Highly Charged States of C$_{60}$ Molecule: a DFT Study

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Introduction

Since the elaboration of the parent fullerene molecule C$_{60}$, tremendous interest in fullerene derivatives, as well as in C$_{60}$ itself, has been devoted. Singly and multiply charged fullerene ions exhibit a wealth of chemistry in the gas phase at room temperature, ranging from electron transfer between fullerene and the substituents, to ion-induced polymerization [1]. A spectacular production of stable and highly charged C$_{60}$, reaching up to C$_{60}^{12+}$, has recently been appeared in the literature [2]. The authors, Bhardwaj and coworkers, claimed that they were able to detect and identify the different ionized C$_{60}^{z+}$ in a laser field. No previous theoretical work has been reported in the literature on such highly charged fullerene. This prompts us to take the initiative to elucidate this kind of highly charged fullerenes. We report here our first results on selected C$_{60}$ cations, ranging from C$_{60}^{+}$ to C$_{60}^{18+}$. Using DFT method, we clarify up to which cationic level the C$_{60}$ can be ionized. We explain the unusual stability of those cations.

Computational details

All calculations have been carried out using the Gaussian 03 suites of program. The calculations were performed at the DFT level of theory. Geometry optimizations were carried out using the B3LYP functional, which consists of a hybrid Becke+Hartree–Fock exchange and Lee–Yang–Parr correlation functional with nonlocal corrections. For the icosahedral (I_h) point group we use the 6-31G(d) basis set implemented in Gaussian 03. For lower symmetries, the 3-21G and the 3-21G(d) basis sets have been used.

Results

It is well known that the C$_{60}$ has the I_h point group which is highly symmetric; however, removing of one electron yields drastic change in the structure. Except C$_{60}^{10+}$ and C$_{60}^{18+}$ cations which possess I_h point group, the symmetry for the other cations will be broken and they adopt lower symmetry. The highest symmetry we could reach for C$_{60}^{+}$, for example, was D_{5d}. Successive ionization leads to further lowering the symmetry. Therefore, we have used the C_2 symmetry, for which the optimization of all cations (up to C$_{60}^{14+}$) could converge, in order to evaluate the curve of the ionization potential for the neutral fullerene C$_{60}$. For this calculation, and owing to computational limitation, we used the 3-21G basis set. The result is shown in Figure 1. As can be deduced from Figure 1, the ionization potential follows a quadratic curvature. Inspection of the geometric structures shows that the carbon-carbon bond lengths increase monotonically as the charge of the fullerene cation is increased, leading to

the expansion of the fullerene cage. Depending on the ionization, the structure of the fullerene cation undergoes a prolate/oblate distortion, in agreement with the experiments done by Bhardwaj *et al.* [2]. Only for C_{60}^{5+}, C_{60}^{10+} and C_{60}^{14+}, where the structure reflects the I_h symmetry, the distortion can be characterized as a breathing mode. This has also consequences on the charge distribution and the bond lengths for carbon atoms in equivalent position. The reason for lowering of the symmetry, distortion of the structure in prolate/oblate forms, can be attributed to orbital relaxation.
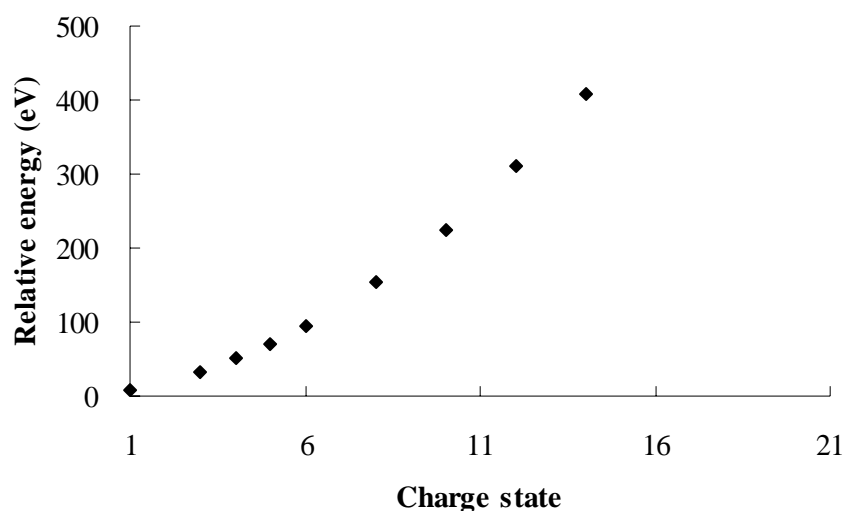

Figure 1. Ionization potential curve of C_{60} calculated at B3LYP/3-21G level using C_2 symmetry.

In fact, in the I_h symmetry, there are 5 degenerated MOs for the HOMO succeeded by 4 degenerated MOs (by 0.048 eV) for HOMO-1 and 5 MOs (by 0.049 eV) for HOMO-2. When all the electrons in the HOMO and/or in the HOMO-1 are removed, no breaking symmetry occurs. The system conserves the I_h symmetry. However, for the other cases, orbital relaxation occurs. As a consequence, a geometric relaxation takes palce in order to compensate the strain in the system.

Identification of the stationary point for selected structures is in progress. More details will be given in the symposium.

References

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[2] V. R. Bhardwaj, P. B. Corkum, and D.M. Rayner, *Phys. Rev. Lett.*, **91**, 203004 (2003).