Photoionization of Ce$^{3+}$-Ce$^{4+}$

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ABSTRACT

Photoionization of the Ce$^{3+}$ - Ce$^{4+}$ process has been studied using the random phase approximation with exchange method in the energy region 100-150 eV. Comparison of our results with the recent measurement [Müller et al, Phys. Rev. Lett. 101, 133001 (2008)] confirms the suppression effect of the carbon cage in the endohedral fullerene Ce@C$_{82}^+$ photoionization. The reasons for the cause of the confinement resonance and the suppression effect are discussed.
1. Introduction

The motivation to study the photoionization of the Ce\(^{3+}\) - Ce\(^{4+}\) process is the disturbing discrepancy between the theoretical calculations and the experimental measurements of the photoionization of an endohedrally confined atom. The theoretical calculations [1-6] indicate the presence of strong confinement resonances for the endohedral fullerenes, such as Xe@C\(_{60}\) [6]. However, the experimental results [7-11] demonstrate a great suppression of the photoionization cross section of an atom encapsulated in the carbon sphere, for example the photoionization of Ce@C\(_{82}\) [7], Pr@C\(_{82}\) [8], Ce@C\(_{82}^+\) [9, 10], and Dy@C\(_{82}\) [11].

Both experiments [12, 13] and theoretical study [14] have indicated that the Ce atom in the endohedral fullerene Ce@C\(_{82}\) is located at an off-centered position adjacent to the carbon cage and the encapsulated Ce atom donates three valence electrons to the carbon sphere. The electronic state of Ce@C\(_{82}\) can be formally described as Ce\(^{3+}\)@C\(_{82}^{3-}\) [13]. The same charge state can be found for the Ce atom in the endohedral molecule Ce@C\(_{82}^+\) [10]. Since the photoelectron ionized from the Ce\(^{3+}\) ion of the Ce@C\(_{82}^+\) molecule will be multiply reflected to different directions by the carbon cage, it is difficult from a theoretical point of view to consider the photoionization of an off-centered Ce\(^{3+}\) ion. However, the photoionization of the Ce\(^{3+}\) ion can be calculated by using our recently developed random phase approximation with exchange (RPAE) method [15] if the necessary modifications in the computer code are made. The results should further confirm the cage suppression effect if agreement is obtained with the experimental data for the Ce\(^{3+}\) - Ce\(^{4+}\) photoionization [10] or a transparent cage model can be set up for the photoelectron if it agrees with the photoionization cross section of the Ce@C\(_{82}^+\).

The RPAE method, which allows for the inclusion of both intrashell and intershell correlations has been developed recently by Chen and Msezane for atoms(ions) with an outer open-shell [15], or with an inner open shell [16] and has been successfully used to study the 4\(d - \epsilon f\) photoionization of the ions Xe\(^+\) [15] and I\(^+\) [16] and the photoelectron angular distribution asymmetry parameter \(\beta\) of the Sc 4s electron [17]. In this calculation our RPAE codes are modified to include the intershell coupling between the Ce\(^{3+}\) 5\(s - \epsilon p, 5p - \epsilon s, d\) and 4\(d - 4f\) transitions. A new computer code is used to study the Ce\(^{3+}\) photoionization.

2. Theory
The RPAE equation and the symbols and operators in the equation for an atom with an outer open-shell is given by Eq. (1) of Ref [15]. Similar terms will be added for the switch of other electron pairs. All the matrix elements have been derived and presented in the Appendices of Refs. [15] and [17]. The Coulomb matrix elements which are needed to evaluate the intershell coupling between the 5s – \( \epsilon p \), 5p – \( \epsilon s, \epsilon d \) and 4d – 4f transitions of the Ce\(^{3+} \) ion, are given in the Appendix of this paper.

The ground state of the Ce\(^{3+} \) ion has the configuration [Xe]4f\((2F)\). Here we assume the 5d and 6s\(^2 \) electrons of the Ce atom, which are located outside the 4f orbital have been transferred to the carbon cage in the endohedral fullerene Ce@C\(_{82}^+\).

Since we try to include the intershell couplings among the 5p – \( \epsilon s, \epsilon d \), 5s – \( \epsilon p \), and 4f – \( \epsilon d, \epsilon g \) transitions, the following combined core with discrete and continuum electron states have been included in the calculation.

We have a total of 21 channels from the 5p + \( h\nu \) → \( \epsilon d, \epsilon s \) transitions to the states:

\[
4d^{10}5s^25p^54f(1D, \ 1G, \ 1F, \ 3D, \ 3G, \ 3F,)\epsilon d(2D, \ 2F, \ 2G),
\]

\[
4d^{10}5s^25p^54f(1D, \ 3D)\epsilon s(2D),
\]

\[
4d^{10}5s^25p^54f(1F, \ 3F)\epsilon s(2F),
\]

\[
4d^{10}5s^25p^54f(1G, \ 3G)\epsilon s(2G),
\]

a total of 6 channels from the 5s + \( h\nu \) → \( \epsilon p \) transition to the states:

\[
4d^{10}5s^25p^54f(1F, \ 3F)\epsilon p(2D, \ 2F, \ 2G),
\]

and a total of 2 channels from the 4f + \( h\nu \) → \( \epsilon d, \epsilon g \) transitions to the states:

\[
4d^{10}5s^25p^6(1S)\epsilon d(2D),
\]

\[
4d^{10}5s^25p^6(1S)\epsilon g(2G).
\]

The closed shells of 1s, 2s, 2p, 3s, 3p, 4s, and 4p are not listed above. As the photoionization process is caused mainly by the autoionization of the 4f subshell our code has several special subroutines to treat the 4d\(^{10}\)4f + \( h\nu \) → 4d\(^9\)4f\(^2\) transition, with a total of 14 channels:

\[
4d^{10}5s^25p^64f + h\nu \rightarrow 4d^95s^25p^6(4f^2(3H))(2F, \ 2G) \quad (1)
\]

\[
4d^{10}5s^25p^64f + h\nu \rightarrow 4d^95s^25p^6(4f^2(3F))(2D, \ 2G) \quad (2)
\]

\[
4d^{10}5s^25p^64f + h\nu \rightarrow 4d^95s^25p^6(4f^2(3P))(2D, \ 2F) \quad (3)
\]

\[
4d^{10}5s^25p^64f + h\nu \rightarrow 4d^95s^25p^6(4f^2(1I))(2G) \quad (4)
\]

\[
4d^{10}5s^25p^64f + h\nu \rightarrow 4d^95s^25p^6(4f^2(1G), \ 1D))(2D, \ 2F, \ 2G) \quad (5)
\]
\[ 4d^{10}5s^25p^64f + h\nu \rightarrow 4d^{10}5s^25p^6(4f^2(1S))(^2D) \quad (6) \]

The Ce\(^{3+}\) ground state and the core wave functions were obtained through the self-consistent Hartree-Fock (HF) calculation. Then the radial functions of the discrete and continuum electron were obtained by solving the linear HF equations without self-consistency using those core wave functions. Each radial function has been represented by 2000 points. After evaluating the dipole matrix elements and the Coulomb matrix elements of the time-forward type and the time-backward type, the RPAE equation was solved to obtain the partial cross sections with a total of 15 \(^2D\) states, 15 \(^2G\) states, and 13 \(^2F\) states. All types of matrix elements are evaluated using the equations found in the Appendices of Ref. [15] and Ref. [16]. Equations for the Coulomb matrix elements of the intershell coupling between the Ce\(^{3+}\) \(5p - \epsilon s, \epsilon d, 5s - \epsilon p\) and \(4d - 4f\) transitions are found in the Appendix of this paper.

**Results**

It is well known that there are two kinds of giant resonances [18]. One is the shape resonance in which the properties of the giant resonance is determined mainly by the effective potential for the \(f\) electron. The overlaps of bound \(f\) orbital with the \(4d\) orbital are very small. Most of the \(4d \rightarrow f\) oscillator strength is associated with the continuum state. The photoionization of the \(4d - \epsilon f\) channel in the atoms Xe, Ba, and I [19] and ions Xe\(^+\) [15] and I\(^+\) [16] are the examples of this type of giant resonance. The resonance results from a one step process: continuum enhancement due to the centrifugal-barrier shape resonance. The second type of giant resonance corresponds to a decaying discrete resonance, which results from a two-step process: photoexcitation of a \(4d\) electron into the \(4f\) subshell, followed by autoionization of the \(4d^04f^{N+1}\) state where \(N\) is the initial occupation number for the \(4f\) electron. An example of this type of giant resonance is found in the photoionization of the rare earths elements. The decaying discrete resonance is related to the so-called collapsed \(f\)-wave function. In this situation the inner well is deep enough to support a bound state and the \(4f\) orbital "collapses" into the inner well.

The photoionization of the Ce\(^{3+}\) \(4d\) electron belongs to the second type of giant resonance. The mean radius of the \(4f\) electrons is only 0.96 a.u., which is much smaller than that of the \(5s\) electrons (1.58 a.u.) and \(5p\) electrons (1.75 a.u.). Most of the \(4d \rightarrow f\) oscillator strength is associated with the \(4f\) state. We performed two calculations: one with the processes represented by equations (1)-(6), and the other without these processes. The results show
that the photoionization cross section without the $4d - 4f$ transition is about only 10% of the results when these transitions are included. It demonstrates that the photoionization cross section is mainly (90%) caused by two processes. The first process is to photoexcite the $4d$ electron to the $4f$ subshell, then the autoionization of the $4f$ subshell causes the photoionization of the $4f, 5s,$ and $5p$ subshells.

Figures 1 gives our calculated photoionization cross sections for the Ce$^{3+}$-Ce$^{4+}$ transition in the energy region 100-150 eV. Dotted, dashed and dash-dotted curves represent, respectively the partial cross sections for the $2F$, $2D$ and $2G$ states. The first peak, located at 101.7 eV, is contributed mainly (88%) by the partial cross section of the $2F$ state. The most important photoexcited states are

$$4d^95s^25p^6(4f^2(^1G))(2F),$$
$$4d^95s^25p^6(4f^2(^3H))(2F).$$

The most important final states through intershell coupling among the $5s - cp$ and $4d - 4f$ transitions are

$$4d^{10}5s^25p^54f(^1G)6d(^2F),$$
$$4d^{10}5s^25p^54f(^3D)6d(^2F),$$
$$4d^{10}5s^25p^54f(^3G)6d(^2F),$$
$$4d^{10}5s^5p^64f(^3F)cp(^2F),$$
$$4d^{10}5s^5p^64f(^1F)cp(^2F).$$

Other transitions will also contribute to the cross section but to a lesser extent. We note that the above five states contribute 86.0% to the partial cross section of the $2F$ state in the first peak at 101.7 eV.

The second peak is at 118.0 eV with a maximum cross section of 47.9 Mb. The $2D$, $2F$ and $2G$ states contribute respectively 2.4 Mb, 3.9 Mb and 41.6 Mb to this peak. The transition to the $2G$ state accounts for 86.8% of the total cross section. Therefore, the most important processes are first $4d$ electron excited to the states

$$4d^95s^25p^6(4f^2(^3H))(2G),$$
$$4d^95s^25p^6(4f^2(^1I))(2G).$$

Then autoionization follows to the final states

$$4d^{10}5s^25p^6(^1S)6g(^2G),$$
$$4d^{10}5s^25p^54f(^3D)6d(^2G),$$
$$4d^{10}5s^25p^54f(^3F)6d(^2G),$$
$$4d^{10}5s^5p^64f(^3F)cp(^2G).$$
Since the $4f - \epsilon g$ transition has the cross section 20.4 Mb, which is almost half the cross section (41.6 Mb) of the $2G$ state, this transition is the most important process for the second peak.

The third peak has a maximum of 57.0 Mb and is due to the partial cross sections for the $2D, 2F$ and $2G$ states whose values are respectively, 23.7 Mb, 26.0 Mb, and 7.3 Mb. Unlike in the first and second peaks, for the third peak the $2D$ and $2F$ states contribute significantly, while the $2G$ state contributes moderately to the cross section. The most important final states are

\begin{align*}
4d^{10}5s^25p^54f(3G)e_d(2D), \\
4d^{10}5s5p^64f(3F)e_p(2D), \\
4d^{10}5s^25p^45f(3F)e_d(2F), \\
4d^{10}5s5p^55f(3G)e_d(2F), \\
4d^{10}5s5p^64f(3F)e_p(2F), \\
4d^{10}5s^25p^6(1S)e_g(3G).
\end{align*}

From the above analysis we can see that the $3D$, $3F$ and $3G$ terms of the core wave function are more important than the $1D$, $1F$ and $1G$ terms.

Figure 2 displays the comparison of our RPAE results with the experimental data. Solid and dotted curves represent, respectively our calculations and the data from the measurement [10]. The agreement is reasonable. The two main peaks in the experiment are closer to each other than those in our calculation. Both the theoretical and experimental results are much larger than the cross section for photoionization of Ce@C$_{82}^+$ (see section a of Figure 2 in Ref. [10]). The photoionization cross section for Ce@C$_{82}^+$ has a maximum of 20 Mb around 123 eV. This value is much smaller than that of our third peak 57.0 Mb at 123.2 eV. The reduction effect from the carbon cage can also be seen from comparison of our results with the experimental data of the endohedral fullerene Ce@C$_{82}$ [7]. The photoionization cross section of the $4d - 4f$ giant dipole resonance in Ce@C$_{82}$ is estimated to be 14.3 Mb at 130 eV, which is also smaller than our results of 20.9 Mb at 130.0 eV. Therefore our calculation further confirms the suppression effect obtained by the experiment when an atom encapsulated inside the carbon cage is photoionized.

Many theoretical calculations demonstrate confinement resonances [1-6]. However, all the experiments show no confinement resonances. The measurements demonstrate a great suppression of the photoionization cross section by the carbon cage. It is hypothesized in Ref. [10] that additional decay channels for the Ce $4d$ vacancy may exist. After analyzing carefully the theoretical models and
the experimental arrangement, we are led to the conclusion that the discrepancy between the theory and measurement may be due to the assumed location of the atom inside the C_{60} by theory. The location of the atom in the calculation of the confinement resonances is always assumed to be at the center of the carbon cage. The photoelectron ionized from the atom will be reflected by the carbon sphere. For the atom assumed to be at the center of the C_{60} the reflected wave and the incoming wave easily interfere with each other and create the resonance. However, the atoms in the current experiments involving the photoionization of Ce@C_{82}^{+}, Ce@C_{82}, Pr@C_{82} etc. are located at off-center positions and adjacent to the carbon cage. This geometrical configuration causes the photoelectron ionized from for example, the Ce^{3+} ion to be multiply reflected to different directions by the carbon cage. The reflected wave and incoming wave do not necessarily readily interfere with each other, but are easily absorbed by the carbon cage in the process of photoionization. This may be the reason for the great suppression observed in the experiment.

To resolve directly the long-standing discrepancy between the measurements on the one hand and theoretical predictions on the other on the photoionization of an endohedral fullerene, we recommend that both measurements and calculations be performed on the photoionization of A@C_{60} (atom at the center of C_{60} cage).

**Conclusion**

In conclusion, we have performed a RPAE calculation for the photoionization of the Ce^{3+} - Ce^{4+} process. The reasonable agreement in magnitude and shape with the recent measurement [10] confirms the suppression effect of the carbon cage in an endohedral fullerene. The plausible reasons for the confinement resonance or suppression effect have been advanced and discussed as well.

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**Appendix: Coulomb matrix elements for the intershell coupling between Ce^{3+} 5s – cp, 5p – cs, d and 4d – 4f transitions**
In the following equations $l_{c}^{n_1}$ is an open shell and the other $l^{n}$ subshells are closed shells. $G^{L_1, S_1}_{L_1, S_1}$ etc. is the fractional parentage coefficient.

(1) For the Coulomb interaction

$$|l_{c}^{n_1-1}[L_3 S_3][L_2 S_2]|^{n_1+1}[L_1 S_1]|L^{n} S^{n} > \rightarrow$$

$$|l_{c}^{n_1}[L_3 S_3][L_2 S_2]|^{n_1}[L_1 S_1]|L_c S_c| l_0 L' S' >$$

the Coulomb matrix element of time forward type is:

$$\sum_{k} G^{L_1, S_1}_{L_c, S_c}[L_{c}', L_1, S_1, S_1']^{1/2}[L', L_1', L_1'+1] \left\{ \begin{array}{c} l_1 \ l_3 \ k \\ L_1 \ L_1' \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_6 \ l_2 \ k \\ L'' \ L' \ L'_1 \end{array} \right\}$$

* $< l_0 ||C^{k}|| l_2 > < l_3 ||C^{k}|| l_1 > R_k(l_0 l_3; l_2 l_1)(-1)^{l_1'+k+l_0+l_1} \sum_{kL_1} G^{L_1, S_1}_{L_c, S_c}[L_{c}', L_1, S_1, S_1']^{1/2}[L', L_1', L_1'+1] \left\{ \begin{array}{c} l_2 \ l_1 \ L_c' \\ l_6 \ L' \ L_1' \end{array} \right\} \left\{ \begin{array}{c} l_6 \ L_1 \ L_1' \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_2 \ L_1 \ L_1' \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_6 \ l_2 \ L_1' \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_6 \ l_2 \ L_1' \ L_1'' \end{array} \right\}$$

(7)

The exchange part of the Coulomb matrix element of time backward type is:

$$-\sum_{k} G^{L_1, S_1}_{L_c, S_c}[L_{c}', L_1, S_1, S_1']^{1/2}[L', L_1', L_1'+1] \left\{ \begin{array}{c} l_6 \ l_1 \ k \\ L'_1 \ L_1 \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_2 \ l_3 \ S_1 \ S_1' \end{array} \right\}$$

* $< l_0 ||C^{k}|| l_3 > < l_1 ||C^{k}|| l_2 > R_k(l_1 l_3; l_2 l_1)(-1)^{2S_c'+1+n_1} \sum_{kL_1} G^{L_1, S_1}_{L_c, S_c}[L_{c}', L_1, S_1, S_1']^{1/2}[L', L_1', L_1'+1] \left\{ \begin{array}{c} l_2 \ l_1 \ L_c' \\ l_3 \ L_1 \ L_1' \end{array} \right\} \left\{ \begin{array}{c} S_1' \ S_1'' \\ S_c' \ S_c'' \end{array} \right\} \left\{ \begin{array}{c} l_2 \ L_1 \ L_1' \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_2 \ L_1 \ L_1' \ L_1'' \end{array} \right\} \left\{ \begin{array}{c} l_2 \ L_1 \ L_1' \ L_1'' \end{array} \right\}$$

where $L_c S_c'$ are from coupling of $l_{c}^{n_2-1}[L_2 S_2'][L_1 S_1']$ etc. is the fractional parentage coefficient. The symbols ( ) and { } are the so-called 3j symbol and 6j symbol, respectively. The symbol { } with three lines and three columns is the so-called 9j symbol. $C^{k}$ is the normalized spherical harmonics,

$$< l_3 ||C^{k}|| l_1 > = (-1)^{l_3}[l_3, l_1]^{1/2} \left\{ \begin{array}{c} l_1 \ k \ l_3 \\ L' \ L_c' \ L \end{array} \right\}$$

(8)

and

$$R_k(l_1 l_3; l_2 l_3) = \int R_{l_1} R_{l_3} \frac{r^k_{l_1}}{r^k_{l_2}} R_{l_2} R_{l_3} r^2 dr$$

(9)

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Figure Captions

Fig. 1. The cross sections for the Ce$^{3+}$-Ce$^{4+}$ photoionization process in the energy region 100-150 eV calculated in the RPAE approximation. Dotted, dashed and dash-dotted curves represent, respectively the partial cross sections for the symmetries $^2F$, $^2D$ and $^2G$. The solid curve is the total photoionization cross section, which equals the sum of these partial cross sections.

Fig. 2. Comparison of our RPAE results with the experimental data for the Ce$^{3+}$-Ce$^{4+}$ photoionization process [10]. Solid and dotted curves are respectively, the calculated and measured results.
