Structural and Spectral Properties of a Nonclassical C₆₆ Isomer with Its Hydrogenated Derivative C₆₆H₄ in Theory

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ABSTRACT: X-ray photoelectron and near-edge X-ray absorption fine structure (NEXAFS) spectra, as well as the ground-state electronic/geometrical structures of a newly discovered nonclassical isomer C₂−C₆₆(NC), and two classical fullerene isomers C₂−C₆₆ and C₂−C₆₆(C₆₆) with their hydrogenated derivatives [C₂−C₆₆H₄(NC)], C₂−C₆₆H₄(H₄) and C₂−C₆₆(C₆₆)H₂ have been calculated at the density functional theory (DFT) level. Significant differences were observed in the electronic structures and simulated X-ray spectra after hydrogenation. Simultaneously, both X-ray photoelectron and NEXAFS spectra reflected conspicuous isomer dependence, indicating that the “fingerprints” in the X-ray spectra can offer an effective method for identifying the above-mentioned fullerene isomers. The simulated ultraviolet–visible (UV–vis) absorption spectroscopy of C₂−C₆₆H₄(NC) has also been generated by means of the time-dependent DFT method, and the calculations are well consistent with the experimental results. Consequently, this work reveals that X-ray and UV–vis spectroscopy techniques can provide valuable information to help researchers explore the fullerene electronic structure and isomer identification on the future experimental and theoretical fullerene domains.

1. INTRODUCTION

The fullerene family has aroused immense attention of scientific researchers both for its characteristic spherical geometry and fascinating properties since the discovery of Buckyball C₆₀ in 1985. In accordance with the empirical isolated-pentagon rule (IPR) proposed by Kroto, the adjacent pentagons enhance the local steric strain, resulting in the instability of the fullerene structure. Thus, the stable fullerene called the IPR fullerene should have all its 12 pentagons surrounded by heptagons. However, among the vast fullerenes consisting of pentagons and hexagons, non-IPR fullerenes that violate the IPR principle are in the majority. Due to the consisting of pentagons and hexagons, non-IPR fullerenes that surrounded by heptagons. However, among the vast fullerenes called the IPR fullerene should have all its 12 pentagons enhance the local steric strain, resulting in the instability of the fullerene structure. Thus, the stable fullerene called the IPR fullerene should have all its 12 pentagons surrounded by heptagons. However, among the vast fullerenes consisting of pentagons and hexagons, non-IPR fullerenes that violate the IPR principle are in the majority. Due to the enhanced local steric strain and lack of resonance stabilization, the non-IPR fullerene isomers containing adjacent pentagons are more reactive and difficult to synthesize. Meanwhile, with the continuous advancement of fullerene research, a novel fullerene called the nonclassical fullerene has been proposed theoretically, which contains additional other kinds of polygons, such as extraordinary squares or heptagons, or both exist at the same time. Through theoretical calculation methods, researchers speculated that fullerenes featuring heptagons were more stable than most comparable classical fullerenes, and until 2002, the first nonclassical fullerene derivative was synthesized by Qian et al. The successful synthesis of the nonclassical fullerene aroused the interest of experimenters, leading to the appearance of a series of nonclassical fullerenes. The nonclassical fullerenes have an essential effect on changing the local strain, electronic properties, and chemical activity of the molecule. Furthermore, researchers think the nonclassical fullerenes are beneficial for studying the fundamental information mechanism of fullerenes since they are reckoned as intermediates of the IPR fullerene formation process. Thus, a deeper comprehension of nonclassical fullerenes is significant, both experimentally and theoretically.

With the continuous exploration of chemists, a certain amount of nonclassical fullerenes containing heptagon had been synthesized in the form of derivatives. In 2005, the first two heptagonal nonclassical fullerenes C₆₆F₁₈ and C₆₆F₁₇(CF₃) were prepared through fluorination of C₆₀ by Troshin et al. Then, a number of nonclassical heptagon-containing fullerenes appeared, and some of them even involved more than one heptagon. Among the nonclassical fullerenes, C₆₆(NC) with C₃ᵥ-symmetry [hereinafter referred to as C₃ᵥ−C₆₆(NC)] is definitely a special one since it is the only hydrogenated nonclassical fullerene reported to date. Most synthetic...
nonclassical isomers were modified and shrunk from conventional fullerenes, while the unique $C_{2v}$-$C_{60}(NC)$ was the first nonclassical fullerene directly captured from low-pressure combustion.\textsuperscript{11} Moreover, it is the smallest cage that contains two heptagons among the nonclassical fullerenes.\textsuperscript{11} Considering the crucial function of heptagons for changing local strain and the formation mechanism of fullerene,\textsuperscript{69} it is significant for nonclassical species to compare with conventional fullerenes by systematic theoretical simulation and calculations. As we know, all of the $4478$ $C_{66}$ classical isomers violate the widely accepted IPR,\textsuperscript{2,12} which brings obstacles in and so forth.\textsuperscript{22} To identify the electronic structures of many molecules, surfaces, qualitative analysis of compounds and have been used to in many respects. These techniques are widely used in the methods would be beneficial to explore the isomer dependence of $C_{66}$ fullerenes with their hydrogenated derivatives. With systematic and comparative theoretical research, we can acquire a comprehensive understanding of the electronic structures of the core, valence, and unoccupied orbitals. Furthermore, the spectroscopic information obtained in this work will give an explicit difference between $C_{66}$ nonclassical fullerenes and conventional isomers, as well as offer a theoretical basis for isomer identification and characterization of the future nonclassical fullerenes.

The following part of this paper is divided into three sections: Section 2 simply describes our computational methods used in the XPS, NEXAFS, and UV-vis spectra. Section 3 describes our study results and detailed discussions. Finally, conclusions are presented in Section 4.

## 2. COMPUTATIONAL METHODS

In this work, the initial coordinates of the nonclassical fullerenes $C_{2v}$-$C_{60}H_{4}(NC)$ and $C_{2v}$-$C_{60}(NC)$ were obtained from the crystallographic information file (CIF) of previous experimental work\textsuperscript{11} and designed by the GaussView program.\textsuperscript{35} The primordial coordinates of two non-IPR isomers $C_{2v}$-$C_{4466}C_{66}$ and $C_{2v}$-$C_{4169}C_{66}$ were acquired from the CaGe program,\textsuperscript{36} which is an excellent software package that can generate mathematical graphs of different chemical molecules and view selected graphs in various ways, as well as save them in several formats. The corresponding hydrogenated derivatives, $C_{2v}$-$C_{4466}C_{60}H_{4}$ and $C_{2v}$-$C_{4169}C_{60}H_{4}$, were designed through the GaussView program. Subsequently, the geometrical structures of the aforesaid $C_{60}$ isomers and their hydrogenated derivatives were optimized at the B3LYP\textsuperscript{57,58} and 6-31G** level by the Gaussian 09 quantum chemical package.\textsuperscript{39} Moreover, to acquire more convincing results, a larger 6-311G** basis set was employed to calculate the single-point energy. All the energies we calculated were corrected by the zero-point energy. The natural atomic charges of the atoms within three hydrogenated derivatives were analyzed by the natural bond orbital (NBO)\textsuperscript{40,41} at the B3LYP\textsuperscript{57,58} and 6-31G level. After using the above methods, the obtained results on the variation tendency of energies and the relative stability of ionization of nuclear electrons, while near-edge X-ray absorption fine structure (NEXAFS) gives the features of virtual orbitals through excitation of core electrons to virtual orbitals. Based on previous studies, XPS is mainly used to identify fullerene isomers with different symmetry and NEXAFS has an excellent isomer dependence between fullerenes and corresponding derivatives. In this work, we present a systematic and comparative description of the theoretical investigation of X-ray photoelectron and NEXAFS spectra at the density functional theory (DFT) level on the above six fullerenes. To obtain a deeper insight into the electronic structures, we also simulated ultraviolet-visible (UV-vis) absorption spectroscopy, a powerful material analysis method, and presented relevant information on the electronic structures, particularly for the system valence band. A number of theoretical groups applied this technique to the investigation of the electric construction of fullerenes as well as their derivatives and achieved some satisfactory results.\textsuperscript{31–34} Herein, a theoretical research of UV-vis spectroscopy about $C_{2v}$-$C_{4466}H_{4}(NC)$ by the time-dependent (TD) DFT method was given, and the simulation spectrum was in accordance with the experimental results. The purpose of this work is to probe the relationships between structure and spectroscopy, as well as to explore the isomer dependence of $C_{66}$ fullerenes with their hydrogenated derivatives. With systematic and comparative theoretical research, we can acquire a comprehensive understanding of the electronic structures of the core, valence, and unoccupied orbitals. Furthermore, the spectroscopic information obtained in this work will give an explicit difference between $C_{66}$ nonclassical fullerenes and conventional isomers, as well as offer a theoretical basis for isomer identification and characterization of the future nonclassical fullerenes.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Electronic Structures

The electronic structures and spectroscopic properties by X-ray methods were beneficial to gain a deeper comprehension in many respects. These techniques are widely used in the qualitative analysis of compounds and have been used to identify the electronic structures of many molecules, surfaces, or bulk materials, such as fullerenes, DNAs, carbon nanotubes, and so forth.\textsuperscript{12,26} Quite a few X-ray spectroscopy calculations for the identification of fullerene isomers and their derivatives have been completed successfully, such as $C_{54}$,\textsuperscript{23} $C_{70}$,\textsuperscript{28} $C_{70}$,\textsuperscript{29} $C_{58}$,\textsuperscript{10} $C_{60}$,\textsuperscript{31} and $C_{72}$,\textsuperscript{52} X-ray photoelectron spectroscopy (XPS) provides the information of the core orbital by
the three isomers correspond well with the previous studies, which implement smaller basis sets, such as 6-31G*. Relatively speaking, our calculation results may be more accurate and cogent owing to our more reliable and reasonable computational level.

The NEXAFS and X-ray photoelectron spectra were derived from the StoBe program with the gradient-corrected Becke (BE88) exchange and Perdew (PD86) correlation functionals at the DFT level. In order to facilitate the convergence of the nuclear hole state, the triple-ζ quality individual gauge for the localized orbital (IGLO-III) basis set of Kutzelnigg et al. was used for the excited carbon atoms, while the nonexcited carbon atoms and hydrogen atoms employed model core potentials. Moreover, to obtain a proper expression of the relaxation effects, a full core-hole (FCH) potential method was utilized to simulate the NEXAFS spectra combining with a double basis set technique, stating a normal orbital basis set for the minimization of the energy and an added augmented diffuse basis set (19s, 19p, 19d) for the excited carbon atom.

Already there is evidence that the FCH method supplied remarkable transition moments and good relative energy positions to evaluate the NEXAFS spectra of fullerenes, and the absolute energy position still required calibration. To determine the absolute energy position of the spectra, the ΔKohn–Sham (ΔKS) method was used in the calculation, which can obtain more accurate ionization potential (IP) values compared with other methods. In the ΔKS approach, optimization was applied to the total energies of the system in the ground state and the N = 1 electron system after the core ionization. The raw spectra were corrected so that the first spectral feature (1s → the LUMO) aligns with the accurate excitation energy of the first spectral feature by the ΔKS approach. Similarly, to solve the differential relativity effect caused by the introduced core hole, a unified correction of +0.2 eV was added to the IPs, which had been acquired as the energy difference between the fully optimized core ionized state and the ground state. Finally, the X-ray photoelectron spectra were obtained by broadening the IP values with a Lorentzian line shape with full width at half-maximum (fwhm) values set at 0.12 eV for spectral lines. The NEXAFS spectra were generated from convoluting the discrete intensities by a Gaussian function with the fwhm set at 0.3 eV below the IP and a Steltjes imaging approach in the region above 12 eV.

The UV–vis absorption spectrum was computed with the TD DFT method at the B3LYP/def2-TZVP level by using the ORCA program. Previous studies suggested that the functionals with various fractions of the Hartree–Fock (HF) exchange have different excitation energies. Thus, we employed several functionals with different HF %, such as TPSSH (10% HF), O3LYP (11.61% HF), B3LYP (20% HF), and PBE0 (25% HF), to simulate the UV–vis spectrum of C_{2v}-C_{66}H_{4}(NC). The B3LYP functional reveals better consequences than the other three ones. The UV–vis spectrum calculations were accelerated through the resolution of identity and chain-of-sphere (RIJCOSX) approximations combining with the def2-TZVP/J auxiliary basis set. Considering the solvation effect of the toluene solution in the experiment, we used the conductor-like screening model (COSMO) to estimate the solvation energies which were already at the optimized geometries in the toluene solution. The program calculated 100 singlet excited states of the vertical excitation energies owing to the computational limitations. The eventual UV–vis spectrum was generated by a Gaussian functional convolution with fwhm set at 3000 cm⁻¹, which constitutes an average width for an absorption band observed in the UV–vis range.

3. RESULTS AND DISCUSSION

3.1. Geometrical and Electronic Structures. Optimized structures of the nonclassical isomer C_{66}(NC), the non-IPR isomers C_{2v}^{#4466}C_{66} and C_{4i109}^{#4466}C_{66} and their hydrogenated derivatives C_{2v}^{#4466}C_{66}H_{4}(NC), C_{2v}^{#4466}C_{66}H_{4}, and C_{4i109}^{#4466}C_{66}H_{4} are shown in Figure 1. The fused pentagons and heptagons are highlighted in blue and red, respectively, and the exohedral hydrogen atoms are highlighted in yellow. The distinct geometrical trait is that all of the molecules involved have two pairs of fused pentagons, and the four hydrogen atoms of the derivatives are attached to the common vertexes of the fused pentagons. Furthermore, the exohedral hydrogen atoms transform the hybridization of hydrogen-linking carbon atoms from sp² to sp³. According to the optimized consequences, the addition of hydrogen atoms does not alter the symmetry of the three C_{66} isomers.

Considering the difference of the singlet state and the triplet state in the above molecules, we calculated the energies of these two states and found that the ground states of the aforesaid fullerenes are the single state. Table 1 shows the calculation data of bond lengths, the relative total energies, and the HOMO–LUMO gaps of the three fullerene isomers, as well as their corresponding hydrogenated derivatives. Despite the shortest and longest bond lengths of the pristine cages being different, their average data are nearly the same (1.434–1.435). This phenomenon also occurs in their corresponding hydrides (1.442). Note that the average lengths of pure cages are shorter than hydrogenated derivatives, indicating that the C–C bond lengths have been elongated in general, especially for those carbon atoms connected to the hydrogen atoms, which illustrate considerable changes in the C_{66} backbone owing to hydrogenation. Among the three original cages, the classical fullerene C_{2v}^{#4169}C_{66} has the lowest energy, which is consistent with the previous studies using different functionals and basis sets. The newly discovered nonclassical isomer C_{2v}^{#4466}C_{66}(NC) is the second stable cage with a relative energy 5.35 kcal/mol higher than C_{4i109}^{#4466}C_{66} and 3.83 kcal/mol smaller than C_{2v}^{#4169}C_{66}. Also, the relative energy of the most active isomer C_{2v}^{#4466}C_{66} is 9.18 kcal/mol. The HOMO–LUMO gap of C_{2v}^{#4466}C_{66}(NC) is 1.819 eV. However, after
hydrogenation, the energy of $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$ becomes the lowest among the hydrogenated fullerenes, and the HOMO–LUMO gap of $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$ is enlarged to 2.390 eV in $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$, illustrating that the hydrogenation process is beneficial to the stability of the $C_{2v}\text{C}_{66}\text{(NC)}$. The calculations are consistent with the results of previous studies.\textsuperscript{1,19,20}

To better understand the interaction between the $C_{66}$ backbone and hydrogen atoms, the NBO analyses of the three hydrofullerenes have also been performed. The NBO charge distribution over the fullerene atoms can qualitatively represent the charge transfer during the process of hydrogenation. As shown in Table 1, the average natural atomic charge of hydrogen atoms is 0.288 in the nonclassical isomer $C_{2v}\text{C}_{66}\text{(NC)}$ and 0.289 in the non-IPR isomers $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$ and $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$. Besides, the charge of carbon is mainly localized in the atoms directly connected to the hydrogen atoms, and the average charge of the four carbons is $0.270$, $0.277$, and $0.277$ for $C_{2v}\text{C}_{66}\text{(NC)}$, $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$, and $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$, respectively. The calculations of NBO are in agreement with the previous study.\textsuperscript{65} Such results indicate strong electron donor and acceptor characteristics of hydrogen atoms and the $C_{66}$ backbone, respectively. In addition, it can be inferred that the exotic hydrogen atoms primarily influence the charge of hydrogen-linking carbon atoms and have little impact on other carbons. The strong electron donation and electrostatic interaction indicate there are large changes in electronic and geometrical structures from the fullerene to the hydrogenated derivative. The structural deformation has been proved by the evident C–C bond length increase (Table 1), while the variations in the electronic structures can be detailly reflected in the X-ray photoelectron and NEXAFS spectra, as discussed below.

In the spectral research studies of fullerenes, it is general to group the carbon atoms of the fullerene according to the local environment. As shown in Figure 2, there are six distinguished types of carbon sites: (1) the pyracylene site $C_1$, where the carbon atom situated on a pentagon is connected through an exo bond to another pentagon, (2) the corannulene site $C_2$, where the carbon atom situated on a pentagon is connected through an exo bond to a hexagon, (3) the pyrene site $C_3$, where the carbon atom is shared by three hexagons, (4) the DFP site $C_4$, where the carbon atom is situated on the common edge of fused pentagons, (5) the TSFP site $C_5$, where the carbon atom is situated on the common edge of the fused TSFPs, and (6) the heptagon site $C_6$, where the carbon atom is part of pentagon, hexagon, and heptagon. The different combinations of these six carbon sites leads to different isomers. For instance, there are 50 pyracylene sites, 4 DFP sites, and 12 heptagon sites for $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$; 34 pyracylene sites, 18 corannulene sites, 10 pyrene sites, and 4 DFP sites for $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}\text{C}_2$; and 36 pyracylene sites, 16 corannulene sites, 10 pyrene sites, and 4 TSFP sites for $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}\text{C}_3$.

![Figure 2. Schematic illustration of the local environment of different types of carbons.](Image)

**Table 1. Statistics of Bond Lengths (Å), HOMO–LUMO Gaps (eV), and Relative Energies (kcal/mol) of the Nonclassical Isomer $C_{2v}\text{C}_{66}\text{(NC)}$, the Non-IPR Isomers $C_{2v}^{\#4466}\text{C}_{66}$ and $C_{2v}^{\#4169}\text{C}_{66}$ and Their Hydrogenated Derivatives $C_{2v}^{\#4466}\text{C}_{66}\text{H}_4\text{(NC)}$, $C_{2v}^{\#4466}\text{C}_{66}\text{H}_4\text{C}_2$, and $C_{2v}^{\#4169}\text{C}_{66}\text{H}_4\text{C}_2$**

| molecule                  | shortest $R_{cc}$ | longest $R_{cc}$ | average $R_{cc}$ | HOMO–LUMO gap | relative energy | NBO(H) |
|---------------------------|-------------------|------------------|------------------|---------------|----------------|---------|
| $C_{2v}\text{C}_{66}\text{(NC)}$ | 1.389             | 1.484            | 1.435            | 1.819         | 5.35           |         |
| $C_{2v}^{\#4466}\text{C}_{66}$ | 1.379             | 1.477            | 1.434            | 1.361         | 9.18           |         |
| $C_{2v}^{\#4169}\text{C}_{66}$ | 1.378             | 1.480            | 1.434            | 1.932         | 0              |         |
| $C_{2v}\text{C}_{66}\text{H}_4\text{(NC)}$ | 1.382             | 1.596            | 1.442            | 2.390         | 0              | 0.288   |
| $C_{2v}^{\#4466}\text{C}_{66}\text{H}_4$ | 1.376             | 1.567            | 1.442            | 1.067         | 18.03          | 0.289   |
| $C_{2v}^{\#4169}\text{C}_{66}\text{H}_4$ | 1.337             | 1.583            | 1.442            | 0.948         | 18.04          | 0.289   |

\*The average of NBO charge on hydrogen atoms for three hydrides is also listed.

3.2. X-ray Photoelectron Spectroscopy. The calculated C 1s X-ray photoelectron spectra of different nonclassical carbon atoms in the nonclassical isomer $C_{2v}\text{C}_{66}\text{(NC)}$, as well as the classical non-IPR isomers $C_{2v}^{\#4466}\text{C}_{66}$ and $C_{2v}^{\#4169}\text{C}_{66}$, are shown in Figure 3a. The spectrum of $C_{2v}^{\#4169}\text{C}_{66}$ coincides with the previous study.\textsuperscript{20} One can easily observe that all of the three isomers have a major peak at around 289.8–289.9 eV. Besides, the non-IPR isomers show two weak peaks, while the nonclassical $C_{2v}\text{C}_{66}\text{(NC)}$ possesses four weak peaks. The high-energy weak peaks of $C_{2v}^{\#4466}\text{C}_{66}$ and $C_{2v}^{\#4169}\text{C}_{66}$ appear at about 290.1–290.2 eV, and their low-energy weak peaks arise at around 289.4–289.5 eV, respectively. Besides, the high-energy weak peak belonging to $C_{2v}^{\#4169}\text{C}_{66}$ is sharper and smaller than the one of $C_{2v}^{\#4169}\text{C}_{66}$, which may be a point to differentiate the two non-IPR fullerenes. The nonclassical isomer has two low-energy peaks at 289.3–289.6 eV and two...
high-energy peaks at 290.0–290.3 eV. Such a visible feature might provide helpful information for distinguishing the nonclassical one from the three C$_{66}$ isomers. In addition, the IP values of different symmetry-independent carbon atoms are discrepant, which results in the X-ray photoelectron spectra being completely different. To gain an insight into the contributions from the carbons of different local environments to the total spectra, the corresponding component spectra for different types of carbon atoms in each isomer are presented in Figure 3b–d. Also, we found that, although in different molecules, the same or similar types of carbon atoms still have semblable IP values. For instance, the pyracylene sites and corannulene sites in these three C$_{66}$ isomers show peaks at 289.7–290.0 eV, the pyrene carbons in C$_{2v}$-C$_{66}$ and C$_{h}$-C$_{66}$ have IP values at 290.1–290.3 eV, and the fused pentagon sites are presented in the lower-energy range. It is worth noting that the nonclassical isomer has no pyrene carbons, but the heptagon sites have similar IP values at 290.0–290.3 eV. The IP value distribution can be reasonably inferred from the stability of the carbon sites. The adjacent pentagons enhance the local steric strain, while the incorporation of heptagons may release the carbon skeleton strain, resulting in low and high ionization energy, respectively. These results are consistent with the previous simulation of X-ray photoelectron spectra of C$_{2v}$-$\text{C}_{66}$H$_{4}$ and C$_{h}$-$\text{C}_{66}$H$_{6}$, and C$_{3v}$-C$_{66}$.

Figure 4 presents the calculated X-ray photoelectron spectra of the three corresponding C$_{66}$ hydrogenated derivatives and the spectral contributions generated by different types of carbon atoms. All the spectra of C$_{2v}$-C$_{66}$H$_{4}$ and C$_{h}$-$\text{C}_{66}$H$_{6}$, and C$_{3v}$-$\text{C}_{66}$H$_{4}$ show a strong peak at about 288.4–288.6 eV with a weak shoulder peak at about 289.7–289.9 eV and a feeble peak at about 290.2–290.7 eV. The peak at higher energy is contributed by the carbon atoms of the adjacent pentagons, which directly connect to the hydrogen atoms, and the pyracylene sites and corannulene sites generate the strong peak. However, the weak shoulder peaks at about 289.7–289.9 of non-IPR hydrides and nonclassical hydrofullerene are created by pyrene sites and heptagon sites, respectively. The increased IP value of fused pentagon sites may be caused by the hybridization of the hydrogen-linking carbon atoms from sp$^3$ to sp$^2$. Analyzing the spectra of pure cages and hydrides, it is not difficult to discover that after hydrogenation, the TSFP and DFP sites directly connected to hydrogen atoms have a blue shift of approximately 1.0 eV. Comparing with the previous XPS studies on chlorides and fluorides, for which the fused pentagon sites have an enhancement of about 2.8–4.0 eV, the blue shift is much smaller. This phenomenon may result from the fact that the binding energy of carbon 1s electrons will increase differently depending on the bond type of fused-pentagon carbon atoms. Such an observation confirms that the geometrical and electronic structures of the C$_{66}$ backbone have made an effective change after hydrogenation.

Furthermore, as shown in Figures 3 and 4, the abundance of distinct carbon atoms is directly related to the spectral intensity. For instance, in the spectrum of the nonclassical fullerene C$_{2v}$-C$_{66}$H$_{4}$, the intensity of corresponding peak of DFP is weak, which accounts for only four sites of the total 66 carbon atoms, while the dominant pyracylene sites contribute the majority of the spectrum. The spectra of the hydrogen derivatives also confirmed this observation. According to the previous studies, it can be reasonably predicted that as the abundance of the fused pentagon sites increases, the contribution to the spectrum will be greater and the features will be more obvious.

3.3. Near-Edge X-ray Absorption Fine Structure. The calculated NEXAFS spectra of the three C$_{66}$ isomers and the contributions from various types of carbons are shown in
Figure 5, which are generated by the weighted (according to their relative abundance) summation of spectral components for different carbon types. The spectrum of $C_{56}^{+}$Cs is consistent with the previous investigation.\textsuperscript{20} As presented in Figure 5a, the major peaks of the three isomers, which are marked differently in the NEXAFS spectra, are labeled A−E, A−F, and A−G. We mainly concentrate on the major peaks in the energy range between 283 and 288 eV to distinguish the three isomers. First, focusing on the higher-energy region about 287−288 eV, there is only a distinct broad feature E at about 287.6 eV in the spectrum of $C_{56}^{+}$Cs, whereas the spectra of $C_{56}^{+}$C and $C_{56}^{+}$Cs show two weak peaks, which are at about 287.2 and 287.9 eV (marked E and F, respectively) in $C_{56}^{+}$C and at about 287.2 and 288.0 eV (marked F and G, respectively) in $C_{56}^{+}$Cs. Then, in the low-energy region, all three spectra possess two absolutely clear features. The two legible peaks are labeled B, D in $C_{56}^{+}$C and C, D in $C_{56}^{+}$Cs as well as C, E in $C_{56}^{+}$Cs. It is noticed that another clear weak peak B appears on the left of the $C_{56}^{+}$Cs peak C, while in the spectrum of $C_{56}^{+}$Cs, the main feature C becomes broad and low due to the existence of its right and left shoulder peaks (labeled B and D, respectively).

Figure 5b−d show the contributions of different carbon types to $C_{56}^{+}$C, $C_{56}^{+}$C, and $C_{56}^{+}$Cs, respectively. As the spectra present, the DFP and TSFP sites give rise to the first absorption feature A at lower energy, and all carbon types contribute to the two distinct main features of these three isomers. In Figure 5b, the unique peak E is mainly generated by heptagon and pyracylene sites, which distinguishes $C_{56}^{+}$C from two non-IPR fullerenes. Notice that the quite weak peak C only arises from the characteristic heptagon sites, which is the left shoulder of feature D. In Figure 5c,d, both the peaks C that can be used to discriminate these two non-IPR isomers ($C_{56}^{+}$C and $C_{56}^{+}$Cs) arise from all carbon types. As for the remaining peaks, every carbon type makes important contributions to them.

Furthermore, we also calculated total NEXAFS spectra of the three corresponding hydrogenated C$_{66}$ fullerenes with the contributions of all carbon types, as presented in Figures 6−8.
In all spectra, several peaks appear in the high-energy region 289−291 eV, which do not exist in the pristine cages. These features labeled F, G for \(C_{2v}\)-\(C_{66}(NC)\) and \(C_{2}-\#4466C_{66}\), as well as E, F, G for \(C_{s}-\#4169C_{66}\), which are mainly generated by DFP or TSFP sites, show a clear difference from parent cages. Besides, there are notable discrepancies among the three hydrides, especially for the two distinct main features at about 284.3 and 285.7 eV in the low-energy region. As shown in Figures 6−8, for \(C_{2v}\)-\(C_{66}(NC)\), the first major peak A at about 284.3 eV is much sharper and more intensive than peak B at about 285.7 eV. Peak B becomes broader owing to the symmetrical left and right shoulders. For \(C_{2}-\#4466C_{66}\), the peak A has a right shoulder and thus turns wider. As for \(C_{s}-\#4169C_{66}\), due to the existence of a small peak A at about 283.7 eV, the two main peaks appear in the second and third positions. Furthermore, by comparing the total spectra before and after hydrogenation, as well as their type-specific contributions in all figures, one can easily find a distinct blue shift of about 5.0 eV for DFP and TSFP sites after hydrogenation in comparison to spectra of the other carbon atoms. According to the previous NEXAFS chlorides and fluorides, the blue shift is about 5.0−6.0 eV, which is similar to the NEXAFS spectra of hydrides in this work. Consequently, the NEXAFS spectra created by the hydrogenated derivatives are visibly different from those of the corresponding parent fullerenes, effectively reflecting the changes in the electronic structure of the carbon cages after hydrogenation. Moreover, we found that the intensity of peaks of the spectra is tightly associated with the abundance of...
different carbon atoms. As shown in the figures, the peaks originating from DFP and TSFP sites represent weak signals since the fused pentagon sites only account for 4 of the total 66 carbon atoms. Meanwhile, the stronger peaks that are contributed by all carbon-type sites constitute the main body of the spectra.

As a result, we have discovered effective differences in the NEXAFS spectra of the three C_{66} isomers and their corresponding hydrogenated species resulting from the isomer difference and hydrogenation effect. Thus, peaks A and B for C_{66}−C_{66}H_4(NC) and C_{66}−C_{4169}C_{66}H_4 as well as peaks B and C for C_{66}−C_{4169}C_{66}H_4 can be reasonably used to identify these three hydrofullerenes. Such a NEXAFS spectrum simulation also illustrates that the nonclassical fullerene C_{66}−C_{66}H_4(NC) can be distinguished from the other two study non-IPR fullerenes by this method.

3.4. UV–Vis Absorption Spectrum. Besides the above-mentioned detailed studies of the X-ray photoelectron and NEXAFS spectra of C_{66} fullerene isomers and the hydrogenated derivatives, the theoretical calculation of the UV–vis absorption spectrum of C_{66}−C_{66}H_4(NC) has also been generated at the TD-DFT level. Considering the effect of the proportion of the HF exchange on results, we have employed functionals with different HF % to simulate the spectrum. The calculation results of simulation UV–vis absorption spectrum are convolved by a Gaussian function with fwhm = 3000 cm^{-1}. As shown in Figure 9, the spectrum created by the B3LYP (20%) functional has five different feature peaks, of which two have larger convolutional intensities at about 312.6 and 340.4 nm and three smaller weak crests at about 399.6, 468.0, and 588.0 nm. The absorption peaks at 626 and 684 nm that are extremely weak in the experimental UV–vis absorption spectrum are not observed in simulation spectrum due to the limitation of our computation conditions. Comparing with the peaks of the experiment, the simulation spectrum is in good agreement with the experimental data.11 Other relevant details are listed in the Supporting Information.

For further clear exposition, the TD-DFT-calculated adsorption wavelengths, excitation energies, oscillator strengths (f_osc), and leading transition compositions for the optically allowed singlet excitation states of C_{66}−C_{66}H_4(NC) are listed in Table 2. Only the excitations with f_osc > 0.001 and the contributions of more than 10% in the transition processes are displayed. One can easily observe that the key molecular orbitals may consist of multiple electronic transitions. For instance, the strongest absorption peak at about 312.6 nm, which corresponds to the experimental value at 312 nm, stems from the cooperative contributions of the electronic excitations with the energies at 312 S95 312.2 3.971 0.00450 H−7→L+6 (40.0), H−8→L+6 (30.4)
S82 312.8 3.964 0.00259 H−13→L (52.4), H−6→L+7 (13.2), H−2→L+8 (10.5)
340 S67 339.3 3.654 0.00105 H−6→L+S(52.1), H−4→L+7 (14.3), H−10→L (10.1)
S66 341.7 3.628 0.01206 H−5→L+5 (59.6), H−12→L (15.8)
400 S35 399.7 3.102 0.00963 H−7→L+1 (37.7), H−1→L+6 (21.3), H−2→L+5 (16.9)
465 S24 468.0 2.649 0.00817 H−1→L+6 (87.7)
S84 S4 587.3 2.111 0.00213 H−1→L (87.2), H−3→L+1 (10.2)
626 684

*Experimental values from ref 11. Only the excitations with f_osc > 0.001 are listed. Contributions of less than 10% are omitted.
orbits involved are presented in the Supporting Information Table S9. The remaining details of the main absorption peaks in the simulation of the \( \text{C}_2v\)-\( \text{C}_{66}\)H\(_4\)(NC) UV–vis absorption spectrum are displayed in Table 2. Although previous studies have demonstrated that the TD-DFT method has a slight overestimation of the excitation energy and leads to a small deviation in wavelength, it could reasonably assume that the UV–vis absorption spectrum obtained by theoretical calculation is in good agreement with the experimental results. In conclusion, the simulation UV–vis absorption spectrum elaborates the detailed assignments of absorption bands to electronic transitions within the molecule and thus could be considered as an effective method for characterizing the electronic structures of fullerenes and their derivatives.

4. CONCLUSIONS
In summary, we have investigated the electronic structures, XPS, and NEXAFS spectra of the nonclassical isomer C\(_{2v}\)-\( \text{C}_{66}\)(NC), the non-IPR isomers C\(_2v\)-\( \text{C}_{66}\)(NC) and C\(_{2v}\)-\( \text{C}_{66}\)(NC) and their hydrogenated derivatives C\(_2v\)-\( \text{C}_{66}\)H\(_4\)(NC), C\(_2v\)-\( \text{C}_{66}\)H\(_4\)(NC) and C\(_{2v}\)-\( \text{C}_{66}\)H\(_4\) at the DFT level. The UV–vis absorption spectrum of the nonclassical hydride C\(_{2v}\)-\( \text{C}_{66}\)H\(_4\)(NC) has also been completed with the TD-DFT method. Both of the XPS and NEXAFS spectra show strong isomer dependence and have a significant effect on the carbon cage after hydrogenation. Particularly, the carbon atoms at the fusions of the pentagon–pentagon rings (DFP or TSFP) exhibit special signals that are characteristic of all the study species. In the NEXAFS and X-ray photoelectron spectra, the fingerprints of the pristine fullerenes and the corresponding hydrogenated derivatives, which originate from the pentagon–pentagon carbon sites (DFP or TSFP), usually appear at the lower- and higher-energy regions, respectively. In addition, there is a small and big blue shift in the XPS and NEXAFS spectra after hydrogenation, respectively. The simulated UV–vis absorption spectrum coincides well with previous experimental results. Hence, the results indicate that X-ray and UV–vis spectroscopy maybe provide practicable methods for further experimental and theoretical investigation of fullerene isomers and their derivatives.

5. EXPERIMENTS
The nonclassical isomer C\(_{2v}\)-\( \text{C}_{66}\)(NC), the non-IPR isomers C\(_2v\)-\( \text{C}_{66}\)(NC) and C\(_{2v}\)-\( \text{C}_{66}\)(NC) and their hydrogenated derivatives C\(_2v\)-\( \text{C}_{66}\)H\(_4\)(NC), C\(_2v\)-\( \text{C}_{66}\)H\(_4\)(NC) and C\(_2v\)-\( \text{C}_{66}\)H\(_4\) have been computed by the Gaussian 09 program \(^{39}\) at the B3LYP37,43 /def2-TZVP level by using the ORCA program. \(^{56}\) More details are provided in the Supporting Information.

Optimized coordinates of C\(_{2v}\)-\( \text{C}_{66}\)(NC), C\(_{2v}\)-\( \text{C}_{66}\)(NC) and C\(_2v\)-\( \text{C}_{66}\)(NC) and their hydrogenated derivatives C\(_2v\)-\( \text{C}_{66}\)H\(_4\)(NC), C\(_2v\)-\( \text{C}_{66}\)H\(_4\)(NC) and C\(_2v\)-\( \text{C}_{66}\)H\(_4\) with details of calculations (PDF)

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**Notes**

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03691.
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