

Density functional study of the electronic properties of doped C₂₀ fullerene

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Abstract. Density functional theory calculations have been performed for structures, stability and electronic properties of C₂₀ fullerene doped by hydrogen, fluorine, and chloride atoms. Doping provides efficient tuning of frontier orbitals and electronic distribution in the pristine C₂₀. Dipole moment, HOMO and LUMO energies as well as energy gaps were calculated and analysed. Hydrogen and chlorine dopants provide the minimal value of the energy gap. Based on presented results, one can choose appropriate radical to achieve the desired value of the band gap, needed for concrete solar cell systems or nanoelectronic devices.

1. Introduction

Fullerenes are buckyballs-like carbon clusters consisted of sp^2 -hybridized carbon atoms. High curvature and small size of these clusters result in their unusual properties which differ from characteristics of graphene and nanotubes. In particular, fullerenes possess a wide variety of their HOMO-LUMO gaps dependent of their sizes. Additional tuning of their gaps is achievable with functional groups [1], substitutional doping [2-3] or forming of endohedral complexes with metal atoms [4].

Here we regard the smallest possible fullerene, C₂₀, as a model of larger fullerenes. Due to small size, it has only pentagons on its surface. C₂₀ cage has been obtained for the first time in 2000 [5]. Then the solid state of C₂₀ has been synthesized using ion beam irradiation and laser ablation approaches [6-7]. Despite its high curvature, molecular dynamics predicts its high kinetic stability [8], because the activation barrier for cage destruction is about 4 eV [9]. This is why C₂₀ cage can be regarded as a stable platform for adsorption of different functional groups.

2. Computational Details

All the electronic structure and the energies calculations were carried out by the GAMESS program [10]. The equilibrium geometries were obtained and the structural and energy characteristics of the equilibrium structures were calculated using the density functional theory with the common Becke's three-parameter hybrid method and the Lee-Yang-Parr exchange-correlation energy functional (B3LYP) coupled with the 6-311G(d) electronic basis set [11].



The HOMO-LUMO gap E_g is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO):

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}}.$$

The doped C_{20} -based species were prepared by doping fullerene C_{20} with H, F or Cl atoms. We denote these species as C_{20}R ($\text{R} = \text{H}, \text{F}$ and Cl). To investigate the thermodynamic stability of doped C_{20} , the binding energies (E_b) were estimated by the following equation

$$E_b[\text{eV/atom}] = (1/N_{\text{at}}) [E(\text{R}) + E(\text{C}_{20}) - E(\text{C}_{20}\text{R})]$$

where $N_{\text{at}} = k + l$ is the total number of atoms in the doped fullerene, k and l are the total numbers of atoms in the radical and fullerene, respectively, $E(\text{C}_{20})$ and $E(\text{R})$ are the energies of pristine fullerene and radical, respectively, and $E(\text{C}_{20}\text{R})$ is the total energy of the doped fullerene. In all our calculations $N_{\text{at}} = 21$, $k = 1$ and $l = 20$.

3. Results and discussion

3.1. The electronic properties of doped fullerene

Atomization energies E_{at} for all structures C_{20} , C_{20}H , C_{20}F , and C_{20}Cl are found to be close to each other: their values are 6.01, 6.00, 6.02 eV and 5.94 eV, respectively. Higher values of E_{at} implies more energetically favorable and therefore more thermodynamically stable structures. Hence, the highest E_{at} yields the most preferable and stable molecule. In this terms, the thermodynamic stabilities of C_{20}F and C_{20}H are almost the same as stability of pristine C_{20} , whereas stability of C_{20}Cl structure is some lower. Nevertheless, all regarded structures, presented in Table 1, are stable and can be investigated in further experimental studies.

Calculated electronic properties of these structures are listed in Table 1. The average dipole moment on pristine C_{20} fullerene is almost zero, as expected. The dipole moments on the doped structures are found to be 1.91 D, 0.99 D and 1.00 D for the C_{20}H , C_{20}F , and C_{20}Cl , respectively. It implies that a single Cl atom in the C_{20} cage causes a significant moment which is, on the other hand, low when a H or F atoms are introduced within the C_{20} . Hence, radicals can result in significant changes in the fullerene electronic structure.

In particular, significant changes in HOMO-LUMO gaps are observed for all considered structures. According to our results, the gaps for C_{20}H and C_{20}Cl structures are equal, whereas C_{20}F cage possesses higher gap.

3.2. The reactivity indices of doped fullerenes

The reactivity indices for pristine C_{20} and doped structures (C_{20}H , C_{20}F , and C_{20}Cl) are given in Table 2. The universal indices of reactivity are quite important parameters because they illustrate the reactivity and stability of these structures.

Table 1. Calculated values for HOMO, LUMO, HOMO-LUMO gap (E_g), and carbon-radical distance ($l_{\text{C-R}}$).

Structure	E_{at} (eV/atom)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	μ_{D} (D)	$l_{\text{C-R}}$ (Å)
C_{20}	6.01	-5.34	-3.41	1.93	0.00	--
C_{20}H	6.00	-5.99	-4.17	0.79	1.91	1.088
C_{20}F	6.02	-4.48	-3.58	0.89	0.99	1.372
C_{20}Cl	5.94	-4.48	-3.69	0.79	1.00	1.815

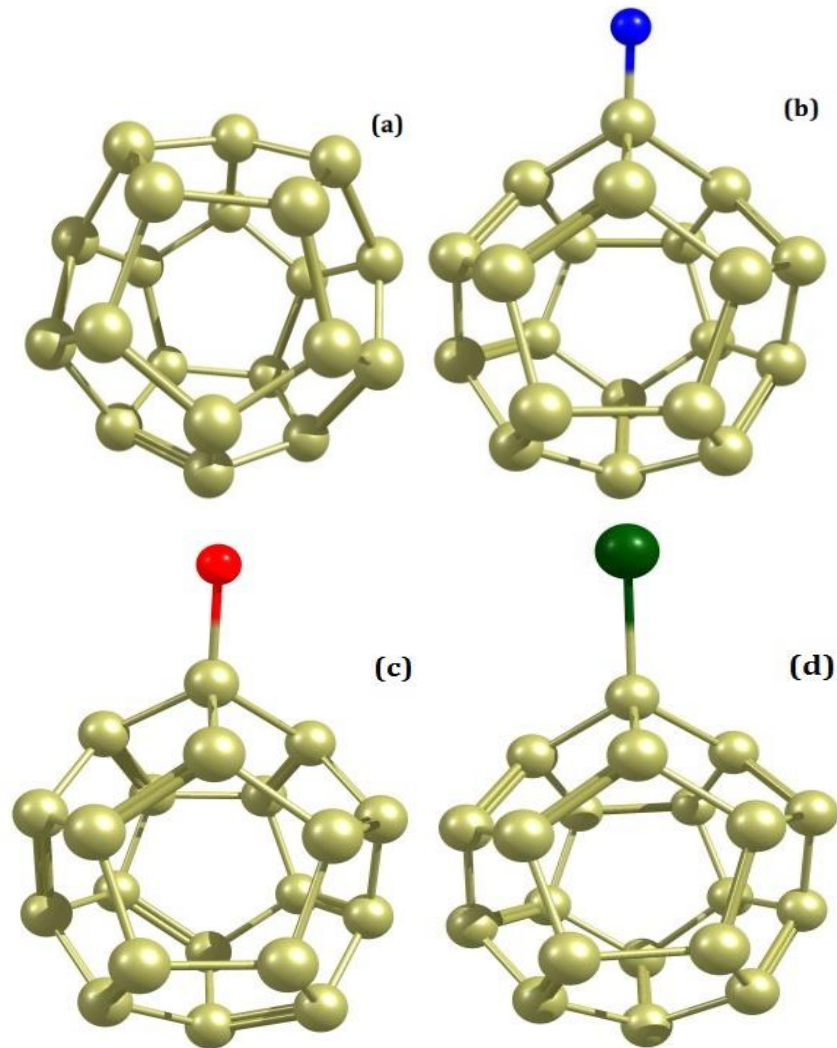


Fig. 1. Optimized structures of fullerenes (a) pristine, (b) $C_{20}H$, (c) $C_{20}F$, and (d) $C_{20}Cl$. Gold, blue, red, and green colors denoted for the carbon, hydrogen, fluorine, and chloride atoms.

Table 2. Chemical potential (μ), chemical hardness (η), softness (S), and electrophilicity (ω) of relaxed structure of C_{20} , $C_{20}H$, $C_{20}F$, and $C_{20}Cl$. All energy parameters are given in eV.

Property	C_{20}	$C_{20}H$	$C_{20}F$	$C_{20}Cl$
$I = -E_{HOMO}$	5.34	5.99	4.48	4.48
$A = -E_{LUMO}$	3.41	4.17	3.58	3.69
$\eta = (I - A)/2$	0.97	0.91	0.45	0.39
$\mu = -(I + A)/2$	-4.38	-5.08	-4.03	-4.09
$S = 1/(2\eta)$	0.52	0.55	1.11	1.27
$\omega = \mu^2/(2\eta)$	9.92	14.18	18.05	21.12

The $C_{20}H$ fullerene has relatively high ionization potential of 5.99 eV, which reflects its stability towards oxidation. The ionization potential of $C_{20}F$ and $C_{20}Cl$ are 4.48 and 4.48 eV, respectively. The lower ionization potentials of $C_{20}F$ and $C_{20}Cl$ are probably due to low ionization potential of F and Cl itself. The ionization potential of C_{20} is higher than that of $C_{20}F$ and $C_{20}Cl$.

4. Conclusion

To summarize, we have investigated electronic properties of the C_{20} fullerene upon doping with the radical atoms with different electronegativity (hydrogen, fluorine, and chloride). For mentioned cages, the order of dipole moment is $C_{20}Cl > C_{20}H > C_{20}F$ which is attributed on the electropositivity of the doped atoms. The analysis of the data reveals that doping with the radical atoms has significant effect on the chemical potential and the chemical hardness indices of these structures.

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