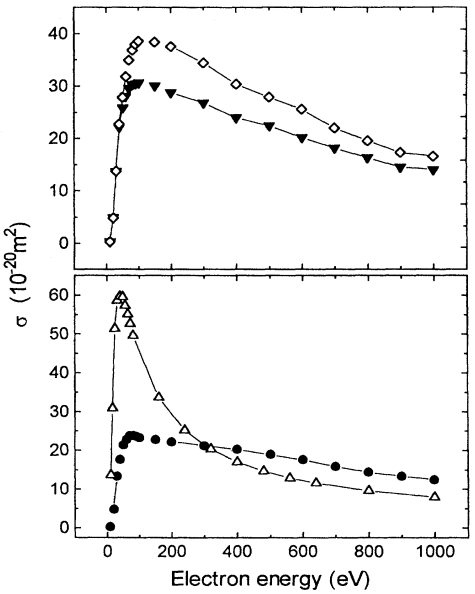

FIG. 3. Absolute total ionization cross section (designated ◇) and total counting cross section (designated ▼) versus electron energy for C_{60} (upper part). In the lower part the sum of the measured cross sections for the production of singly charged ions of C_{60} (designated ●) is compared with calculated values (designated △) using a semiclassical approach similar to the one described in Refs. [21,22].

charged ions known so far is xenon with approximately 12% [19]). The reason for these enhanced production cross sections lies, on the one hand, in the fact that the production of doubly and triply charged ions is energetically more favorable than the production of fragment ions (the appearance energy of C_{60}^{2+} and C_{60}^{3+} lies below that of any fragment ion of C_{60} [17]). In addition the sheer size of C_{60} and the fact that secondary electrons from an initial single-ionization process may be ejected into the empty center of the cage and subsequently interact anew with the electron cloud of the C_{60} enhances the chance for the occurrence of inelastic multiple-electron collisions within this quantum system, thereby increasing the probability for the production of multiply charged ions. Similar effects have been observed for the production of multiply ionized van der Waals clusters [20] and metal clusters [21]. This also explains the anomalous situation encountered in the case of the *fragment* ion cross sections depicted in Fig. 2, where the maximum values for doubly charged ions is of the same magnitude as that of the respective singly charged ion.

The absolute total ionization and total counting cross sections are given in Fig. 3 (upper part). In the lower part of Fig. 3 we have plotted the sum of all single ionization cross sections. This quantity can be calculated using a combination of binary encounter approximation and the Born-Bethe approximation [22,23], and there appears to be good agreement between the experimental data and the predicted values for energies above 200 eV. The discrepancy at the lower electron energies is typical for this type of calculation. Whereas this semiclassical approach takes into account the special geometry of the C_{60} molecule, the simple additivity rule approach [24] (assuming sp^2 hybridization) gives a measure for the total counting ionization cross section at an electron energy of 70 eV of approximately 103×10^{-20} m^2 which is much higher than the present value of 30×10^{-20} m^2 and the simple geometric cross section of $(38 - 78) \times 10^{-20}$ m^2 (the lower limit corresponding to the cage radius and the upper limit to the hard sphere radius of C_{60}). It is interesting to note that the one previous calibration [3]—using a Knudsen cell approach—leads to total counting cross sections which are also larger than these geometric cross sections.

In conclusion, we have measured the first absolute ionization and dissociative ionization cross section functions for the C_{60} molecule using a novel calibration method. C_{60} ionizes primarily to the singly charged parent ion, but with significant cross sections for the doubly charged (≈20% of the singly charged) and higher-charged parent ions. The dissociative ionization channels are at least about a factor of 50 smaller than the parent ion production. The total ionization cross section derived from the single-ionization partial cross sections is in good agreement with a semiclassical calculation for energies above 200 eV. The novel calibration method introduced here should be applicable to measurements of electron impact ionization (or attachment) cross sections of many other substances that are solid at room temperature.

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