Multiple Ionization and Fragmentation of Negatively Charged Fullerene Ions by Electron Impact

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(Received 15 September 1999)

Cross sections for the electron-impact multiple ionization and fragmentation of negatively charged fullerene ions $C_n{}^-$ ($n = 60, 70$) to $C_{n-m}{}^{q+}$ ($q = 1, 2, 3$ and $m = 0, 2, 4$) have been measured for electron energies up to 1 keV. In the case of pure ionization all threshold energies are about 10 eV higher than the values expected. This shift, however, is not observed for the fragment ions. The experimental data indicate that there is no strong electron-electron interaction between the incident electron and the attached electron. A novel ionization mechanism is proposed which can be expected to be valid for all negatively charged molecular or cluster ions which are able to shield the attached electron from the incident electron.

PACS numbers: 36.40.Qv, 34.80.Gs, 34.80.Ht, 36.40.Wa

Fullerenes have been the subject of intense research within the last decade. The interaction of these molecules with various projectiles has been investigated extensively. Ionization of neutral fullerenes has been studied employing electrons [1], fast atoms [2], ions up to very high charge states [3], molecular, as well as cluster ions [4], and photons from the infrared region [5] to photon energies up to 340 eV [6]. Several theoretical studies of the ionization of fullerenes have been published [7–10]. The calculated ionization energies and the electron affinity agree very well with experimental data [11,12]. In general, neutral fullerenes have been used as targets but in a few cases also positively charged fullerene ions have been used [13–15]. As for negatively charged fullerenes, only the photodetachment process has been investigated up to now [16–18].

In this Letter we report the first investigation of electron-impact ionization and fragmentation of negatively charged fullerene ions. Apparent cross sections for the multiple ionization up to quintuple ionization with and without accompanied fragmentation of the fullerene ions $C_{60}{}^-$, and $C_{70}{}^-$ have been measured for electron energies from below the ionization thresholds up to 1000 eV.

For the experiments we employed our electron-ion crossed-beams technique which has been described in detail earlier [19]. A commercially available mixture of fullerenes mainly containing C_{60} and C_{70}, but also trace amounts of larger fullerenes, was evaporated in an electrically heated oven. The neutral vapor was introduced into a 10 GHz electron cyclotron resonance (ECR) ion source [20]. Ion yields of negatively charged fullerenes in the order of 20 nA and stable conditions of the ECR plasma were found after argon at a pressure of about 10^{-4} Pa was introduced into the ion source. The electron-impact ionization of Ar leads to slow electrons which may attach to the fullerenes. In order to avoid undesired strong stray fields of the 90° analyzing magnet, the acceleration voltage had to be reduced for the cross section measurements of the singly charged product ions from nominal 10 kV down to only 4 kV in the case of $C_{70}{}^-$. The ion beam was collimated to about 2×2 mm^2 after mass and energy analysis. The fullerene ions were crossed about 200 μs after production in the ECR ion source with an intense electron beam (up to 450 mA) [21]. The energy of the electrons can be varied between 10 and 1000 eV. After the electron-ion interaction the product ions were separated from the incident ion beam by a second 90° magnet and detected several 10 μs after the interaction by a channeltron-based single-particle detector. The current of the parent ion beam was measured simultaneously in a Faraday cup. Employing the animated crossed-beams technique [22], where the electron beam is moved through the ion beam with simultaneous registration of the primary and the product ion intensity, apparent cross sections were measured.

Figure 1 shows as an example the cross section curves measured for the product ions of the $C_{70}{}^-$ primary ion. The maximum cross section values are summarized in Table I and compared with cross section values obtained by electron-impact ionization of neutral C_{70} [23]. The difference in the magnitude of the cross sections for the production of $C_{70}{}^+$ from $C_{70}{}^-$ and from neutral C_{70}, respectively, is surprisingly small. However, this difference becomes larger for higher charge states of the product ion. The ratio of the intensities of the fragment ions and the corresponding $C_{70}{}^{q+}$ product ion with the same charge state q is about a factor of 3.5 larger for negatively charged precursor ions (see Table II).

The threshold regions up to the maxima of the cross section curves are shown in Fig. 2. Additionally, ion-efficiency curves obtained by Matt *et al.* [23] for electron-impact ionization of neutral C_{70} are plotted. In order to

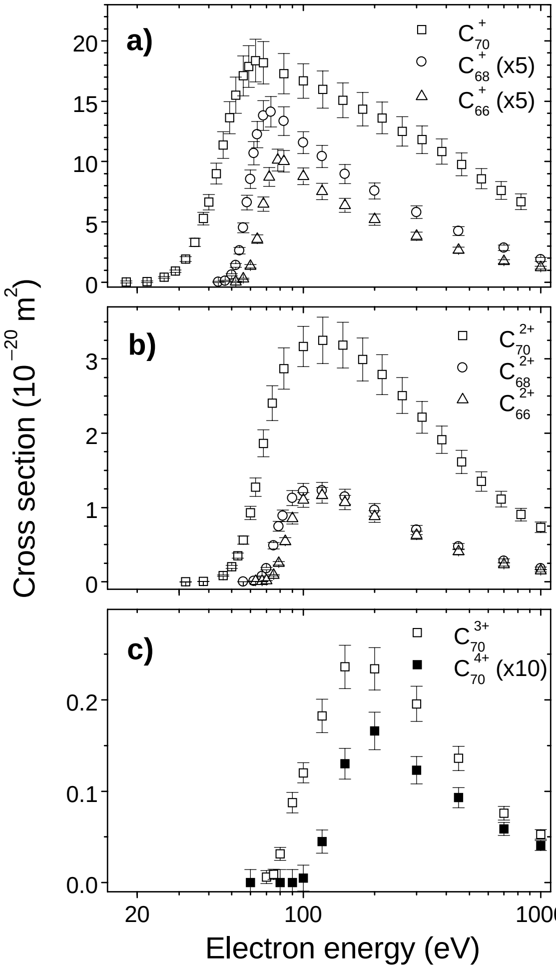

FIG. 1. Cross section data for the electron-impact double, triple, quadruple, and quintuple ionization of C_{70}^- ions into various product ions. The squares represent the cross section data for pure ionization. The circles and triangles correspond to the fragment ions C_{68}^{q+} and C_{66}^{q+}, respectively ($q = 1$ and 2). The error bars represent the total experimental uncertainties including the statistical error at 90% confidence level.

match these curves with the cross section data the ion intensity was multiplied by a first parameter and the energy scale was shifted by a second parameter. A fitting routine was used to minimize the sum of the square of the deviations. Each ion-efficiency curve was used to fit two cross section curves, i.e., (i) leading to the same product ion and (ii) removing the same number of electrons. The single ionization of the C_{70}^- ion could not be measured in the present study as the product is a neutral particle. The ion-efficiency curves can be matched perfectly with the cross section data of the same product ion. In contrast, the removal of the same number of electrons does not lead to similar cross section curves in the case of neutral and negatively charged C_{70}^-.

The binding energy of an electron attached to C_{60} and C_{70} has been determined both experimentally [16,17] and theoretically [7]. In order to create a positively charged ion from a precursor anion, one would expect that the kinetic energy of the electron has to be enlarged by the electron affinity compared to a neutral precursor fullerene. For C_{70} the electron affinity is 2.68 eV [17]. This is much less than the shifts observed which range between 9.9 and 13.4 eV. A similarly large shift could be observed for the cross sections for the pure ionization of C_{60}^-. However, the threshold of the cross sections for the formation of fragment ions is—within the experimental uncertainty—the same for neutral and negatively charged fullerenes. Table III shows the energy shifts between the ionization-efficiency curves of the electron-impact ionization of neutral fullerenes and the corresponding cross section curves measured by electron-impact ionization of mass-selected negatively charged fullerene ions.

The large shifts of the cross section curves towards higher electron energies in the case of electron-impact ionization of negatively charged fullerene ions lead to the conclusion that the projectile electron does not remove the attached electron in a direct process. The following simple model describes a mechanism which agrees well with all experimental findings.

(1) During the approach of the projectile electron the attached electron is pushed to the back side of the fullerene by Coulomb repulsion. Thereby the attached electron is shielded by the fullerene itself and does not interact with the projectile strong enough to be detached. The approach of the projectile electron against the repulsive force of the fullerene anion needs about 2 eV (the Coulomb energy of two charges at a distance of 7 Å) which is taken from the kinetic energy of the projectile. An intermediate highly

TABLE I. Maximum values of the cross sections for the electron-impact ionization of negatively charged and neutral [23] C_{70}. The number in the columns designated E_e (eV) is the electron energy at the maximum of the corresponding cross section function.

	$C_{70}^- \rightarrow C_{70-m}^{q+}$		$C_{70} \rightarrow C_{70-m}^{q+}$	
	σ (10^{-20} m^2)	E_e (eV)	σ (10^{-20} m^2)	E_e (eV)
C_{70}^+	18.5	64	19.64	50
C_{70}^{2+}	3.16	122	10.1	95
C_{70}^{3+}	0.229	170	1.49	160
C_{70}^{4+}	0.016	208	0.136	200
C_{68}^+	2.79	72	0.85	65
C_{68}^{2+}	1.23	111	1.1	93
C_{66}^+	2.01	80	0.53	73
C_{66}^{2+}	1.16	118	0.98	99

TABLE II. Ratios of the cross sections for the production of a fragment ion C_{70-m}^{q+} ($m = 2, 4$ and $q = 1, 2$) and the corresponding ion C_{70}^{q+}. The maximum values of the cross section function listed in Table I were used.

	Precursor	
	C_{70}^-	C_{70} (neutral)
$\sigma(C_{68}^+)/\sigma(C_{70}^+)$	0.151	0.043
$\sigma(C_{66}^+)/\sigma(C_{70}^+)$	0.109	0.027
$\sigma(C_{68}^{2+})/\sigma(C_{70}^{2+})$	0.389	0.109
$\sigma(C_{66}^{2+})/\sigma(C_{70}^{2+})$	0.367	0.097

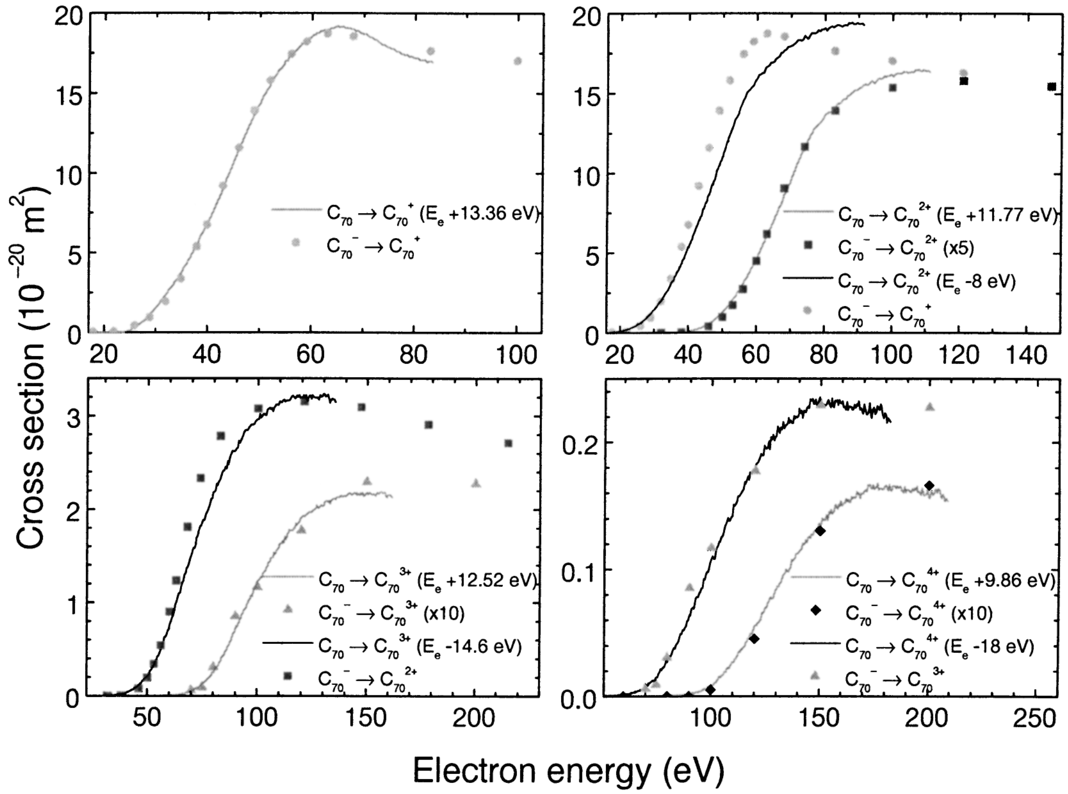

FIG. 2. Threshold regions of the cross section curves measured for the electron-impact ionization of C_{70}^{-} ions. The lines are ion efficiency curves by Matt *et al.* [23] which have been normalized and shifted on the energy scale in order to get the best agreement with the symbols (see text).

excited dianion is formed. The electron affinities of some fullerene dianions (C_{60}^{2-}, and C_{84}^{2-}) have been determined to be very small [7,25]. In other words, the binding energy of the attached electron has been reduced from 2.65 eV to almost zero.

(2) The incident electron collides with the fullerene and ejects several electrons from the fully occupied pi-orbital of the fullerene with the lowest energy. The kinetic energy of the ejected electrons from the former dianion is supplied by the approaching projectile taking into account the potential barrier formed by the Coulomb repulsion, the interaction with the image charge the electron forms at close distances [26], and the attractive force between the emitted electrons and the charged fullerene ion.

(3) The attached electron drops into the vacancies of the HOMO. The energy difference is transferred into vibrational degrees of freedom.

Qualitatively, this model explains the following experimental findings: (i) More energy is needed for pure ionization of a negatively charged fullerene ion than can be expected from the sum of the electron affinity and the ionization energies of the neutral fullerene. (ii) The extra energy is transferred into the vibrational degrees of freedom and therefore this is in agreement with the small shift between the threshold energies of the fragment ions for neutral and negatively charged precursor ions. (iii) The transfer of electronic energy into the vibrational modes of the fullerene increases the probability for fragmentation

TABLE III. Appearance energies of C_{n-m}^{q+} ions produced by electron-impact ionization of neutral and negatively charged C_{70} and C_{60}, respectively. Values are given in eV.

	C_{70}^{-}	C_{70} [12,24]	Δ		C_{60}^{-}	C_{60} [10]	Δ
C_{70}^{+}	20.9	7.5	13.4	C_{60}^{+}	21.9	7.6	14.3
C_{70}^{2+}	30.6	18.8	11.8	C_{60}^{2+}	31.8	19.1	12.7
C_{70}^{3+}	47.8	35.3	12.5	C_{60}^{3+}	47.0	35.7	11.3
C_{70}^{4+}	64.4	54.5	9.9				
			Fragment ions				
C_{68}^{+}	47.1	49.4	−2.3	C_{58}^{+}	43.9	43.8	0.1
C_{66}^{+}	53.3	54.0	−0.7	C_{56}^{+}	50.6	49.9	0.7
C_{68}^{2+}	61.1	61.5	−0.4	C_{58}^{2+}	54.7	54.1	0.6
C_{66}^{2+}	68.2	66.1	2.1	C_{56}^{2+}	61.2	59.9	1.3

processes. The relative amount of fragment ions is in the case of negatively charged precursor ions about 3.5 times larger than for neutral fullerenes (see Table II).

In addition, this model can be used to determine quantitatively the difference of the electron energies which have to be used in order to ionize negatively charged and neutral fullerenes, respectively. The electron affinity of C_{60} is 2.65 eV [16]. The ionization energy to produce a ${C_{60}}^+$ ion from neutral C_{60} is 7.6 eV [27]. This is also the depth of the HOMO orbital which is 5-fold degenerated in the case of neutral C_{60}. Therefore, the electronic energy which is released by the attached electron moving into a vacancy of the HOMO orbital is in the order of 5 eV. According to the present model, however, the attached electron is shifted to the opposite site of the incoming projectile electron and its binding energy is reduced by about 2.5 eV. The sum of these two energies leads to an excitation of the positively charged ${C_{60}}^{q+}$ ion which is formed. So even if the removal of the electrons does not transfer energy into the internal degrees of freedom, the excitation energy will be in the order of 7.5 eV. Taking into account the energy of 2 eV, which the incident projectile needs to approach the negatively charged fullerene ion (which finally is given back to the ejected electrons), and the minimum excitation of the fullerene according to the present model (7.5 eV), one can explain the experimentally observed shift of about 10 eV. In order to produce a ${C_{60}}^+$ ion by electron impact the kinetic energy of the electron has to be at least 10 eV larger if the precursor fullerene is negatively charged compared to a neutral fullerene. This value predicted by the present model is in perfect agreement with the experimentally observed shifts which are summarized in Table III.

The described mechanism for the electron-impact ionization of negatively charged fullerene ions can be expected to be found also for other large molecular and cluster anions. The only necessity is that the attached electron has to be mobile enough in order to avoid a direct collision with the projectile electron.

This work was supported by Deutsche Forschungsgemeinschaft (DFG). It is a pleasure to thank Dr. Verena Grill, Innsbruck, Professor Aleksandar Stamatovic, Belgrade, and Professor Olof Echt, Durham, for helpful discussions.

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