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Experimental studies on photoabsorption by endohedral fullerene ions with a focus on $Xe@C_{60}^{+}$ confinement resonances

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Abstract

A brief overview on the status of experimental investigations into photoionization and fragmentation of fullerenes and endohedral fullerenes by absorption of a single short-wavelength photon is presented. The focus of this paper is on the endohedral $Xe@C_{60}^{+}$ molecular ion in which a xenon atom is centrally encapsulated inside a C_{60}^{+} fullerene cage. Confinement resonances that result from the interference of Xe photoelectron matter waves emerging from the C_{60}^{+} cavity were studied by exposing $Xe@C_{60}^{+}$ ions to synchrotron radiation of 60 to 150 eV energy which is the region of the well-known giant atomic Xe $4d$ excitation resonance. Photoions $Xe@C_{n}^{q+}$ (with final charge states $q = 2, 3, 4$ of the product ions and numbers $n = 60, 58, 56, 54$ of carbon atoms left in the cage) were recorded as a function of photon energy and cross sections for the individual reaction channels were determined. In addition to previous work, new final channels ($q = 2$; $n = 60, 58$ and $q = 4$; $n = 58, 56$) were observed, and thus, about 70% of the oscillator strength expected for the encapsulated Xe atom in the investigated energy range could be recovered. The present results establish the first and, so far, only conclusive experimental observation of confinement resonances in an endohedral fullerene. The data are in remarkable agreement with relativistic R-matrix calculations that accompanied the previous experimental work.

1. Introduction

Endohedral fullerenes have attracted enormous interest during the last three decades. The reason for this are the numerous possible applications [1] of atoms encapsulated inside spherical or near-spherical carbon molecules and the fundamental aspects of an atom confined inside a nanometer-sized quantum cavity [2]. While the confinement of atoms in fullerene cages has been addressed by numerous theoretical approaches, experimental attempts to understand the behavior of encaged atoms have been relatively scarce. The main reason for the lack of experiments is the limited availability of endohedral fullerene materials due to the technical difficulties in producing them in sizable quantities and with high purity. Only a few endohedral fullerene species are commercially available. None of them feature an encapsulated nobel gas atom, such as Xe, which is in the focus of the present communication. The most definitive experimental measurements to directly access the physics of confined atoms is the observation of their response to irradiation by photons. Targets for photoabsorption measurements can be provided by evaporating endohedral fullerene powders which requires high-purity sample materials. An alternative and unique experimental approach is the exposure of mass- and charge-selected endohedral fullerene ions to photon beams in a merged-beams arrangement, for which sample purity is not critical. It is useful to distinguish between different light sources employed in the photoabsorption experiments. Visible and infrared lasers, often pulsed and with high power, were extensively employed to study reactions of neutral endohedral fullerenes ([3] and references therein). Alternatively, high-energy photons from synchrotron radiation or free-electron laser sources have been employed. The associated range of VUV to soft-x-ray wavelengths is the focus of the present paper.

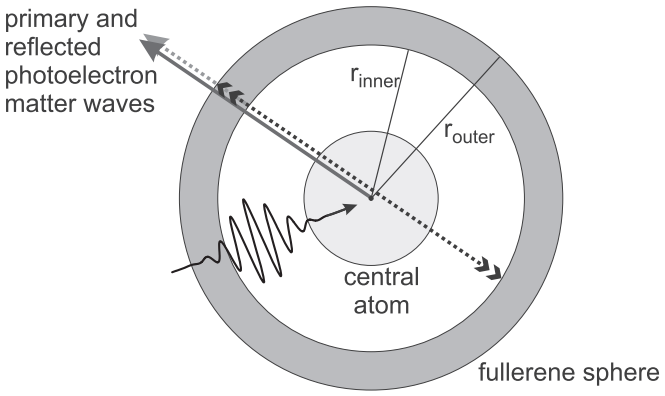

Figure 1. Illustration of the occurrence of confinement resonances in the photoionization of an atom centrally encapsulated inside a fullerene shell with inner and outer radii r_{inner} and r_{outer}, respectively. Only selected pathways of the reflected photoelectron wave are shown.

Most of the experimental work associated with VUV and soft-x-ray photoabsorption by endohedral fullerenes was driven by the stimulating ten or more years of theoretical predictions of confinement resonances [4] which are due to the interference of photoelectron matter waves emitted from a confined atom with and without reflections from the surrounding fullerene cage. A sketch illustrating the conceptual mechanism of confinement resonances is shown in figure 1. The incoming photon releases a photoelectron which can either directly leave the endohedral fullerene or be reflected from the inner and/or outer surfaces of the fullerene shell. The outgoing direct and reflected photoelectron matter waves can interfere with one another and thus give rise to an interference pattern in the cross section, namely, the confinement resonances. First calculations on such phenomena were performed by Puska and Nieminen [5, 6] for xenon and barium atoms encapsulated within a spherical C_{60} molecular cage. Soon after, a further calculation on Ba@C_{60} was published by Wendin and Wästberg [7]. Numerous calculations addressing photoabsorption by endohedral fullerenes followed. A review of theoretical approaches to photoionization of atoms encaged in spherical fullerenes was provided by Dolmatov [8]. Among the most recent theoretical treatments of VUV photoabsorption by confined atoms are those by Amusia *et al* [9], Saha *et al* [10], and Thuppilakkadan *et al* [11].

First experiments on VUV photoabsorption by neutral gas-phase endohedral molecules were conducted by Mitsuke *et al* on Ce@C_{82} [12], Dy@C_{82} [13] and Pr@C_{82} [14] metallofullerenes exposed to synchrotron radiation. The prime goal of these experiments was the observation of confinement resonances; however, the data were challenged by large experimental uncertainties. A different approach to the investigation of photoprocesses with fullerenes and endohedral fullerenes was pursued by employing the photon-ion merged-beams technique with synchrotron radiation [15]. By the use of magnetically selected beams of ions with given mass, charge and energy, even isotopically pure beams of endohedral fullerenes could be provided as targets for photoionization and photofragmentation measurements. The method makes it possible to observe and differentiate between different final ionic products resulting from an initial photoabsorption by the ionic target species. An advantage is the potential for the measurement of absolute cross sections for different final reaction channels that involve ionization or fragmentation of the initial ion. Studies of photoprocesses of fullerene ions by employing the merged-beams technique comprise single ionization of C_{60}^{q+} with $q = 1, 2, 3$ [16], single ionization of $Sc_3N@C_{80}^+$ and Ce@C_{82}^+ [17], single ionization of C_{60}^+ and C_{80}^+ [18], single and double ionization of Ce@C_{82}^+ and C_{82}^+ [19], double ionization of Ce@C_{82}^+ [20], double ionization of Xe@C_{60}^+ accompanied by ejection of a C_2 dimer [21], double and triple detachment of C_{60}^- ions [22], double ionization of Xe@C_{60}^+ and C_{60}^+ with ejection of N C_2 dimers ($N = 0, 1, 2, 3$) [23], single and multiple ionization with fragmentation of $Lu_3N@C_{80}^{q+}$ ($q = 1, 2, 3$) [24], single ionization of C_{60}^+ with ejection of N C_2 ($N = 0, 1, 2, 3, 4, 5, 6, 7$) dimers [25], single ionization of C_n^+ ($n = 40, 50, 70, 76, 78, 84$) [26], ionization and fragmentation of $Sc_3N@C_{80}^+$ and $Sc_3N@C_{80}^-$ ions [27].

Recent experiments on ionization and fragmentation dynamics with high-energy photons were conducted with neutral vapor targets of $Sc_3N@C_{80}$ and $Ho_3N@C_{80}$ employing coincidence velocity mapping spectroscopy at different light sources [28–30].

The present paper specifically reviews and updates the experimental status of photoionization and photofragmentation of Xe@C_{60}^+ ions in the $4d \rightarrow 4f$ excitation energy region where confinement resonances had been theoretically predicted and were subsequently experimentally demonstrated. It adds new experimental results on single and triple ionization with fragmentation of Xe@C_{60}^+ ions and thus considerably extends the available information about the reaction channels that contribute to the phenomenon of confinement

resonances in the Xe@C_{60} molecule. The relations between experimental observables and the cross sections calculated for the free and the encapsulated xenon atom on the basis of theoretical modelling are thoroughly discussed. The caveats that have to be considered when comparing theoretical and experimental results are addressed in detail. This is important because the measurements described in this article provide the first and, to date, the only experimental evidence for the phenomenon of confinement resonances in endohedral fullerence molecules. All the related experiments were performed at the photon-ion merged-beams facility [31] that was previously available at the Advanced Light Source (ALS) in Berkeley, California.

2. Experimental approach

The merged-beams technique employed at the ALS has been described in detail previously [31, 32]. Further developments were described more recently [33]. Detailed accounts of the production of Xe@C_{60} samples were provided by Kilcoyne *et al* [21] and Phaneuf *et al* [23] along with descriptions of the techniques specific to the measurement of cross sections for photoionization and photofragmentation of Xe@C_{60}^{+} ions. Measurements were carried out with endohedral Xe@C_{60}^{+} as well as with C_{60}^{+} ions. Electrical currents of Xe@C_{60}^{+} ions available in the experiments were at most a few picoAmperes. Relative yields obtained for the observed reaction channels after photoabsorption by Xe@C_{60}^{+} were normalized to separately measured absolute cross sections for the associated empty-fullerene ion [23, 25]. For the reaction Xe@$C_{60}^{+} \rightarrow$ Xe@C_{56}^{4+} the relative energy-scan measurement could be normalized to an absolute cross section measurement. The total systematic uncertainties of the cross sections for the fullerene ions are $\pm$22%. The uncertainty of the photon energy scale is less than $\pm$0.5 eV.

3. Results and discussion

Up to the present time, theoretical work on confinement resonances in the photoionization of Xe@C_{60} molecules has addressed the reaction

$$\mathrm{Xe@C_{60}} + \gamma \rightarrow \mathrm{Xe^{+}@C_{60}} + e \tag{1}$$

where γ denotes a photon with energy E_γ. The product of this reaction, a Xe ion inside a C_{60} molecular cage, is at most a very short lived theoretical construct. Theory has not been extended yet to the rearrangement and inelastic electron scattering processes that accompany or follow after the reaction described by equation 1.

For the steady undisturbed state of the endohedral Xe@C_{60} molecule it can be assumed that the charge state of the confined Xe atom is zero even if the endohedral molecule is electrically charged. This has been discussed in the context of recent measurements with $Sc_3N@C_{80}^{q+}$ ($q = -1,\ 0,\ +1$) and associated calculations [27]. The photoelectron in equation (1) is released near the center of the C_{60} cage. It can leave the endohedral molecule directly, or it can be reflected by the inner or outer surfaces of the fullerene cage, bounce back and forth and then leave the molecule. Interference of the direct and the reflected electron matter waves leads to the phenomenon of confinement resonances. Such resonances can be made visible by varying E_γ over a region where the photoionization cross section changes only slowly with E_γ. The de Broglie wavelength λ_e of the photoelectron is directly related to its energy $E_e = E_\gamma - E_{th}$ where E_{th} is the binding energy of the electron in its initial state. For a cage potential that can be described by a δ function, as assumed by Amusia *et al* [34] for Xe@C_{60}, pronounced interference maxima and minima occur which simply depend on the number of half waves that fit within the diameter of the cage. The free neutral xenon atom features a large slowly varying cross section, a broad peak in the region 60 to 150eV, predominantly associated with excitation of a $4d$ electron to ϵf, the so-called giant Xe atomic $4d$ resonance. Thus, Xe@C_{60} is a particularly suitable candidate for the observation of confinement resonances in the total photoionization cross section of an endohedral fullerene.

As mentioned in the introduction, the first treatment of confinement resonances in Xe@C_{60} was published by Puska and Nieminen [5, 6] who employed time-dependent density-functional theory (TDDFT) in combination with a jellium model for describing the fullerene cage potential. Dramatic oscillations of the confined-atom Xe $4d$ cross section were reported by Amusia *et al* [34], based on the random-phase approximation with exchange (RPAE) method, that was applied to a cage model with an infinitely thin shell potential. Subsequently, Dolmatov and Manson [35] also applied the RPAE method but modelled the confining C_{60} cage by a spherical, short-range, attractive potential of given radius, thickness and depth. Their result indicates much smaller excursions of the confined-Xe cross section from the free-atom case than the preceding calculation by Amusia *et al.* A similar RPAE approach was employed by Chen and Msezane [36] with the result of much larger oscillations in the confined-Xe cross section. Madjet *et al* [37] used the time-dependent local-density approximation and a classical jellium cage model. Their result showed smaller excursions again, but at different photon energies. Chen and Msezane [38] followed with an RPAE approach and soon after that with a TDDFT calculation and a density-functional

approximation for modelling the structure of the cage [39]. R-matrix methods were applied by Gorczyca *et al* [40] and Li *et al* [41] to the problem of confinement resonances in the Xe $4d - \epsilon f$ energy range of Xe@C_{60}. All the theoretical results obtained exhibited resonance structures that differed from one another and there was no sign of convergence within the various theories.

Theory predominantly provided cross sections for the process described by equation (1) and the related photoionization cross section of the free Xe atom. Most of the Xe cross section in the energy range 60 to 150 eV is related to $4d \rightarrow \epsilon f,\ \epsilon p$ transitions but also contains contributions of photoionization starting from other subshells as well as from associated ionization with excitation and double ionization processes. According to the Thomas-Reiche-Kuhn sum rule [42–44] the total absorption oscillator strength for the 4*d* subshell with its 10 electrons is $f_{abs} = 10$. Most of this oscillator strength is contained in the atomic 4*d* giant (shape) resonance. Partial 4*d* ionization cross sections have been measured by several groups ([45, 46] and references therein). From these measurements an oscillator strength $f_{abs} = 8.3 \pm 0.5$ can be inferred for the 4*d* giant resonance alone, that is, about 83% of the total oscillator strength of the 4*d* subshell contributes to this resonance peak. The total photoabsorption cross section of Xe in the energy range 60 to 150eV has been measured several times with results that mostly agree with one another within a few percent. As the basis for the present discussion the data published by Samson and Stolte [47] for energies up to 125 eV and the data provided by Suzuki and Saito [48] for energies above 85 eV have been chosen. The small relative uncertainties of these measurements were quoted to be less than 1% and 1%–2%, respectively. However, the cross sections of Suzuki and Saito are about 3% above those of Samson and Stolte. In order to obtain a consistent set of Xe absorption cross sections for reference, the Suzuki and Saito data were normalized by a factor 0.97 suitable for the energy range of the giant 4*d* absorption resonance in Xe. Comparing the partial 4*d* cross section with the total absorption cross section yields a ratio of 0.78. In other words, the 4*d* giant resonance contributes 78% of the total Xe absorption cross section in the energy range. The oscillator strength of the total Xe absorption cross section in the associated energy range 60-150 eV is $f_{abs} = 10.5 \pm 0.3$.

Equation (1) is a simplification of the actual photoabsorption process. Since reabsorption of the photoelectron inside the endohedral molecule is unlikely, equation (1) describes the realistic first step of most of the possible reaction pathways that involve the encapsulated Xe atom. The perturbation caused by the photoionization of that atom results in a multitude of final reaction channels. It is known from previous experiments (e.g., [45, 46]) that the ejection of a 4*d* electron from a neutral Xe atom may be accompanied by the additional excitation and even ejection of an outer shell electron. Moreover, the 4*d* vacancy dominantly produced in the process described by equation (1) in the photon energy range 60-150eV can decay by the Auger process. As a result, the final product of the photoabsorption can also be a multiply charged residual ion. In addition, the electron rearrangement processes during or after the initial photoabsorption can lead to the fragmentation of the fullerene cage. All these processes occur rapidly and cannot be temporally resolved in the present experiments. Thus, in order to make a meaningful comparison of theory and experiment, either the individual final product channels of an initial photoabsorption have to be calculated -which is apparently very difficult- or as many final channels as possible have to be accounted for, experimentally, so that an approximate, but lower bounded, total absorption cross section of the Xe@C_{60} molecule and of the confined Xe atom can be reconstructed. In the present study the latter approach was pursued employing Xe@C_{60}^+ ions instead of neutral Xe@C_{60} molecules.

Possible reaction channels in the photon energy range 60–150 eV are I. net single ionization without or with fragmentations in which a number *N* of C_2 dimers are released

$$\mathrm{Xe@C_{60}^+} + \gamma \rightarrow \mathrm{Xe@C_{60-2N}^{2+}} + e + N\mathrm{C_2} \quad N = 0,\ 1,\ 2,\ 3,\ldots \tag{2}$$

II. net double ionization without or with fragmentations in which a number *N* of C_2 dimers are released

$$\mathrm{Xe@C_{60}^+} + \gamma \rightarrow \mathrm{Xe@C_{60-2N}^{3+}} + 2e + N\mathrm{C_2} \quad N = 0,\ 1,\ 2,\ 3,\ldots \tag{3}$$

III. net triple ionization without or with fragmentations in which a number *N* of C_2 dimers are released

$$\mathrm{Xe@C_{60}^+} + \gamma \rightarrow \mathrm{Xe@C_{60-2N}^{4+}} + 3e + N\mathrm{C_2} \quad N = 0,\ 1,\ 2,\ 3,\ldots \tag{4}$$

In principle, other types of disintegration of the fullerene cage are possible [29] and higher final charge states may also be reached. However, the present study indicates that II. and III. comprise the most important reaction channels for Xe@C_{60}^+ ions in the present photon energy range of the giant Xe atomic 4*d* resonance.

Figure 2 shows the experimental data for net single ionization of Xe@C_{60}^+ and C_{60}^+ ions with ejection of $N = 1$ and $N = 2$ C_2 dimers [49], respectively. Within the experimental uncertainties, the cross sections for producing Xe@C_{58}^{2+} and C_{58}^{2+} do not significantly differ from one another. The same is true for the production of Xe@C_{56}^{2+} and C_{56}^{2+}. The endohedral molecule and the empty carbon cage have identical cross sections in both cases. Thus, there is no measurable contribution of photoabsorption by the encapsulated Xe atom in this energy range that leads to net single ionization with fragmentation. This finding can be rationalized on the basis of measured cross sections for Xe^{q+} photo-ion production ($q = 1,\ 2,\ 3$) from neutral Xe as a function of the

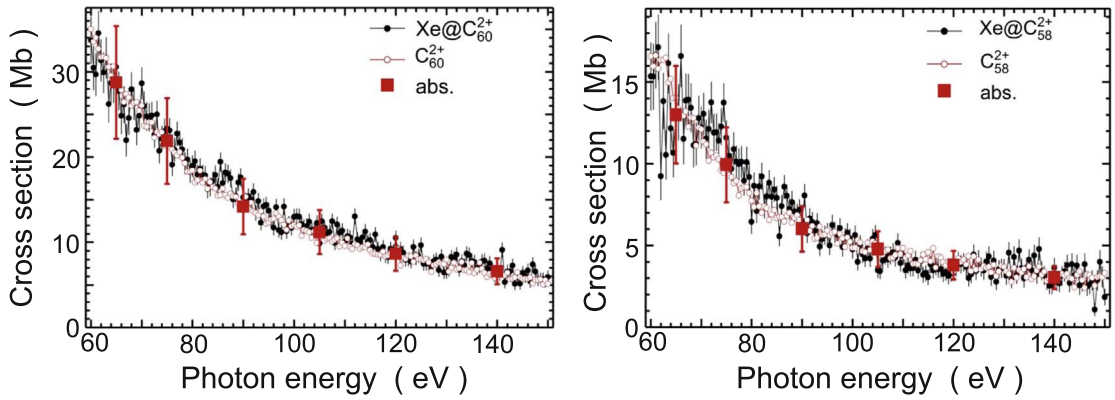

Figure 2. Single ionization of $Xe@C_{60}^{+}$ and C_{60}^{+} with fragmentation to $Xe@C_{58}^{2+}$ and C_{58}^{2+}, respectively (left panel) and, alternatively, to $Xe@C_{56}^{2+}$ and C_{56}^{2+} (right panel). The solid (red) squares are absolute experimental data for the empty fullerene cage.

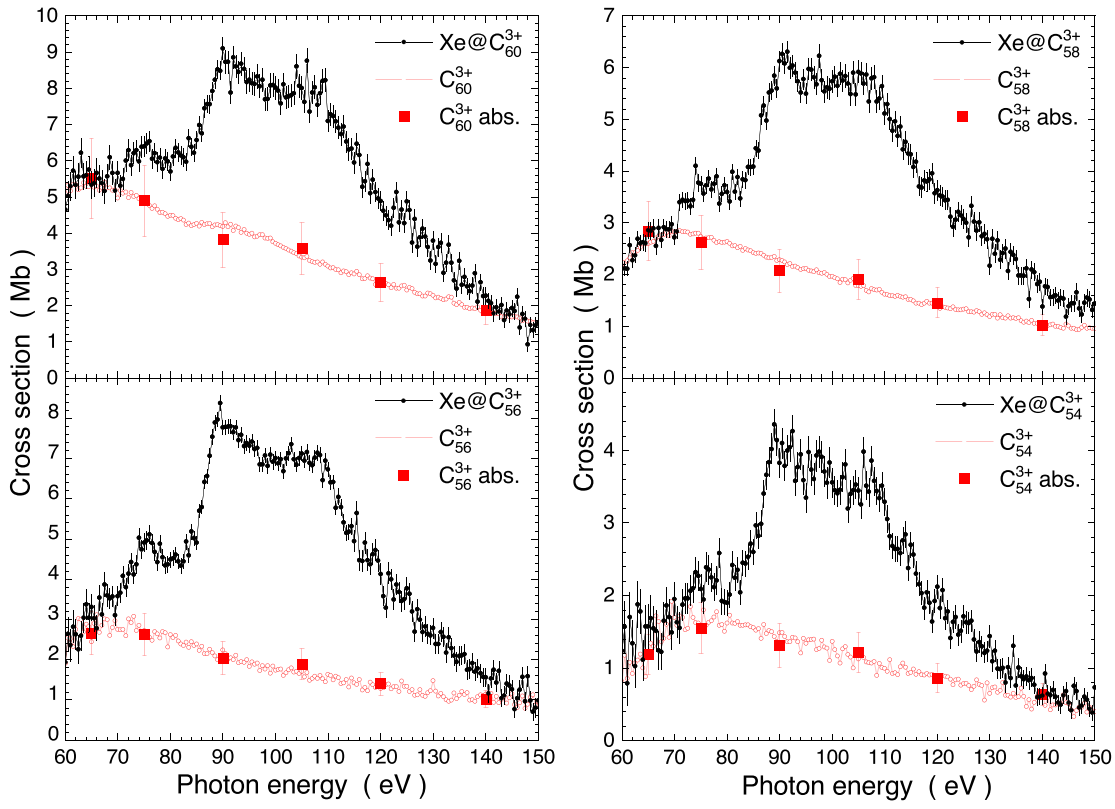

Figure 3. Double ionization of $Xe@C_{60}^{+}$ and C_{60}^{+} yielding $Xe@C_{60}^{3+}$ and C_{60}^{3+}, respectively (top left panel); $Xe@C_{58}^{3+}$ and C_{58}^{3+} (top right panel); $Xe@C_{56}^{3+}$ and C_{56}^{3+} (bottom left panel); $Xe@C_{54}^{3+}$ and C_{54}^{3+} (bottom right panel). 'Background' arising from the fullerene cage is shown by the lighter (red) data points (see also figure 2).

photon energy. Such data have been reported for example by Becker *et al* [46] and by Saito and Suzuki [50, 51]. The maximum cross sections in the energy range 60-150eV are [51]: for Xe^{+} 1.63 Mb at 86 eV, for Xe^{2+} 18.63 Mb at 100 eV, for Xe^{3+} 7.28 Mb at 105 eV, and for Xe^{4+} 0.257 Mb at 150 eV. Obviously, the present experiment is not sufficiently sensitive to a 1.6 Mb Xe cross-section contribution to single ionization of $Xe@C_{60}^{+}$ that is distributed among all possible $Xe@C_{60-2N}^{2+}$ final channels ($N = 0, 1, 2, 3,\ldots$). In addition, the cross sections for single ionization of C_{60}^{+} with fragmentation are relatively large (see figure 2), which hinders the detection of such a small Xe contribution on top of a large 'background'.

Figure 3 shows the experimental data for net double ionization of $Xe@C_{60}^{+}$ and C_{60}^{+} ions with ejection of $N = 0, 1, 2$ and 3 C_2 dimers [23]. The cross sections for the empty C_{60}^{+} cage are considerably reduced in comparison with those for single ionization (see figure 2). As a consequence, excess cross-section contributions arising from the encapsulated Xe atom are very clearly visible. These partial contributions can be obtained

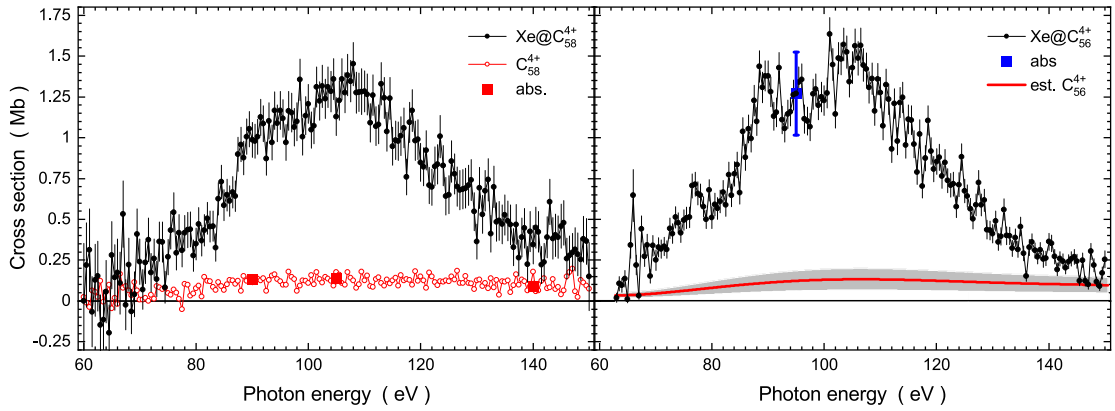

Figure 4. Triple ionization of $Xe@C_{60}^{+}$ and C_{60}^{+} with fragmentation to $Xe@C_{58}^{4+}$ and C_{58}^{4+}, respectively (left panel) and, alternatively, to $Xe@C_{56}^{4+}$ and estimated C_{56}^{4+} (right panel). 'Background' arising from the fullerene cage is shown by the lighter (red) data points in the left panel. The estimated contribution arising from the cage is shown as a solid (red) line in the right panel. The gray-shaded area indicates the uncertainty to be expected for this estimate. The solid (red and blue) squares are absolute data points for the associated observation channels.

straightforwardly by subtracting the measured empty-cage cross sections from the associated cross sections for the endohedral $Xe@C_{60}^{+}$ molecular ion. By integrating the Xe contributions over photon energies from 60 to 150eV one obtains the overall resonance strength S from which the absorption oscillator strength of each resonance peak is obtained [52] as $f_{abs} = S/(109.761\text{Mb eV})$. The numerical results of this procedure are $f_{abs} = 1.71 \pm 0.38$ (N=0), $f_{abs} = 1.51 \pm 0.33$ ($N = 1$), $f_{abs} = 2.10 \pm 0.46$ ($N = 2$), and $f_{abs} = 0.85 \pm 0.19$ ($N = 3$). The total oscillator strength found in the four investigated double-ionization channels amounts to $f_{abs} = 6.17 \pm 1.4$. This is already more than half of the oscillator strength of Xe in the energy range 60-150 eV. Clearly, additional Xe oscillator strength would have likely been found in the fragmentation channels associated with $Xe@C_{60-2N}^{3+}$ and $N \geqslant 4$.

After photoabsorption in the 60-150 eV energy range the Xe atom is found to be triply ionized with a probability of almost 40% of the double-ionization contribution [46, 50, 51]. Hence, one also expects contributions of Xe to be observable in the triple ionization of $Xe@C_{60}^{+}$. Measurements have been carried out for the final reaction channels $Xe@C_{58}^{4+}$ [49] and $Xe@C_{56}^{4+}$ [53]. The measured cross sections are shown in figure 4. The 'background' introduced by the carbon cage itself in the $Xe@C_{58}^{4+}$ channel, that is the cross section for the production of C_{58}^{4+} after photoabsorption by C_{60}^{+}, was also measured. For the $Xe@C_{56}^{4+}$ channel the cage background was estimated to be similar to the cross section for the production of C_{58}^{4+}. This assumption is considered to provide an upper limit of this cross section. Usually, the cross sections for ionization plus fragmentation of fullerenes decrease with increasing number N of C_2 dimers ejected. In double ionization the cross section for the production of C_{58}^{3+} was measured to be almost identical to that for the production of C_{56}^{3+}. Hence, the estimate for the C_{56}^{4+} channel seems justified and an uncertainty of $\pm$ 50% has been assigned.

Overall, the cross sections measured for the two triple-ionization channels are substantially smaller than those for double ionization. The statistical error bars are relatively large due to the low signal rates. Nevertheless, the contributions arising from the encapsulated Xe atom are evident in the measurements. As before they can be determined quantitatively by subtracting the empty-cage contributions from the cross sections of the whole endohedral molecule. Integration of the associated resonance strengths results in a contribution $f_{abs} = 1.05 \pm 0.25$ from the two investigated triple-ionization channels.

The cross section for the production of $Xe@C_{58}^{4+}$ shows less structure than the other product channels that were investigated. This may be attributable to a contribution to this channel arising from 4d ionization accompanied by additional ejection of a 5p electron and a subsequent single-Auger decay. The simultaneous ejection of two electrons in the first step of photoionization implies that the two electrons share the excess energy and therefore have continuous energy distributions that do not support distinct structures arising from confinement resonances. However, most of the contribution to net triple ionization may still come from the process described by equation (1) plus subsequent emission of two Auger electrons. The shape of the cross section for the production of $Xe@C_{56}^{4+}$ supports this assumption. The statistical uncertainties must be considered when drawing conclusions.

By adding the partial cross sections found in the eight investigated final reaction channels populated subsequent to photoabsorption by the confined Xe atom inside a C_{60}^{+} cage, a structured peak (the gray open circles in figure 5) is found in the energy range 60-150 eV. The typical total experimental uncertainty of these data is indicated by the large error bars on the measured point at 93 eV. The resonance strength contained in the

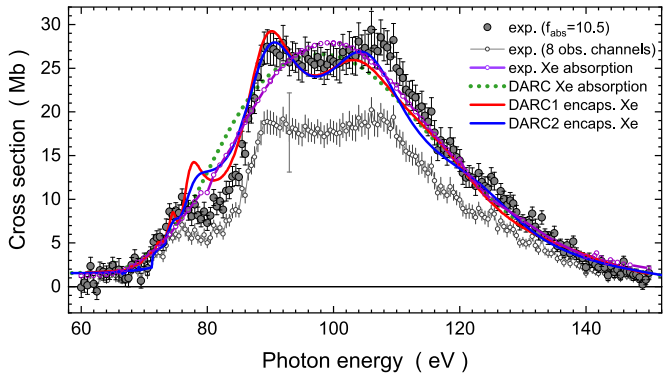

Figure 5. Comparison of theory and experiment, both quantifying the excess cross section due to the encapsulated xenon atom in the Xe@C_{60}^{+} molecule. For details see main text.

Xe peak yields an oscillator strength $f_{abs} = 7.22 \pm 1.7$. This is 69 ± 16% of the total oscillator strength of 10.5 expected in the photoabsorption cross section of the neutral free Xe atom in the energy range 60-150 eV. It is likely that the remaining 31% would be recovered if all possible fragmentation channels remaining in I, II, and III were investigated. For comparison with theory it is appropriate therefore, to multiply the measured cross-section sum by a scaling factor of 10.5/7.22. The resulting data are shown in figure 5 as solid (dark gray-shaded) circles with their statistical error bars. The oscillations modulating the smooth giant Xe 4*d* resonance cross section (given by the magenta line with symbols for the measurements [47, 48], see above) unambiguously provide the only experimental demonstration to date of the phenomenon of confinement resonances in an endohedral fullerene.

The previous publication of experimental results for double ionization without and with fragmentation (cases from II) were accompanied by calculations on the basis of the relativistic Dirac atomic R-matrix code (DARC) [23]. The dotted (green) line in figure 5 is the DARC result for photoabsorption by a free Xe atom. The dark (blue) solid line labeled DARC1 was calculated by describing the cage by a spherical square-well potential of depth 8.2 V with inner and outer radii $r_{inner} = 0.33$ nm and $r_{outer} = 0.39$ nm, respectively. The lighter (red) solid line labeled DARC2 was calculated for a potential of depth 8.8 V with inner and outer radii $r_{inner} = 0.31$ nm and $r_{outer} = 0.40$ nm, respectively. Small changes of the parameters have a sizable effect on the shape of the cross section curve. It is also clear that a simple spherical square-well potential with a single set of parameters cannot adequately describe the C_{60} cage.

The magnitudes of the inner and outer radii of the C_{60} shell have been an issue of debate in the literature (see e.g. reference [54]). Only the radius of the nuclear skeleton $R = 0.35$ nm [55] of the C_{60} molecule appears to be generally accepted. Considering the simplicity of the spherical square-wave potential, the actual geometrical properties of C_{60}, upon which the radii and depths were chosen for this model potential, are not obvious. Recommended radial parameters extend over fairly large ranges. For the inner radius, values are found (without a claim for completeness) between $r_{inner} = 0.279$ nm [56] and $r_{inner} = 0.326$ nm [57]. Similarly, the outer radius has been determined to be between $r_{outer} = 0.384$ nm [58] and $r_{outer} = 0.429$ nm [56]. The parameters estimated from the present experiment are well within these ranges.

4. Summary and outlook

The first and only experimental demonstration, to date, of confinement resonances in an endohedral fullerene has been accomplished for the Xe@C_{60}^{+} molecular ion. Eight final channels that can be populated in connection with the absorption of a single photon by Xe@C_{60}^{+} were investigated, the results for four of them not previously published. Among all possible channels, the eight investigated final products of the kind Xe@C_{60-2N}^{q+} with selected combinations of $N = 0, 1, 2, 3$ and $q = 2, 3, 4$ contain about 70% of the absorption oscillator strength to be expected for the Xe atom in the energy range 60-150 eV. Relativistic R-matrix calculations modelling the influence of the C_{60}^{+} cage by a spherical square-well potential are in satisfying agreement with the experimental findings, both in cross section magnitude and their dependence on the photon energy.

With the present technique of implanting Xe ions into C_{60} fullerenes it would in principle be possible to produce additional endohedral fullerenes with different carbon cages and encapsulated atoms of other elements. By optimizing the parameters of the implantation process, higher yields of sample materials should be attainable. Enhancing the purity of the samples by high performance liquid chromatography or other possible techniques would increase the ion beam currents and therefore the signal rates achievable in the photon-ion merged-beams experiments. For the present Xe@C_{60} it would be of interest to investigate the missing product

channels contributing to the total photoabsorption cross section. Moreover, in addition to 4*d* excitation, 3*d* excitation at higher photon energies is predicted to support a different group of confinement resonances that could provide a deeper insight into the quantum-cavity effects of the carbon cage. Numerous additional confinement-resonance phenomena have been theoretically postulated in endohedral fullerenes with encapsulated atoms from a large part of the periodic table and await experimental confirmation. However, considering the substantial effort in time, manpower and the equipment that made the present investigation possible, it is clear that extending this experimental program would be challenging, but could be facilitated by progress in experimental synthesis techniques.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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