Ultraviolet Photoelectron Spectroscopy of Fullerenes C$_{60}$ and C$_{70}$: A Model Study[*]

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Abstract   Geometrical optimizations of two fullerenes, C$_{60}$ and C$_{70}$, have been performed by means of density-functional theory techniques. Based on the Gelius model, ultraviolet photoelectron spectra (UPS) of C$_{60}$ and C$_{70}$ have been simulated. We have shown how the different local arrangements of carbon atoms of C$_{70}$ are responsible for the spectra. Our calculated spectra are in good agreement with the experimental counterparts.

Key words   ultraviolet photoelectron spectroscopy, fullerene, density-functional theory, Gelius model

1   Introduction

Fullerene, being the prototype of an entirely new class of carbon compound, has captured the attention of researchers worldwide since the discovery of C$_{60}$ in 1985[1].

Among various different spectroscopic properties, ultraviolet photoelectron spectroscopy (UPS) studies are those most directly connected with the electronic structure, especially, the valence band.

Simultaneously, the simulation of UPS for fullerenes has been performed by several groups, but most of them are more sophisticated, as it involves evaluation of the excited electron[2].

In this work, we investigated the electronic structure of fullerenes C$_{60}$ and C$_{70}$ using UPS experiment, and performed density-functional theory calculations to optimize the geometrical structures of C$_{60}$ and C$_{70}$. Based on the Gelius model[3, 4], we generated the spectra of C$_{60}$ and C$_{70}$ theoretically which are in

good agreement with the experimental ones.

2   Theoretical details

Full geometry optimizations were performed for C$_{60}$ and C$_{70}$. Becke's three-parameter (B3) hybrid functional[5] incorporating exact exchange in combination with Lee, Yang and Parr's (LYP) correlation functional[6] was used throughout this work. The 6-31G(d,p) basis set was used in the optimization for all atoms. All the calculations were performed using Gaussian 03[7].

Gelius[3, 4] has reported that the intensity of jth molecular orbital I_j^{MO} for photoelectron spectra could be written as follows,

$$I_j^{\mathrm{MO}} \propto \sum_{A,\lambda} P_{A\lambda_j} \frac{\sigma_{A\lambda}^{AO}}{\sigma_{A_0\lambda_0}^{AO}}. \tag{1}$$

Here $P_{A\lambda_j}$ is the gross atomic population on atom A from the atomic $A\lambda$ orbital in the jth molecular orbital, $\sigma_{A\lambda}^{AO}$ is the atomic $A\lambda$ subshell photoionization

cross section that could be obtained from Ref. [8] and $\sigma_{A_0\lambda_0}^{AO}$ is the photoionization cross section of a particular atomic subshell $A_0\lambda_0$.

3　Results and discussion

3.1　Optimized geometry

The optimized bond lengths from present calculations on C$_{60}$ and C$_{70}$ are listed in Table 1. Being a molecule with symmetry I_h, C$_{60}$ has only one unique atom and two different bond distances (as shown in Table 1).

Table 1. Bond distances (in Å) of C$_{60}$ and C$_{70}$ from the present calculations compared to previous theoretical results[9] and experiment[10, 11]. The point group of fullerenes C$_{60}$ and C$_{70}$ were shown in parentheses.

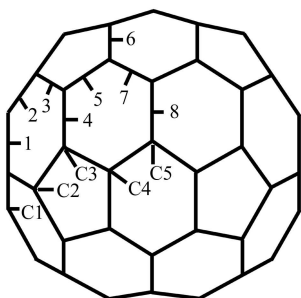| system	this work	previous theory	experiment
C$_{60}$(I_h)			
bond 1	1.395	1.403	1.40±0.015[10]
bond 2	1.453	1.455	1.45±0.015[10]
C$_{70}$ (D_{5h})			
bond 1	1.452	1.460	1.46[11]
bond 2	1.400	1.408	1.38[11]
bond 3	1.448	1.455	1.45[11]
bond 4	1.388	1.400	1.37[11]
bond 5	1.449	1.455	1.43[11]
bond 6	1.434	1.443	1.44[11]
bond 7	1.421	1.430	1.42[11]
bond 8	1.472	1.476	1.46[11]

Fig. 1. Optimized structure for C$_{70}$. The five nonequivalent carbon atoms are labelled C1—C5, and the eight different bonds are labelled with numbers 1—8.

The optimized geometry of C$_{70}$ is shown in Fig. 1, where we label the five symmetry nonequivalent carbon atoms C1—C5 and eight different bonds with numbers 1—8. From Table 1, we could see that our results are found to be slightly different from Ref. [9].

This is mainly because that in Ref. [9], double-ζ plus double polarization (DZP) basis sets were employed while in present calculation we use 6—31G(d,p) basis sets.

3.2　Electronic structure and atomic charge

The energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of C$_{60}$ is about 2.77eV, while for C$_{70}$ is about 2.69 eV. The large energy gap (HOMO-LUMO) indicates that C$_{60}$ and C$_{70}$ are thermally stable.

According to Mulliken population analysis, we found that atoms on C$_{60}$ are almost neutral. As for C$_{70}$, the Mulliken charge is 0.003, −0.002, −0.005, −0.022 and 0.054 for C1—C5 nonequivalent atoms respectively, which suggested that the local environment of C5 is more different from others.

3.3　Ultraviolet photoelectron spectra

The calculated spectrum of C$_{60}$ is shown in Fig. 2 together with the experimental ones[12]. From our calculations, the first two peaks can be assigned as HOMO and HOMO-1. The well reproduction of spectrum via simulation shows that the Gelius model is accurate enough to represent UPS of fullerenes.
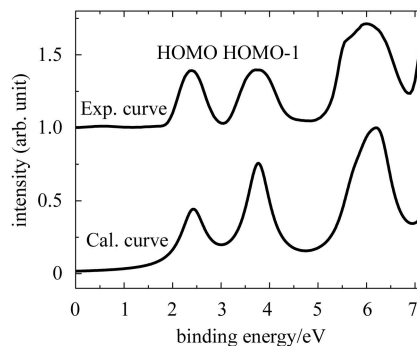

Fig. 2. Ultraviolet photoelectron spectra for C$_{60}$. The incident photon energy is 21.2eV. The theoretical curve has been convoluted with Lorentzian function with half-width at half-maximum (HWHM)=0.4eV.

Fig. 3 shows the calculated spectra for C$_{70}$. From the individual components and the total spectrum, we can see that the spectra of those nonequivalent carbon atoms are slightly different except for C5 whose local environment is more different compared with C1—C4. However, the contribution of C5 type atom
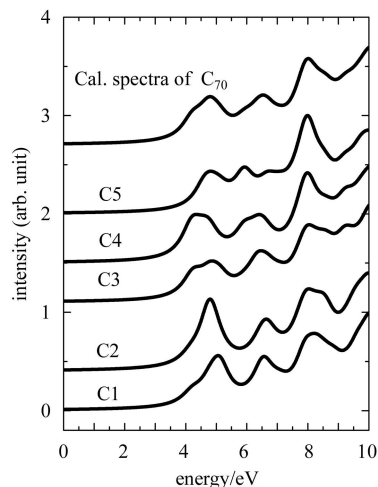
Fig. 3. Calculated spectra for C_{70}. The individual components for the five different types of carbon atoms, C1—C5, are shown together with the total spectra. The incident photon energy is 21.2eV. The theoretical curve has been convoluted with Lorentzian function with HWHM=0.4eV.

(10 atoms) is less than C1—C4 type because of the relative abundance.

4 Summary

We have investigated the electronic structure of fullerenes C_{60} and C_{70} using UPS and theoretical calculations. Our work shows that the Gelius model is suitable for reproducing the ultraviolet photoelectron spectra of fullerenes. Because of the different symmetry, the valence band of fullerenes exhibits significant difference which can be reflected from the ultraviolet photoelectron spectra. Therefore, our research method proposes a direct technique to characterize fullerenes.

Further studies, such as isomers of fullerenes and endohedral metal fullerenes, are in progress.

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基于Gelius模型计算的C_{60}和C_{70}的紫外光电子能谱*

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摘要 在B3LYP/6-31G(d,p)水平上对两种富勒烯C_{60}和C_{70}进行了构型优化. 在此基础上, 并基于Gelius模型, 计算了这两种富勒烯的紫外光电子能谱曲线. 理论计算的曲线同实验曲线符合的很好. 此外, 从理论曲线并结合量子化学计算的结果, 可以看到, C_{70}分子上不同化学环境的的碳原子对紫外光电子能谱曲线的贡献是不同的.

关键词 紫外光电子能谱 富勒烯 密度泛函理论 Gelius模型