Significant Redistribution of Ce 4*d* Oscillator Strength Observed in Photoionization of Endohedral $Ce@C_{82}^{+}$ Ions

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Mass-selected beams of atomic Ce^{q+} ions ($q = 2, 3, 4$), of C_{82}^{+} and of endohedral $Ce@C_{82}^{+}$ ions were employed to study photoionization of free and encaged cerium atoms. The Ce 4*d* inner-shell contributions to single and double ionization of the endohedral $Ce@C_{82}^{+}$ fullerene have been extracted from the data and compared with expectations based on theory and the experiments with atomic Ce ions. Dramatic reduction and redistribution of the ionization contributions to 4*d* photoabsorption is observed. More than half of the Ce 4*d* oscillator strength appears to be diverted to the additional decay channels opened by the fullerene cage surrounding the Ce atom.

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Since the discovery of endohedral $La@C_{60}$ fullerene [1] the concept of an atom inside a fullerene molecule has fascinated chemists and physicists alike. Encapsulating an atom within a sphere of subnanometer size is of highest fundamental and applied interest. Endohedral fullerenes [2] have thus stimulated the imaginations of researchers from many different fields concerning what could happen to an atom in the unique environment of a carbon cage. New possibilities for applications in nanostructure science and technology are being vigorously explored. For example, confinement within a fullerene could have some unique advantages in isolating an atom from its environment, thereby providing a building block for the qubits of a quantum computer [3]. The chemical isolation of reactive and poisonous atoms may also open up new possibilities in medical imaging and cancer therapy [4,5].

Numerous theoretical studies have explored the response of atoms encapsulated in fullerene cages to ionizing electromagnetic radiation. While there are almost no experimental results available for endohedral molecules in the gas phase, theoretical work flourishes without constraints [6]. Clearly, experiments are needed to test and guide the theoretical developments; however, measurements with free endohedral molecules in the gas phase are almost prohibitively difficult. Challenges include the availability of sufficient amounts of target material for gas phase experiments and the purity of the samples to be investigated. Obtaining absolute cross sections for interactions of endohedral species with any kind of radiation is presently close to impossible. The only gas phase experiments with endohedral fullerenes reported to date were conducted by Mitsuke and co-workers on vapors of $Ce@C_{82}$ [7], $Dy@C_{82}$ [8] and $Pr@C_{82}$ [9] exposed to synchrotron light. Cross sections for photoionization with different exit channels have been inferred and evidence was claimed for oscillations as predicted in the $4d - 4f$ atomic inner-shell contributions to photoionization of $Xe@C_{60}$ [6].

The present experiment employs a different approach to overcome problems with the characterization of the endohedral fullerene target and with quantifying its properties. Evaporated fullerenes are efficiently ionized in a low-power plasma of an electron cyclotron resonance (ECR) ion source. The ions are extracted and accelerated by several kV and a beam with defined particle energies is formed. Mass selection by a subsequent dipole magnet provides the desired ion species in the form of a well-characterized fullerene ion beam which then serves as the target for a beam of synchrotron radiation from undulator beam line 10.0.1 of the Advanced Light Source (ALS) in a merged beam geometry. The merged-beams technique for photon-ion interactions is well established [10] and can provide absolute cross sections taking advantage of the availability of energetic projectile and target beams in the experiments. Density profiles and intensities are readily measured for such beams and complete registration of product ions in a suitable detector can be ensured [11]. Different product ion beams are dispersed by a second dipole analyzing magnet and a subsequent electrostatic spherical 90° deflector, thereby sorted with respect to their energy, mass and charge state. By using merged beams, many systematic problems with measurements on static neutral endohedral species can be avoided. However, the availability and sufficient quantities of the desired species remain a problem. Efficient production and purification processes of the endohedral fullerenes [2] have to be combined with high ion yield from dilute vapors ($\sim 10^{-6}$ hPa), high detection probabilities (close to 100%) and low levels of detector background [12]. For the present experiments cerium fullerene soot was prepared by a standard arc

burning process [13]. Given the mass separation capability of the photoionization experiment, the purification process was limited to the 20% level of the $Ce@C_{82}$ component. Milligram quantities of endohedral $Ce@C_{82}$ fullerenes were sufficient to provide picoAmpere ion currents continuously over several days.

The goal of the present experiment was to investigate possible differences in the behavior of free and of caged atomic ions exposed to monochromatic ultraviolet radiation, a topic that is presently of utmost interest [14,15]. In particular, the decay of $4d$ vacancies in the encapsulated cerium is the focus of the present study, relating to theoretical considerations recently summarized by Amusia [6]. For the purpose of comparison, cross sections for single and double photoionization of $Ce@C_{82}^+$, C_{82}^+ as well as of Ce^{2+}, Ce^{3+}, and Ce^{4+} ions were determined.

One of the first questions to be answered when studying metal atoms encapsulated within a fullerene is that of the valence state of the atom in the reductive environment of the cage. Previous investigations showed that the cerium atom in $Ce@C_{82}$ is trivalent [16]. As a result, the endohedral fullerene, although electrically neutral as a whole, can be described as $Ce^{3+}@C_{82}^{3-}$. A recent density functional study [17] explains details of the charge transfer from and to the different subshells of the cerium atom within $Ce@C_{82}$ and provides an explanation to the preferential Ce off-center bonding site on the inner surface of the carbon sphere. Since the present object of investigation is the singly charged $Ce@C_{82}^+$ ion, the effective charge state of the encaged Ce atom might be higher than $q = +3$. Therefore, several charge states of atomic Ce were included in this study. Photoionization of Ce atoms and low charge ions is dominated by resonance features associated with excitation of the $4d$ shell [10]. Modification of the cross section of the $Ce@C_{82}^+$ ion by the encapsulated Ce atom is to be expected, especially in the energy region of $4d \rightarrow nl$ resonances. The photon energy range covered in the experiments was between 17 eV and about 190 eV depending on the observable signals. Photon energy spreads were below 0.5 eV. Special attention was devoted to the energy range 80 to 190 eV where the $4d$ spectral fingerprints of cerium occur.

Mass spectra recorded for the endohedral fullerene ion beam showed that $Ce@C_{82}^+$ ions with mass number 1124 could not be completely separated from C_{94}^+ with mass number 1128. By increasing the resolution of the analyzer, i.e., by narrowing slits, the contamination of the primary ion beam could be estimated to be about 25%. Considering the presence of an admixture to the parent ion beam and the fact that measurements of cross sections at the low ion currents available for the measurements imply large uncertainties of at least 30%, the experimental data were normalized to scaled cross sections for C_{60}^+ ions obtained with the identical apparatus [18]. At energies from about 50 eV up to the carbon K-shell threshold the measurements for single ionization of C_{60}^+ ions are found [19] to have an energy dependence as predicted by the Henke model [20] where the photoabsorption of a molecule is just given by the sum of the cross sections for each single atom in the molecule. For C_{60} this implies 60 times the absorption of a carbon atom. The cross sections found for single ionization of C_{60}^+ are 12% below the absorption cross section predicted by the model calculation. Previous experiments with higher fullerenes [19] agreed with the prediction that cross sections of empty fullerenes scale with the number of carbon atoms. Hence, the expected cross section for the empty C_{82} is 82/60 times that of C_{60} and, accordingly, the measured yields for single ionization of C_{82}^+ and of $Ce@C_{82}^+$ were normalized to the expectation in the energy range 80 to 100 eV where cerium does not significantly contribute. Much care was taken to measure the ratios of double versus single ionization cross sections for both the endohedral and the empty-fullerene ion, thus providing the basis for normalizing the double-ionization yields to the scaled C_{60}^+ results.

Figure 1 shows the cross sections obtained for single and double ionization of $Ce@C_{82}^+$ ions together with data for single ionization of the empty C_{82}^+ fullerene ion. The cross section for the empty cage ion is smooth in the present

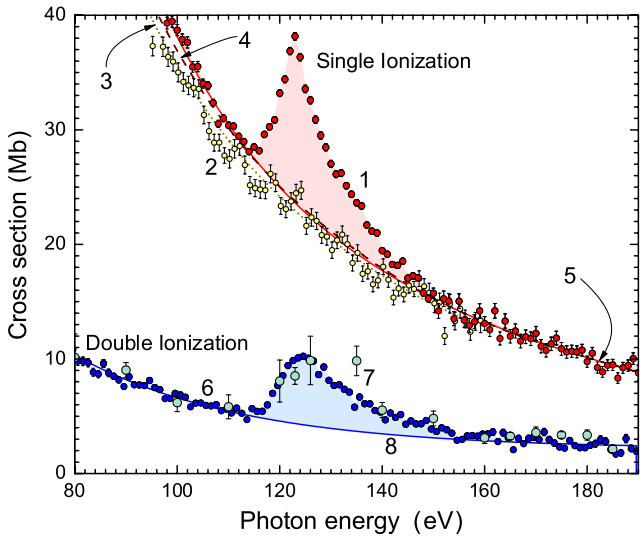

FIG. 1 (color online). Cross sections $\sigma_{i,j}$ for photoionization from initial charge state i to final charge state j in the energy region of Ce $4d$ excitation: (1) $\sigma_{1,2}$ of $Ce@C_{82}^+$; (2) $\sigma_{1,2}$ of C_{82}^+; (3) $\sigma_{1,2}$ of C_{82}^+ scaled from results for C_{60}^+ (see text); (4) scaled $\sigma_{1,2}$ of $Ce@C_{82}^+$ accounting for a 25% contamination of the parent ion beam with C_{94}^+; (5) fit curve representing the empty-fullerene background under the Ce $4d$ contribution to single ionization of $Ce@C_{82}^+$; (6) scan measurement of $\sigma_{1,3}$ of $Ce@C_{82}^+$ normalized to (7), i.e., data points (with larger error bars) obtained from measured cross section ratios $\sigma_{1,2}/\sigma_{1,3}$ and the normalized data set (1); (8) fit curve representing the empty-fullerene background under the Ce $4d$ contribution to double ionization of $Ce@C_{82}^+$. Error bars are statistical only.

energy range of interest which is also true for the double ionization (not shown). Because of the 25% contamination of the primary $Ce@C_{82}^+$ ion beam, the expected "background" corresponding to 75% C_{82}^+ and 25% C_{94}^+ is enhanced by only 3.7% (curve 4 in Fig. 1). The effects of $4d$ excitation of the encapsulated cerium atom on the ionization cross sections of $Ce@C_{82}^+$ are clearly seen.

For clarification of the valency of the Ce atom residing within the $Ce@C_{82}^+$ ion, data obtained for single ionization of atomic Ce^{2+}, Ce^{3+} and Ce^{4+} are compared in Fig. 2 with the Ce $4d$ excess cross section in single ionization of the endohedral $Ce@C_{82}^+$ ions. The difference between the data set (1) in Fig. 1 and the background fit (curve 5) was divided by the fraction (0.75) of $Ce@C_{82}^+$ ions in the parent beam. The excess cross section is relatively structureless indicating the hybridization of the outer levels of the Ce atom and the fullerene cage and the resulting increase of resonance widths. In spite of this difference, the comparison clearly shows the best match of resonance energies for the endohedral Ce atom with $\sigma_{3,4}$ for atomic Ce^{3+}. As in the neutral $Ce@C_{82}$ molecule the valency of Ce in the $Ce@C_{82}^+$ ion is 3. A similar comparison for double ionization of the same ions with the best match for Ce^{3+} confirms this conclusion.

For atomic Ce^{3+} ions, photoabsorption in the present energy range is expected to be dominated by $4d$-shell excitations resulting in single and double ionization of the absorbing ion. Triple ionization with a threshold near 180 eV is energetically not allowed and radiative stabilization of a $4d$ vacancy can be neglected. On that basis one would expect a total oscillator strength f_a of 10 for the absorption by ten $4d$ electrons. Integration of the cross section sum $\sigma_{3,4} + \sigma_{3,5}$ for Ce^{3+} ions (see the upper chain curve in Fig. 3) in the energy range 100 to 170 eV yields $f_a = 8.5$. With the limitation of the integration range, a possible small contribution of fluorescence stabilization and the expected total uncertainty of the ionization cross sections for atomic Ce^{3+} of at least 20% the total experimental oscillator strength is in good agreement with the expectation. In strong contrast to that, absorption by the encapsulated Ce atom involving $4d$ excitation and subsequent ionization is much smaller (see Fig. 3). The excess cross sections for single and double ionization of the endohedral fullerene obtained from Fig. 1 and their sum are much smaller than the corresponding data for atomic Ce^{3+}. Integration over the investigated energy range is shown by the lower chain curve in Fig. 3. The difference is more than a factor of 2. Integration of the endohedral data to 180 eV results in $f_a = 3.6$, i.e., only 36% of the expected total oscillator strength or 42% of the number observed in photoionization of Ce^{3+}. The missing strength cannot be explained by uncertainties in the normalization procedures used here. Actually, the total *absorption* expected for 82 carbon atoms must be considered an upper limit for the empty-endohedral background *ionization* cross section. In that respect, the derived Ce $4d$ contributions to single and double ionization of endohedral $Ce@C_{82}^+$ are also at their upper limits. Apparently, $4d$ vacancy decay via autoionizing channels is greatly sup-

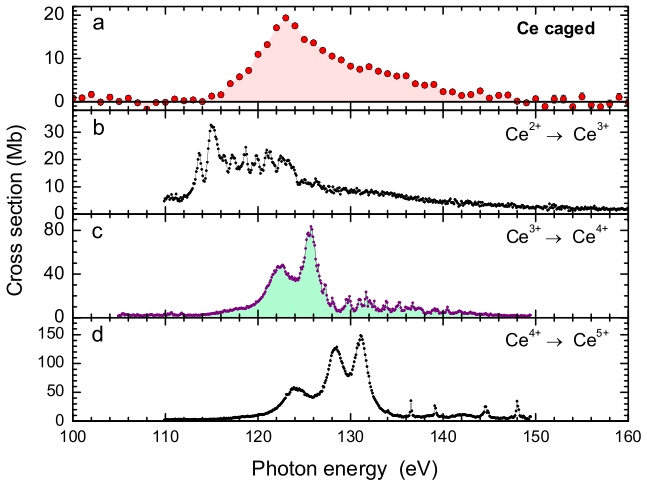

FIG. 2 (color online). Comparison of absolute cross sections for single photoionization of atomic Ce^{q+} ions $q = 2$ (b), $q = 3$ (c), $q = 4$ (d) with the excess cross section (a) obtained by subtracting curve (5) in Fig. 1 from the data set (1) and correcting for the contamination of the parent ion beam.

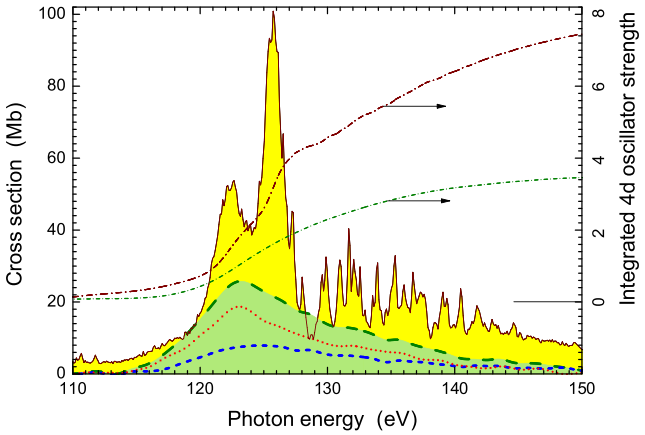

FIG. 3 (color online). Cross sections and integrated oscillator strengths for photoionization of atomic Ce^{3+} ions and for the Ce $4d$ contributions to single and double ionization of $Ce@C_{82}^+$. Solid (brown) line with shading (yellow): $\sigma_{3,4} + \sigma_{3,5}$ for Ce^{3+}; long-dashed (green) line with shading (light green): sum of the Ce $4d$ contributions to single ionization, represented by the dotted (red) line, and double ionization of $Ce@C_{82}^+$, represented by the short-dashed (blue) line. The chain curves correspond to the oscillator strength scale on the right (note the offset). The upper (brown) curve is the energy-integrated total absorption oscillator strength of Ce^{3+} in the energy region of $4d$ excitations, and the lower (green) curve results from the integration of the long-dashed (green) curve, i.e., from the $4d$ contributions to single and double ionization of $Ce@C_{82}^+$.

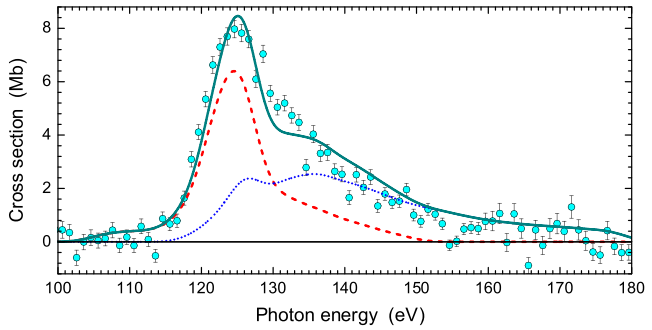

FIG. 4 (color online). Cross section [(cyan) shaded circles with statistical error bars] for the Ce 4*d* contribution to double ionization of $Ce@C_{82}^{+}$ obtained by subtracting curve (8) from the data set (6) shown in Fig. 1. The dashed (red) curve is the cross section $\sigma_{3,4}$ for atomic Ce^{3+} convoluted with a 5-eV Gaussian and multiplied by a factor 0.15, the dotted (blue) curve is the cross section $\sigma_{3,5}$ for atomic Ce^{3+} convoluted with a 5-eV Gaussian and multiplied by a factor 0.22. The solid (dark cyan) line is the sum of the two latter curves.

pressed for Ce^{3+} encapsulated inside a fullerene cage relative to free Ce^{3+}.

Since the cage of the endohedral fullerene is transparent to the incident EUV photons, one has to conclude that most of the absorption oscillator strength of the 4*d* electrons in the encapsulated Ce is diverted to decay channels other than net single and double ionization which were isolated and individually observed in the present experiment. A test measurement showed that triple ionization, though energetically possible in the endohedral fullerene, does not significantly contribute to the total 4*d* absorption cross section. It is hypothesized that the most likely additional decay channels for the relaxation of the Ce 4*d* vacancy in the endohedral $Ce@C_{82}^{+}$ ions opened up by the presence of the fullerene cage are related to ionization with fragmentation. First evidence for this hypothesis was obtained by observing a Ce 4*d* enhancement in the photo-ion yield of mass/charge separated $Ce@C_{78}^{2+}$ produced from the parent $Ce@C_{82}^{+}$ beam.

In an attempt to quantify the 4*d* suppression for single and double ionization of $Ce@C_{82}^{+}$ the cross sections for atomic Ce^{3+} ions were convoluted with a 5 eV Gaussian which appears to give a reasonable representation of the smearing effect of the hybridization in the endohedral system. It turns out that 45% of the resulting convoluted cross section $\sigma_{3,4}$ gives a fairly good representation of the measured 4*d* single ionization contribution in $Ce@C_{82}^{+}$ (the dotted curve in Fig. 3), which is well compatible with the overall 42% of the total absorption contribution. Trying the same with double ionization immediately shows that the measured 5-eV Gaussian-convoluted cross section $\sigma_{3,5}$ (dotted curve in Fig. 4) contributes only 22% to the inferred 4*d* double-ionization contribution (short-dashed line in Fig. 3 and circles in Fig. 4) in $Ce@C_{82}^{+}$. Reasonable agreement with the measured 4*d* double-ionization function is only obtained by including an additional 15% contribution of the 5-eV Gaussian-convoluted cross section $\sigma_{3,4}$ (dashed curve in Fig. 4). This redistribution of partial oscillator strengths is a consequence of "post-decay" interactions of the ejected Auger electrons with the fullerene cage. Possibilities are electron scattering, electron capture, electron-impact ionization and fragmentation subsequent to ionization of the encapsulated Ce atom.

In summary, clear spectral fingerprints of 4*d* excitation of Ce atoms encapsulated in a fullerene have been observed both in single and double photoionization. For the first time, the anticipated redistribution of decay probabilities of a caged atom versus its free counterpart has been clearly demonstrated. Detailed energy-dependent information has been obtained on the effects of the electrons ejected from the encapsulated atom on the surrounding carbon sphere.

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[1] Y. Chai *et al.*, J. Phys. Chem. **95**, 7564 (1991).
[2] L. Dunsch and S. Yang, Small **3**, 1298 (2007).
[3] W. Harneit *et al.*, Phys. Rev. Lett. **98**, 216601 (2007).
[4] C.-Y. Shu *et al.*, Bioconjugate Chemistry **19**, 651 (2008).
[5] K. B. Hartman, L. J. Wilson, and M. G. Rosenblum, Molecular Diagnosis & Therapy **12**, 1 (2008).
[6] M. Ya. Amusia, J. Electron Spectrosc. Relat. Phenom. **161**, 112 (2007).
[7] K. Mitsuke *et al.*, J. Chem. Phys. **122**, 064304 (2005).
[8] K. Mitsuke *et al.*, Int. J. Mass Spectrom. **243**, 121 (2005).
[9] H. Katayanagi *et al.*, J. Quant. Spectrosc. Radiat. Transfer **109**, 1590 (2008).
[10] H. Kjeldsen, J. Phys. B **39**, R325 (2006).
[11] A. M. Covington *et al.*, Phys. Rev. A **66**, 062710 (2002).
[12] A. Müller *et al.*, J. Phys. Conf. Ser. **88**, 012038 (2007).
[13] L. Dunsch *et al.*, Synth. Met. **121**, 1113 (2001).
[14] V. Averbukh and L. S. Cederbaum, Phys. Rev. Lett. **96**, 053401 (2006).
[15] M. E. Madjet, H. S. Chakraborty, and S. T. Manson, Phys. Rev. Lett. **99**, 243003 (2007).
[16] W. Sato *et al.*, J. Radiol. Nucl. Chem. **239**, 187 (1999).
[17] K. Muthukumar and J. A. Larsson, J. Phys. Chem. A **112**, 1071 (2008).
[18] S. W. J. Scully *et al.*, Phys. Rev. Lett. **94**, 065503 (2005).
[19] A. Müller *et al.*, in Latest Advances in Atomic Cluster Collisions, edited by J.-P.- Connerade and A. V. Solov'yov [Imperial College Press, London, (to be published)].
[20] B. L. Henke, E. M. Gullikson, and J. C. Davis, At. Data Nucl. Data Tables **54**, 181 (1993).