Electron-Impact Induced Fragmentation of Fullerene Ions

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(Received 19 June 2000)

The C_2 fragmentation of fullerene ions ${C_{60}}^{q+}$ ($q = 1, 2, 3$) induced by electron impact was studied for the first time. The cross sections for the loss of a C_2 fragment indicate the presence of two different processes. At low electron energies the projectile electron leads to the direct excitation of the giant plasmon resonance. At electron energies larger than 100 eV the fragmentation of the fullerene ions can be described as an unsuccessful ionization. Only this second part of the cross section shows a dependence on the charge state q of the precursor ion.

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

The exceptionally high stability of fullerenes in general and the buckminster fullerene C_{60} in particular have drawn the attention of both experimentalists and theoreticians to study the mechanisms that lead to the excitation and relaxation of fullerenes. Excitation has been realized by various methods, i.e., thermal heating [1], single-photon [2] or multiphoton [3] absorption, electron impact [4], collisions with neutral particles [5], atomic [6–8], molecular [9], and cluster ions [10], and surface collisions [11]. Three different cooling mechanisms for excited fullerenes have been observed, i.e., the evaporation of electrons (thermoionization) [3], the release of neutral or charged particles (fragmentation) [12,13], and radiative cooling [14]. The importance of these three mechanisms strongly depends on the excitation energy [15].

Although the dissociation of fullerenes upon excitation has been studied for almost 15 years, some important questions could be answered only recently. For example, the value of the binding energy of C_2 to ${C_{58}}^{q+}$ (for $q = 0, 1, 2, \ldots$) was leading to a lot of controversy. Presently there seems to be a commonly accepted value of about 11 eV for this binding energy [16]. Furthermore, experiments based on mass-spectrometric techniques clearly demonstrated that sequential C_2 loss is the dominant process for the formation of smaller fragments from fullerene ions [17].

However, there are other experimental observations concerning the fragmentation of fullerenes which still lack an explanation. For instance, there is no answer to why large multiply charged fragment ions are so abundant in mass spectra compared to the corresponding parent ions [18].

In order to observe a fragmentation, the deposition of just the binding energy into the vibrational degrees of freedom is not sufficient. For a fragmentation in the μs time regime about 38 eV are needed [19]. According to single-photoionization studies [2,20] and an earlier theoretical investigation [21] the most efficient way to deposit that amount of energy is the collective excitation of the fullerene via a plasmon. Up to now, most of the studies of the fragmentation of fullerenes were investigations of the dissociative ionization processes with neutral fullerenes as precursors [22,23].

The present paper is a novel approach to the investigation of the pure C_2 fragmentation of fullerenes applying the electron-impact induced fragmentation of mass selected cations ${C_{60}}^{q+}$ ($q = 1, 2, 3$). For the first time cross sections for this C_2 loss have been determined from the respective threshold up to an electron energy of 1 keV.

The measurements were performed employing the electron-ion crossed-beam setup described in detail by Tinschert *et al.* [24]. A commercially available powder of fullerenes was evaporated with an electrically heated oven. The neutral vapor was introduced into a 10 GHz Electron Cyclotron Resonance Ion Source (ECRIS) [25]. The extracted ion beam was collimated to 2×2 mm^2 after mass to charge analysis and crossed with an intense electron beam [26]. The energy of the electrons can be varied between 10 and 1000 eV. After the electron-ion interaction the fragment ions ${C_{58}}^{q+}$ were separated from the incident ion beam of ${C_{60}}^{q+}$ by a 90° magnet and detected by a single-particle detector. The flight time between the interaction of the ${C_{60}}^{q+}$ ions and the analysis of the product ions is in the order of 10 μs. The current of the parent ion beam was measured simultaneously in a Faraday cup. Employing the dynamic crossed-beam method described by Müller *et al.* [27], where the electron gun is moved through the ion beam with simultaneous registration of the primary and the product ion intensity, absolute cross sections were obtained.

Cross sections for the electron-impact induced fragmentation of ${C_{60}}^{q+}$ ($q = 1, 2, 3$) are shown in Fig. 1. It should be mentioned that these are apparent cross sections and depend on the chosen time scale due to the statistical nature of the evaporation process. For all three measured charge states the cross sections show a characteristic shape. At energies below 100 eV a well pronounced peaklike structure can be observed and at higher energies the cross sections behave like a typical ionization cross section. In order to

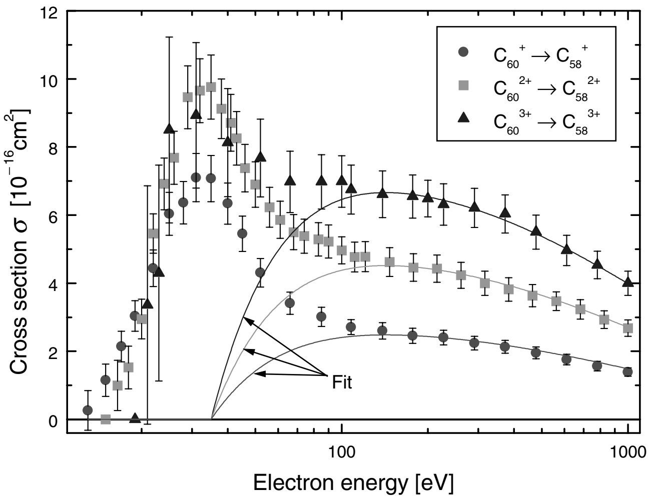

FIG. 1. Absolute cross sections σ for the electron-impact induced C_2 fragmentation of $C_{60}{}^{q+}$ ions: circles, $q = 1$; squares, $q = 2$; triangles, $q = 3$. The error bars indicate the total experimental uncertainties. The solid lines are fits through the respective data points at energies higher than 120 eV. For more detail, see text.

separate the two fractions the high energy part was fitted applying the Lotz formula [28], normally used to calculate electron-impact ionization cross sections. This second contribution to the fragmentation cross sections scales linearly with the charge state of the fullerene ions (see Fig. 2).

It is interesting to note that also the cross sections for fragment ions produced by electron-impact ionization of neutral [22] and charged [29] fullerenes exhibit an unusual peak in the low energy region. Whereas all these previous investigations were combined ionization-fragmentation processes, in the present study the pure fragmentation was investigated. In order to separate the two contributions the fits shown in Fig. 1 are subtracted from the measured cross section. The results of this procedure are shown in Fig. 3. The similarity of the resulting peak with the giant plasmon resonance observed in Ref. [30] suggests that the fragmentation process induced by the electron impact at low energies is predominantly caused by a plasmon excitation. Note that the shape of this peak does not depend on the charge state of the ion. The width of the presently observed peak, however, is much larger than the peaks that have been observed by the excitation of a single plasmon by both photons and electrons [2,20,30]. In contrast to the previous investigations where neutral fullerenes were used as a target the internal energy of the $C_{60}{}^{q+}$ ions will have a much larger spread. Cold ions will need the excitation of two plasmons for the C_2 fragmentation similarly to the cold neutral fullerenes used in Ref. [23]. $C_{60}{}^{q+}$ ions that contain at least the energy of one plasmon from the ionization in the ECRIS will decay upon the excitation of only one additional plasmon.

The good agreement of the second part of the cross sections with the Lotz fitting indicates that the fragmentation in this energy range is actually caused by an ionization process. However, as the charge of the system does not change one of the two outgoing electrons has to be recaptured. The onset energy for this process according to the fitting routine is roughly 35 eV and thus in good agreement with the position of the maximum of the first peak that could be attributed to a plasmon resonance. According to the peak shown in Fig. 3 C_2 fragmentation can be achieved most efficiently with electrons of about 35 eV of kinetic energy. Therefore, at high projectile energies, preferentially the slow electron will inelastically scatter with the fullerene ion during their separation [31]. If the electron energy after the collision is low enough, the electron will attach to the ionized fullerene and recombine by a further release of energy. However, if the electron is still

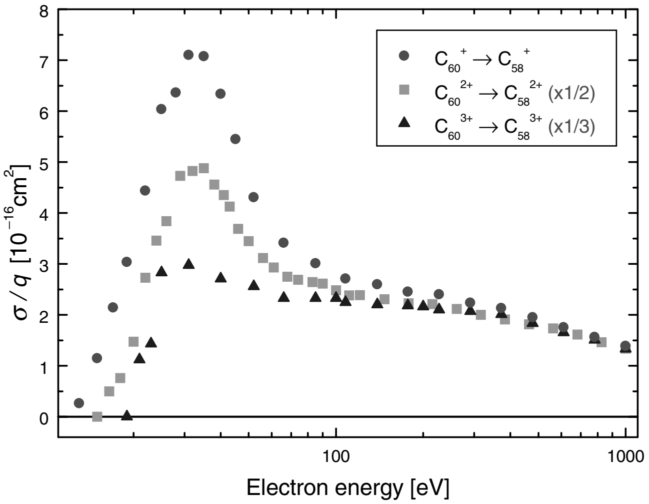

FIG. 2. Absolute cross sections σ for the electron-impact induced C_2 fragmentation of $C_{60}{}^{q+}$ ions divided by the respective charge state q: circles, $q = 1$; squares, $q = 2$; triangles, $q = 3$.

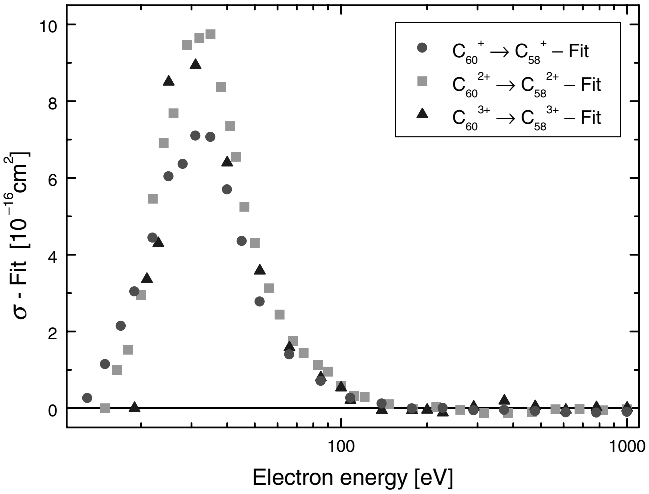

FIG. 3. Differences between the absolute cross sections σ for the electron-impact induced C_2 fragmentation of $C_{60}{}^{q+}$ ions and the fits in Fig. 1: circles, $q = 1$; squares, $q = 2$; triangles, $q = 3$.

too fast it might simply leave the excited fullerene and the finally observed process will be either a pure ionization or a combined fragmentation ionization. These processes feature competitive reaction channels to the pure fragmentation.

The idea of an unsuccessful ionization process by a recapture of one of the outgoing electrons explains the charge state dependence of the higher energy part of the fragmentation cross section. Higher charged fullerenes are able to recapture faster electrons. This charge dependence gives a sound explanation of the large abundance of multiply charged fragment ions in the mass spectrum obtained by electron impact of fullerenes. Single-differential cross sections (SDCS) obtained by a large number of e-$2e$ experiments and theoretical models for both atoms and molecules clearly show that for fast projectile electrons the energy distribution between the two leaving electrons is generally very asymmetric [32,33]. This means that even at projectile energies of 1 keV the probability for a slow leaving electron that has a kinetic energy in the order of 20 to 40 eV is sufficiently large.

Finally it has to be explained why the second part of the fragmentation cross section shows the energy dependence of a pure ionization. One would expect that the first step, i.e., the ejection of a bound electron should exhibit this kind of an energy behavior. However, for a fragmentation in the present case one of the secondary electrons has to be slowed down sufficiently by an inelastic scattering mechanism (for instance, the plasmon excitation) and then has to be recaptured by the fullerene. Using a modified Mott formula [33] one can show that the integration over the SDCS, in the energy range interesting for electron recapture, gives a value which is practically independent of the energy of the projectile electron for energies larger than 50 eV. This means that the energy dependence of the cross section for the complete process is defined only by the first step that is the ionization of the fullerene ion.

For the first time the electron-impact induced C_2 fragmentation of fullerene ions has been investigated. At electron energies below 100 eV, the direct excitation of one or two plasmons leads to a well pronounced peak that is independent of the charge state of the parent ion. The second part of the cross section at higher energies can be explained as the result of a recapturing process of a secondary electron. This unsuccessful ionization could also contribute to the fragmentation of other large molecules or clusters after electron impact. However, a mechanism has to exist that effectively converts kinetic energy of the electrons into vibrational degrees of freedom of the target molecule. In the present case of fullerenes this is the plasmon excitation. In addition, unsuccessful ionization explains in a novel way the more destructive nature of electron impact compared to photoionization of large molecules.

This work was supported by Deutsche Forschungsgemeinschaft (DFG) and the APART-program of the Austrian Academy of Sciences.

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