

Research Article

Metastable One-Electron Excited States of Charged Fullerenes

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We study the spontaneous emission processes for the quantum transitions between electron states of a charged C_{60} fullerene. Lifetimes for the transitions between the volume-localized electron levels and the surface-localized electron levels are evaluated and compared with the transitions between two surface-localized electron levels. We find the lifetimes by computing the transition dipole moments on the basis of the numeric calculations of the three-dimensional electron wave functions of a charged fullerene by making use of the density functional theory method implemented in the QuantumEspresso package. We show that the lifetime of a volume-localized level is of order of $1 \mu s$ for a transition energy of about 5 eV. This suggests to consider the possibility of using charged fullerenes for generating short-wavelength radiation, including coherent radiation in this range.

1. Introduction

Fullerenes are sufficiently well studied experimentally and theoretically. Recently, there was a growing interest in the physics of charged fullerenes [1–5]. In particular, a number of experimental studies demonstrate the existence of metastable cations C_{60}^{+Z} with charges Z up to +10 [4, 5]. Earlier, by making use of analytical estimates in the approximation of a spherically symmetric model, it was shown that along with the well-known surface-localized electron states, there are volume-localized states for which the electron wave function has the maximum at the center of the fullerene [6, 7]. The existence of volume-localized electron states for charged fullerenes was subsequently confirmed by means of the three-dimensional numeric calculations with the help of the widely available QuantumEspresso software package for quantum-mechanical computations.

It is worthwhile to note that it is well known (since the early theoretical and experimental studies of the mesoatom in the middle of the last century) about situations when a charged light particle can be localized inside a charged heavy nucleus. In particular, for heavy nuclei with a charge Z greater than 50, the radius of the Bohr orbit of the μ^- meson is $a_{0\mu} < m_e/m_\mu Z$ a.u. smaller than the size of the nucleus.

Although the spatial scale and characteristic energies are of course different, such a situation is analogous to the case of charged fullerenes.

In this paper, we analyze the spontaneous emission processes for the quantum transitions between electron states of a charged C_{60} fullerene and evaluate the corresponding lifetimes.

Our calculations show that volume-localized electron states are metastable with the typical lifetimes of $1 \mu s$. These times are essentially longer than the characteristic values that we previously obtained on the basis of a simple estimate for the transition dipole moment [7]. For example, the lifetime obtained with such a simple estimate was 0.1 ns for the transition energy of 10 eV, whereas now with the 3D numeric calculations for 10 eV, we find $0.1 \mu s$.

2. Methods and Approaches

In order to calculate numerically the energies of single-electron states and to find the corresponding wave functions for the case of the charged fullerene, we use here the method based on the electron density functional theory (DFT) [8], which was implemented in the QuantumEspresso software package [9], which demonstrated good results in the earlier

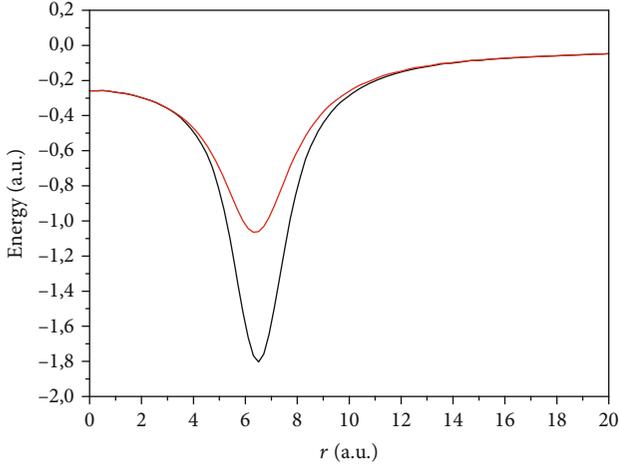


FIGURE 1: Cross-sections of the calculated potential for the charged fullerene with $Z = 2$, passing through the atom of carbon (black) and through the center of the segment connecting the neighboring atoms (red).

numeric evaluation of the electron structure of neutral fullerenes [10]. The electron wave functions are decomposed in the plane wave basis, and the pseudopotential method is used to reduce the dimension of the basis. In the study of low dimensional materials, we use the supercell method with a translation vector length of 100 a.u. to exclude interactions between fullerenes, whereas for the pseudopotential, we take the norm-preserving Perdew-Wang potentials [11] in the framework of the local density approximation (LDA). In the basis, we take into account plane waves with energies less than 40 Ry. For the structure optimization, we use the method based on the Broyden-Fletcher-Goldfarb-Shanno algorithm. The position of ions is varied to the state when the interatomic forces become less than 10^{-4} Ry/a.u., and the unit cell parameters are varied to the values when the stress in the cell becomes less than 0.5 kbar. The numeric computations were carried out on a high-performance cluster computer K-100 at the M.V. Keldysh Institute of Applied Mathematics, RAS.

We find the lifetimes by evaluating the components of the electric dipole moment of the quantum transition between the initial (i) and the final (f) states, which is defined by

$$d_{fi} = e \int d^3x \psi_f^*(x) r \psi_i(x), \quad (1)$$

where $\psi_f(x)$ and $\psi_i(x)$ are the electron wave functions of the final and initial states, respectively. Then, the photon emission rate (probability per time of an electric dipole transition between the initial and the final states) can be calculated as

$$P_{fi} = \frac{|d_{fi}|^2 (\Delta E_{fi})^3}{3\pi\epsilon_0 \hbar^4 c^3}, \quad (2)$$

where $\Delta E_{fi} = E_f - E_i$ is the difference of energies of the final and initial quantum levels. The radiative lifetime is the inverse of (2).

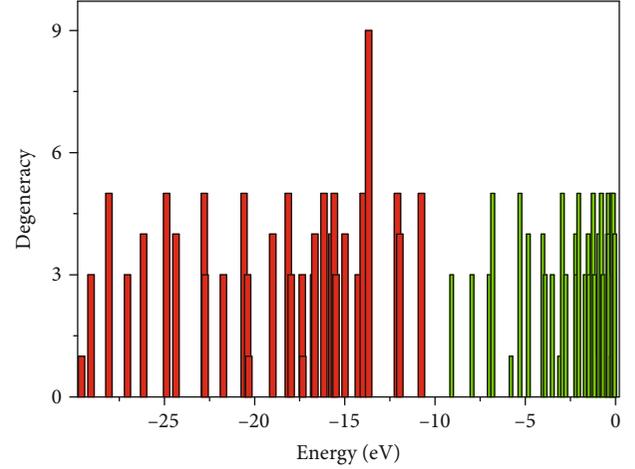


FIGURE 2: Occupied (red) and unoccupied (green) electron states of the fullerene ion C_{60}^{+2} .

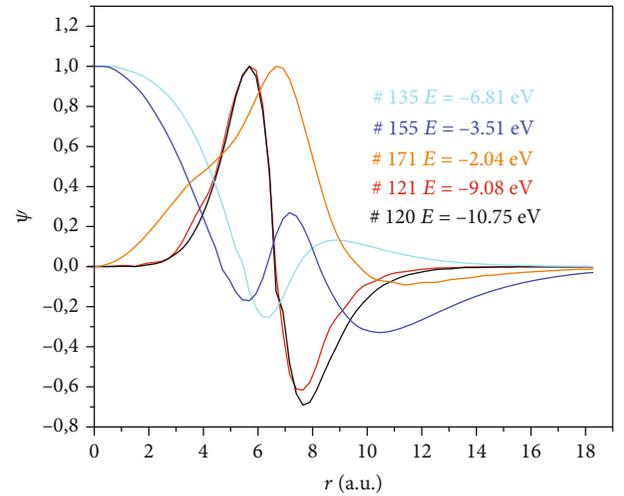


FIGURE 3: Cross-sections of wave functions of electron states of a molecule C_{60}^{+2} .

We calculate the components d_{fi} of the electric dipole moment (1) by numerically integrating the electron wave functions obtained with the help of the QuantumEspresso software package. The wave functions are normalized to 1, as usual. The dimension of the 3D grid for the wave function values is $500 \times 500 \times 500$ points in a cube of the size $100 \times 100 \times 100$ a.u.

3. Results and Discussion

We evaluate the lifetimes of volume- and surface-localized electron states of charged fullerenes with the help of a three-dimensional numeric calculation of the C_{60}^{+2} fullerene potentials by making use of the method based on the electron density functional theory. The resulting potential is presented in Figure 1, where we show the cross-section passing through the center of the fullerene and the carbon atom and the section through the center of the fullerene and the center of the segment connecting two adjacent

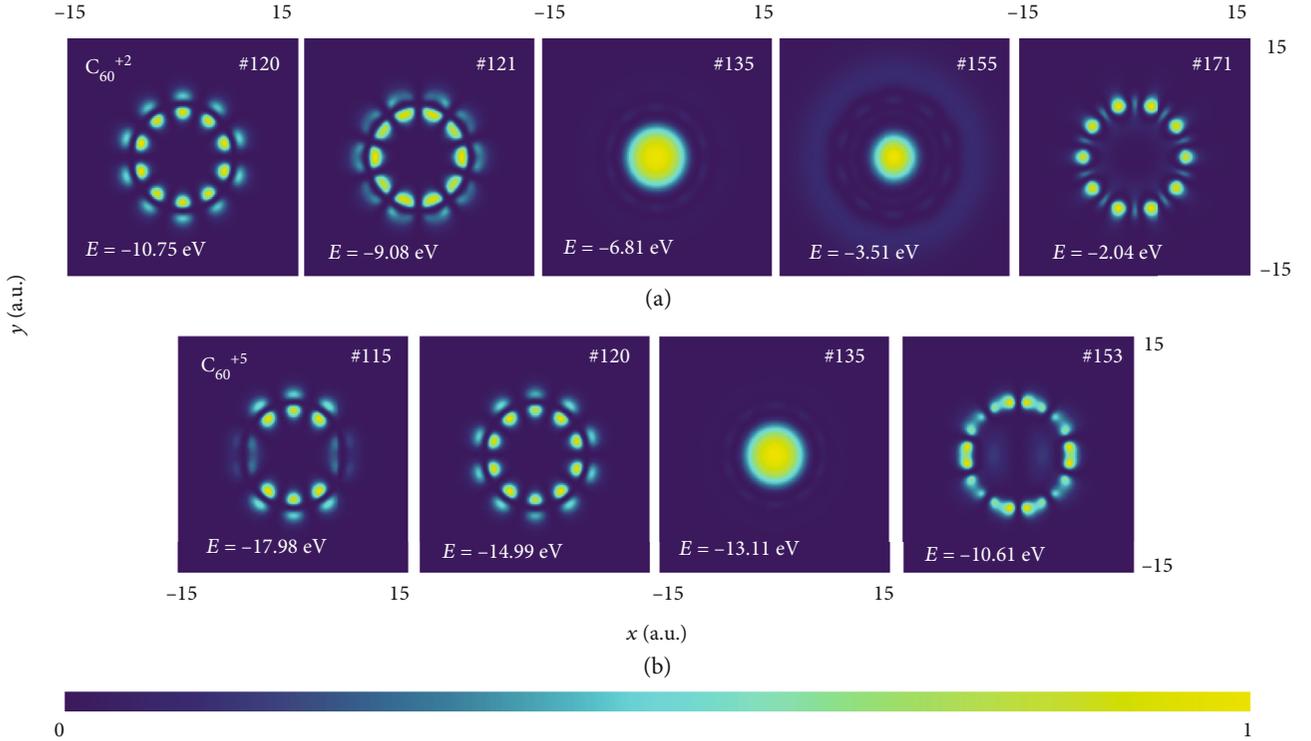


FIGURE 4: Two-dimensional cross-sections of the squares of the wave functions of the single-particle excited states of the C_{60}^{+2} molecule (a) in comparison to the C_{60}^{+5} molecule [12] (b).

TABLE 1: Estimated transition lifetimes of C_{60}^{+2} .

| Initial state | Final state | ΔE (eV) | Lifetime (μs) |
|---------------|-------------|-----------------|----------------------|
| 135 | 121 | 3.29 | 6.94 |
| 135 | 120 | 4.96 | 1.94 |
| 155 | 121 | 5.99 | 14.3 |
| 155 | 120 | 7.66 | 1.91 |
| 171 | 121 | 7.04 | 0.607 |
| 171 | 120 | 8.71 | 0.501 |

carbon atoms. Similar to the findings of our previous works [7, 12], we observe that the value of the potential in the center is lower for the charged C_{60}^{+2} than for the neutral fullerene.

For the energies above the potential value at the center of the fullerene, we find both the well-studied surface-localized electron states (SLES) and volume-localized electron states (VLES). At the same time, for the energies below the potential value at the center, only surface-localized states are found.

The results of the numerical modeling for the energy levels and the wave functions of single-particle excited states of an electron in the field of a charged fullerene C_{60}^{+2} are shown in Figures 2–4. In particular, Figure 2 shows the energies and the degree of degeneracy of single-electron states of a charged fullerene. Occupied states are marked in red, while unoccupied states are highlighted in green.

When calculating with the help of the pseudopotential method, in which the electrons of completely filled shells

are removed from the consideration, we find that the first 118 states are occupied. This should be compared with the neutral fullerene C_{60} , for which the first 120 electron states are occupied. The volume-localized levels are not degenerate (multiplicity equal 1). Using this numbering for the energy levels, the first volume-localized electron state is # 135 and # 155 is the second volume-localized state. The numeric calculation of the energies for these states yields the values -5.79 eV and -3.09 eV, respectively. The excited electron states # 120 and # 121 have the energies -10.75 eV and -9.08 eV, respectively.

Figures 3 and 4 show the 2D cross-sections of the electron wave functions calculated for these states. In particular, Figure 3 depicts a cross-section, passing through the center of the fullerene and a carbon atom, for the single-electron wave functions of volume-localized (VLES) and surface-localized (SLES) states. One can clearly see that the wave functions for the states # 135 and # 155 have a maximum in the center of fullerene, and therefore, these are VLES. The remaining states turn out to be SLES.

Figure 4 shows the two-dimensional cross-sections of the squares of wave functions for the charged fullerene C_{60}^{+2} (Figure 4(a)), and for comparison, the cross-sections for the C_{60}^{+5} fullerene are presented (Figure 4(b)) (see [12]).

On the basis of the numeric data for wave functions, one can evaluate the dipole moments and the lifetimes of the quantum transitions between VLES and SLES and between SLES and SLES. Table 1 contains the values for the lifetimes for the transitions from the first and second VLES to states # 120 and # 121, which are HOMO and LUMO, respectively,

in the neutral fullerene. For comparison, we also give the lifetimes of transitions with SLES # 171.

As one can see from Table 1, the lifetimes of quantum transitions from VLES are of the order of $1 \mu\text{s}$ for the energy difference about 5 eV. At the same time, for transitions from SLES # 171, the lifetime is about $0.5 \mu\text{s}$. These times are significantly greater than the characteristic values that were previously obtained on the basis of a simple estimate for the transition dipole moment [7].

4. Conclusion

In this work, we have analyzed the spontaneous emission processes for the quantum transitions between the volume-localized electron levels and the surface-localized electron levels of the charged C_{60} fullerene, as well as between two surface-localized electron levels, and estimated the corresponding lifetimes.

The numeric calculations demonstrate that the volume-localized electron states are metastable with the typical lifetimes of $1 \mu\text{s}$. These times are essentially greater than the characteristic values that were previously obtained on the basis of a simple estimate for the transition dipole moment [7]. For the energy transition of 10 eV, the lifetime obtained using such an estimate was 0.1 ns, while the results obtained on the basis of the 3D calculations for 10 eV now give $0.1 \mu\text{s}$.

The results obtained for the lifetimes of charged fullerenes are thus encouraging and suggest to consider the possibility of using the charged fullerenes for generating the short-wavelength radiation in the energy range of the order of 10 eV, including coherent radiation in this range.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

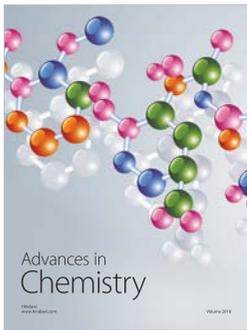
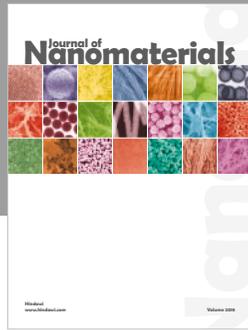
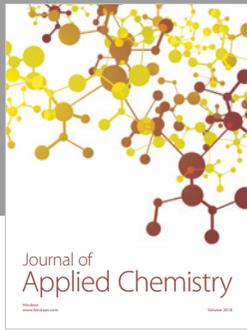
The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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