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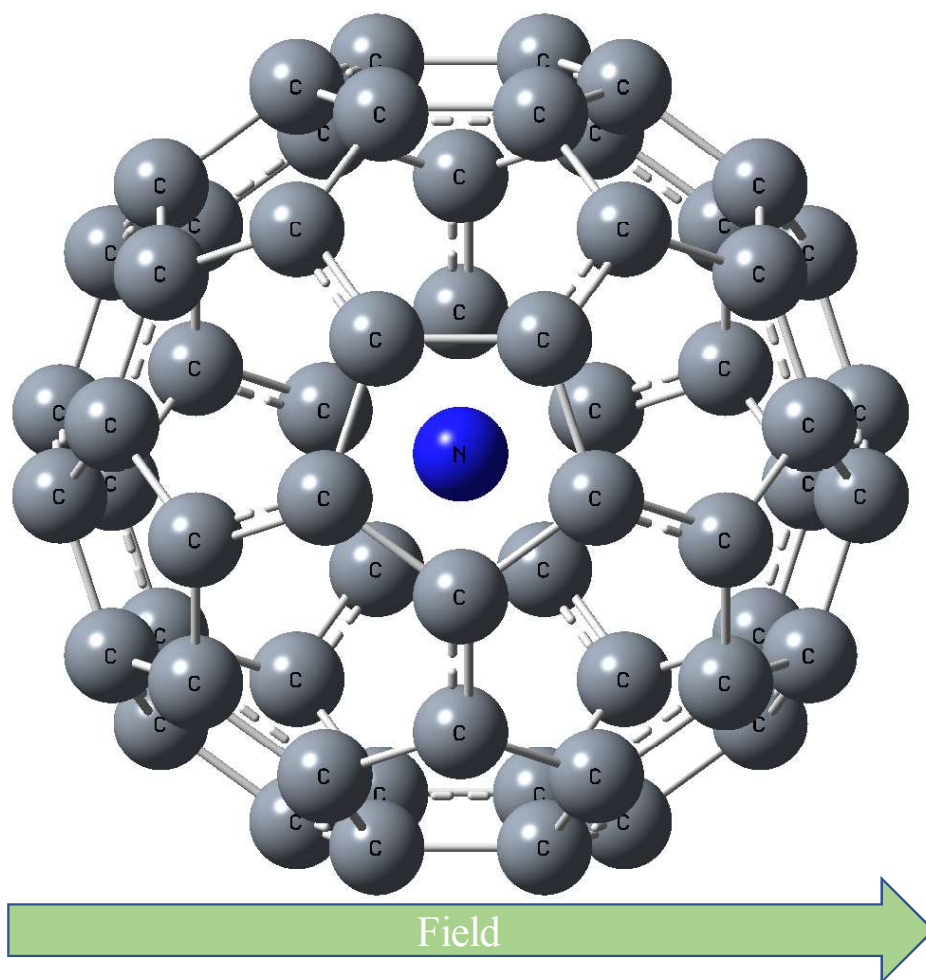
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Abstract: In recent years, endohedral fullerene materials in recent years have been booming. In this work, the N@C60 molecule was selected as an example to demonstrate the effectiveness of this modulation method based on external electric field. The total energy, LUMO energy, HOMO energy, energy gap, infrared spectrum and Raman spectrum of N@C60 were investigated using density functional theory at the B3LYP/3-21G level. The results obtained fully illustrate that the modulation method proposed in this work has extremely high application value, and it is expected to play a vital role in the application of fullerene materials.

### Highlights

1. A new modulation method of endohedral fullerene material has been introduced.
2. N@C<sub>60</sub> was taken an example to illustrate the modulation method with external electric field.
3. The total energy, LUMO energy, HOMO energy and LUMO-HOMO energy gap of N@C<sub>60</sub> under the external electric field have been studied for the first time.
4. The infrared spectrum and Raman spectrum of N@C<sub>60</sub> under the external electric field have been investigated for the first time.



# A Modulation Method of Endohedral Fullerene Material: Using the external electric field

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**Abstract:** In recent years, endohedral fullerene materials in recent years have been booming. In this work, the N@C<sub>60</sub> molecule was selected as an example to demonstrate the effectiveness of this modulation method based on external electric field. The total energy, LUMO energy, HOMO energy, energy gap, infrared spectrum and Raman spectrum of N@C<sub>60</sub> were investigated using density functional theory at the B3LYP/3-21G level. The results obtained fully illustrate that the modulation method proposed in this work has extremely high application value, and it is expected to play a vital role in the application of fullerene materials.

**Keywords:** Modulation method, External electric field, Endohedral fullerene, N@C<sub>60</sub>

## 1. Introduction

Since C<sub>60</sub> was discovered in 1985 [1], the unique chemical and physical properties of fullerenes, as well as their potential applications in technology, are of great interest to scientists, especially in materials science, electronics and nanotechnology [2-6]. The most special property of the structure of fullerenes is that their carbon cage is a cavity structure [1, 7-9], so some special species (atoms, ions or clusters of atoms) can be embedded in the cavity. The resulting fullerenes are called endohedral fullerenes. Due to their peculiar structure, endohedral fullerenes may even play a more important role than parent fullerenes in some frontier fields. For example, the endohedral fullerenes material can be used to make small portable atomic clocks, making the Global Positioning System (GPS) navigation system of

1 driverless cars accurate to 1 mm. Therefore, in the past decades, researchers have made a lot  
2 of reports on the endohedral fullerenes to pave the way for their practical application in the  
3 near future [3-4, 10-13].  
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6 N@C<sub>60</sub>, as an endohedral fullerene that can already be produced [14], is of great research  
7 value. For instance, in the previous study, Gao et al. demonstrated that N@C<sub>60</sub> is potential  
8 cathode catalyst in hydrogen fuel cells [15]. It was found that N@C<sub>60</sub> is very suitable as a  
9 non-destructive structural probe for fullerene nanomaterials [16]. Although N@C<sub>60</sub> has broad  
10 application value in the near future, it is a pity that no study has been reported on the  
11 influence of the external electric field (EEF) on the spectrum and physical properties of  
12 N@C<sub>60</sub>. Generally speaking, molecules are often exposed to the EEF in their natural habitat  
13 or some experiment conditions like a scanning tunneling microscope (STM) [17]. What's  
14 more, it is well known that the EEF, being an effective means to modulate, has been used in  
15 all kinds of material modulation [17-22]. Therefore, N@C<sub>60</sub> was taken as an example to  
16 illustrate the modulation method of endohedral fullerene materials based on EEF.  
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19 In this work, the variation of the total energy, frontier orbital, infrared (IR) spectra and the  
20 Raman spectra of N@C<sub>60</sub> under different EEFs were studied by the density functional theory  
21 (DFT) at the B3LYP/3-21G level. The results are helpful to have a better understanding on  
22 the effect of the EEF on the endohedral fullerene N@C<sub>60</sub>, which can provide a reference for  
23 the all kinds of application or experiment settings on endohedral fullerene N@C<sub>60</sub> for further  
24 study.  
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## 29 2. Computation details

30 Under the effect of the EEF, the Hamiltonian of the molecular system is written as:

$$31 H = H_0 + H_{int} \quad (1)$$

32 Where  $H_0$  is the Hamiltonian without EEF and the  $H_{int}$  is the interaction Hamiltonian between  
33 the EEF and the molecular. Under the dipole approximately,  $H_{int}$  can be expressed as:

$$34 H_{int} = -\mu \cdot F \quad (2)$$

35 Where  $\mu$  is the dipole moment of the molecular system, and the  $F$  denotes the EEF. In this  
36 work, the EEF discussed is ranging from 0 atomic units (a.u.) to 0.02 a.u., where 1a.u.  
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=5.14225 V/nm.

All the results calculated in this work are obtained by Gaussian 09 program [23]. The density functional theory Becke's hybrid exchange functional [24] and Lee-Yang-Parr correlation functional [25] (B3LYP) has been demonstrated to perform excellently in the electronic structure calculations, geometry optimizations and frequency calculations [26]. Therefore, in this work, the DFT at the B3LYP/3-21G level is employed to optimize the geometry of the endohedral fullerene N@C<sub>60</sub>, and the result calculated is shown in Fig. 1. Then, the EEF is applied on the endohedral fullerene N@C<sub>60</sub> molecule along the green arrow, which is shown in Fig. 1. The total energy, frontier orbital, infrared spectra and Raman spectra under the different EEF of N@C<sub>60</sub> were investigated by the DFT at the B3LYP/3-21G level.

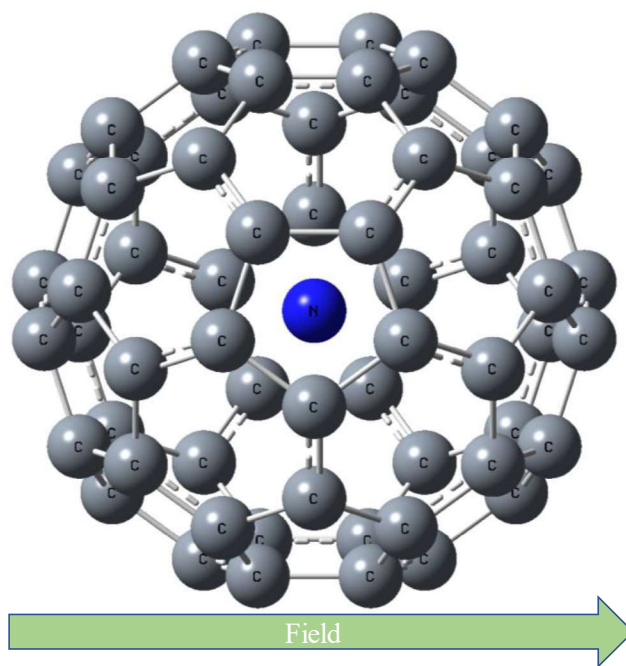


Figure 1. The optimized geometry of ground states of endohedral fullerenes N@C<sub>60</sub> and the arrow represents the direction of the applied EEF

### 3. Results and discussion

#### 3.1 The total energy, frontier orbital of endohedral fullerenes N@C<sub>60</sub> under the EEF

The total energy of endohedral fullerenes N@C<sub>60</sub> under different EEFs are obtained using

1 B3LYP/3-21G level. The results are shown in Fig. 2. According to results, the total energy of  
2 ground states of endohedral fullerenes N@C<sub>60</sub> is -2327.77285278 Hartree. The stronger the  
3 strength of the EEF, the more the effect on total energy by the EEF. When the strength of the  
4 EEF increases to 0.20 a.u., the total energy of endohedral fullerenes N@C<sub>60</sub> decreases to  
5 -2327.86165942 Hartree. Compared to the total energy of the ground state of the endohedral  
6 fullerenes N@C<sub>60</sub>, the deviation is about -233.16183 kJ/mol (1 Hartree=2625.5 KJ/mol).  
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11 As for one molecule, the orbital energies reflect its ability of taking part in the chemical  
12 reaction. The highest occupied molecular orbital (HOMO, E<sub>H</sub>), the lowest unoccupied  
13 molecular orbital (LUMO, E<sub>L</sub>), and the energy gap (E<sub>G</sub>) of alpha molecular orbital(MOs) and  
14 Beta MOs of the endohedral fullerenes N@C<sub>60</sub> under the EEF were obtained, as is shown in  
15 Fig. 3, Fig. 4 and Fig. 5. And the energy gap can be written as:  
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$$22 E_G=(E_L-E_H)\times 27.2114\text{eV} \quad (3)$$

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24 According to the frontier theory, the electrons in the frontier orbitals, like the valence  
25 electrons in the atomic orbitals, are the most reactive electrons in the chemical reactions and  
26 the core of the organic chemical reactions. The electron of the HOMO has the highest energy  
27 and can easily escape, while the LUMO has lowest energy among all the unoccupied  
28 molecular orbitals, which is equivalent to the molecular electron affinity and can accept  
29 electrons easier. Therefore, the E<sub>G</sub> reflects the ability of the electron transition from occupied  
30 orbitals to unoccupied orbitals.  
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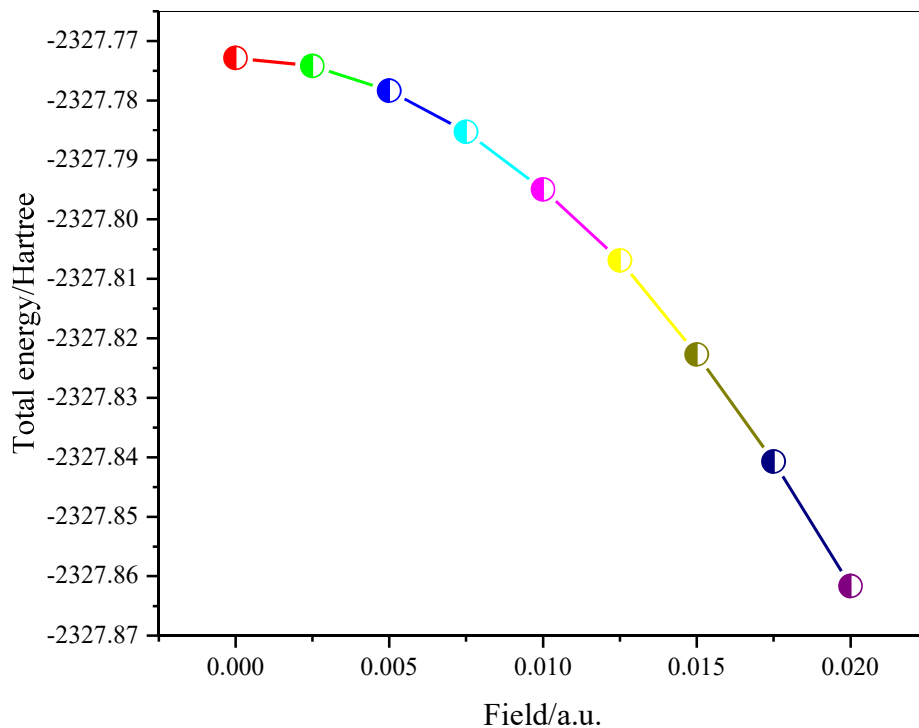


Figure 2. The total energy of endohedral fullerenes  $N@C_{60}$  under the different EEFs

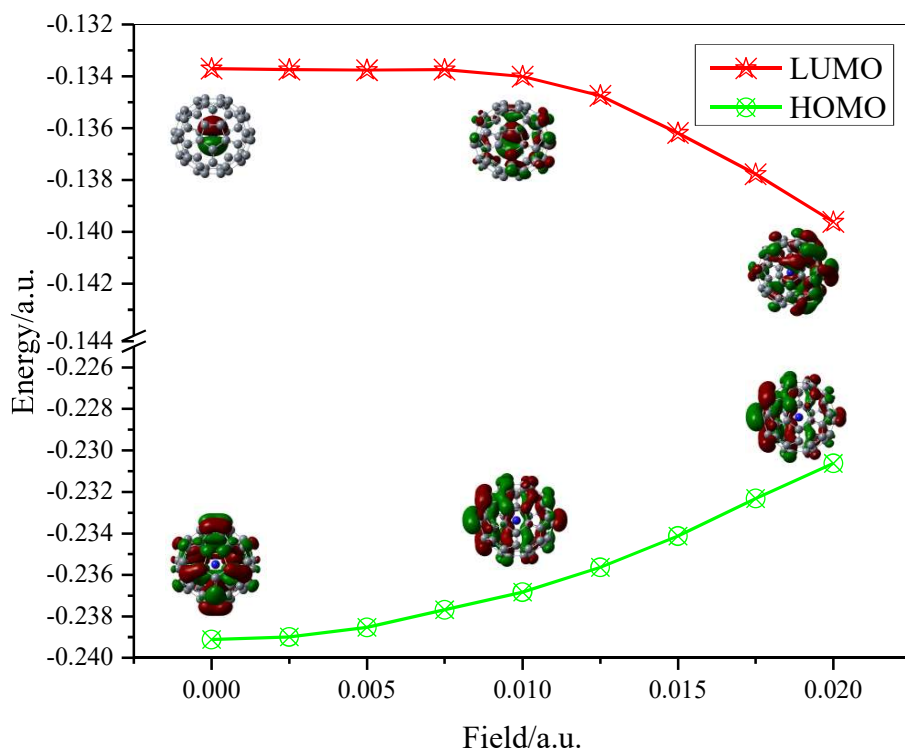


Figure 3. The LUMO energy and HOMO energy of alpha MOs of endohedral fullerenes  $N@C_{60}$  under the different EEFs



As is shown in Fig. 3, when the EEF below 0.01 a.u., the electric field almost has no difference on the LUMO energy of alpha MOs of N@C<sub>60</sub>. Only when the EEF exceed 0.01 a.u., the EEF begins to take effect and the LUMO energy of alpha MOs of N@C<sub>60</sub> decreases from -0.13401 a.u. to -0.13962 a.u.. With the enhancement of the EEF, the HOMO energy of alpha MOs of the endohedral fullerenes N@C<sub>60</sub> increases, reaching the maximum -0.23063 a.u. when the F is 0.02 a.u..

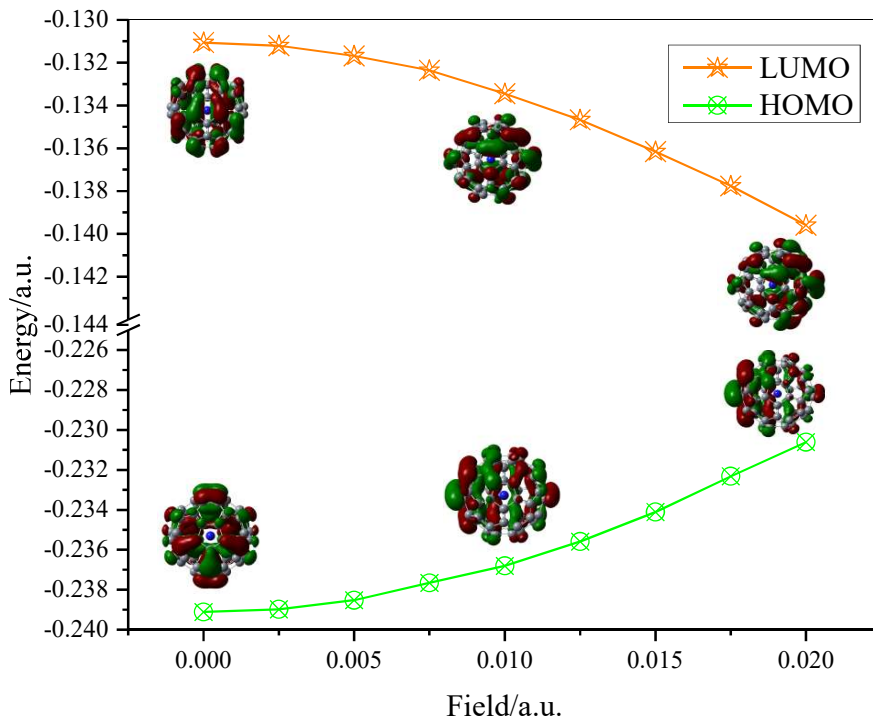


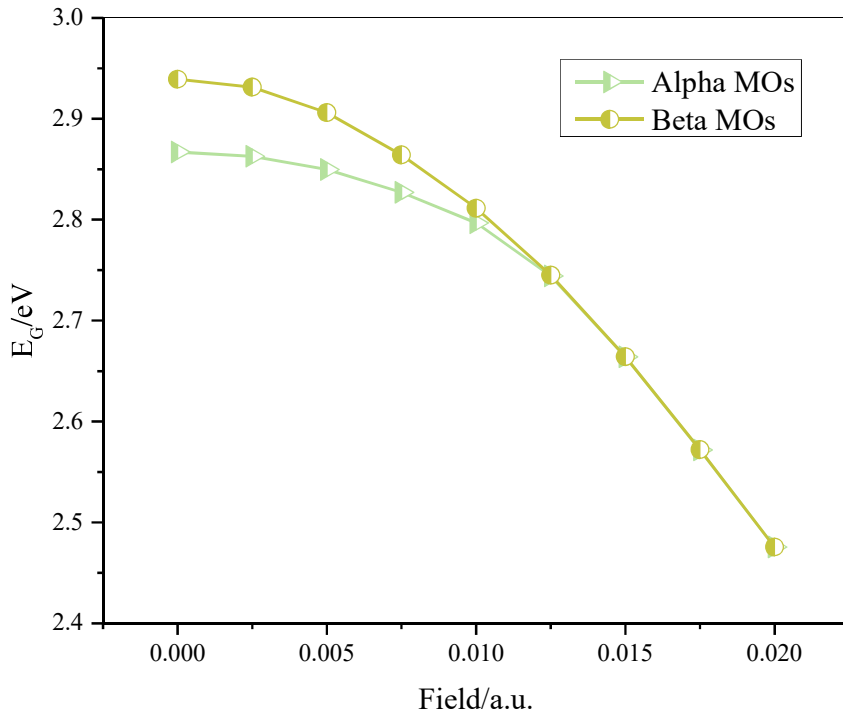
Figure 4. The LUMO energy and HOMO energy of beta MOs of endohedral fullerenes N@C<sub>60</sub> under the different EEFs

There exist some differences about the effect of the EEF on the beta MOs compared to alpha MOs. As is shown in Fig. 4, with the increase of EEF, the LUMO energy of beta MOs of endohedral fullerenes N@C<sub>60</sub> decreases contiguously, while the HOMO energy of beta MOs of endohedral fullerenes N@C<sub>60</sub> increases steadily. The deviations of the LUMO and HOMO energy of beta MOs of endohedral fullerenes N@C<sub>60</sub> under the effect of EEF are -0.00854 a.u. and 0.00851 a.u. respectively.

The tiny difference between alpha MOs and beta MOs of endohedral fullerenes N@C<sub>60</sub> under the EEF determine that the energy gap of endohedral fullerenes N@C<sub>60</sub> can appear two different variations. According to the calculated results, the energy gap of alpha MOs and

1 beta MOs of N@C<sub>60</sub> in ground states were obtained and the value of them are 2.867 eV and  
2 2.939 eV respectively. Compared with the Suzuki's work [27], the results of E<sub>G</sub> obtained in  
3 this work are in closer to the experiment value (2.7eV) of C60 on Au (887) [28]. As is shown  
4 Fig. 5, with the enhancement of the EEF, both the E<sub>G</sub> of alpha MOs and beta MOs decrease.  
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6 It obviously seen that the effect of the EEF on beta MOs is bigger than alpha MOs. Moreover,  
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8 when the strength of the EEF exceeds 0.0125 a.u., the E<sub>G</sub> of alpha MOs and beta MOs of  
9 endohedral fullerenes N@C<sub>60</sub> have a same behavior.  
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15 To display the effect of the EEF on LUMO and HOMO vividly, The LUMO and HOMO  
16 of alpha MOs and beta MOs are shown in Fig. 3 and Fig. 4, respectively. It is quite clear that  
17 the HOMO of alpha MOs is similar to the HOMO of beta MOs due to the energy of them are  
18 very close together. With the electric field increasing, the HOMO shifts in the opposite  
19 direction of the electric field. The LUMO of alpha MOs of endohedral fullerenes N@C<sub>60</sub> in  
20 ground states is different from the LUMO of beta MOs due to energy difference. With the  
21 increasing of EEF, the LUMO shift in the direction of EEF due to attracting electrons by EEF.  
22 When the EEF is 0.20 a.u., the LUMO of alpha MOs is also similar to the beta MOs on  
23 account of the energy difference of them almost decrease to 0 a.u. by the EEF.  
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1 Figure 5. The energy gap of endohedral fullerenes N@C<sub>60</sub> under the different EEFs

2 **3.2 The infrared spectrum of endohedral fullerenes N@C<sub>60</sub> under the effect of the EEF**

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4 The infrared spectrum of endohedral fullerenes N@C<sub>60</sub> can reflect some important  
5 chemical and physical properties. The infrared spectrum of endohedral fullerenes N@C<sub>60</sub>  
6 under the EEF were obtained by DFT at B3LYP/3-21G level. According to the results,  
7 endohedral fullerenes N@C<sub>60</sub> have 177 vibrational modes on account of having 61 atoms.  
8 Compared to fullerene C<sub>60</sub>, endohedral fullerenes N@C<sub>60</sub> owns 3 more vibrational modes,  
9 which are related to the vibrations of N (Nitrogen) atom. As is shown in Table 1, the intensity  
10 of the three different vibrational modes of N atom is very weak. What's more, with the  
11 climbing of the EEF, the intensity of the three different vibrational modes always fluctuate  
12 between 0 a.u. to 0.003 a.u., which indicates that the carbon cage is very good at binding N  
13 atom, even being subjected to the EEF. In a word, endohedral fullerenes N@C<sub>60</sub> can exist  
14 steadily and have broad application value in this aspect.  
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27 Table 1. The frequencies and intensities of vibrations of N atom of endohedral fullerenes  
28 N@C<sub>60</sub> in ground states (frequencies in cm<sup>-1</sup> and intensities in a.u.)  
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Frequency	Intensity
40.72	0.0016
64.16	0.0024
79.50	0.0020

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40 As is shown in Fig. 6, the infrared spectrum of endohedral fullerenes N@C<sub>60</sub> owns only  
41 four absorption peaks in ground states, which is similar to fullerene C<sub>60</sub> [29]. According to  
42 Table 2, it can be found that the frequencies of absorption peaks of IR spectrum of N@C<sub>60</sub> in  
43 ground states is consistent with the frequencies of absorption peaks of C<sub>60</sub> in ground states  
44 [29-32]. This phenomenon is caused by N atom being bound in the carbon cage, which makes  
45 N's vibration very weak and has little effect on the infrared spectrum. With the climbing of  
46 the EEF, the more absorption peaks began to emerge. In this work, the peaks, which are  
47 affected greatly by the EEF, were studied carefully.  
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56 Table 2. The comparison between the absorption peaks of IR spectrum of N@C<sub>60</sub> in ground  
57 states and the calculated and experimental values of absorption peaks of IR spectrum of C<sub>60</sub> in  
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ground states (frequencies in  $\text{cm}^{-1}$ )

This work	Calculated			Experimental
	Schettino et	Giannozzi et	Schettino et	Menendez et
	al. [29]	al. [30]	al. [31]	al. [32]
504.16	528	527	525	526
582.41	577	586	578	578
1175.63	1189	1218	1180	1182
1452.50	1431	1462	1430	1429

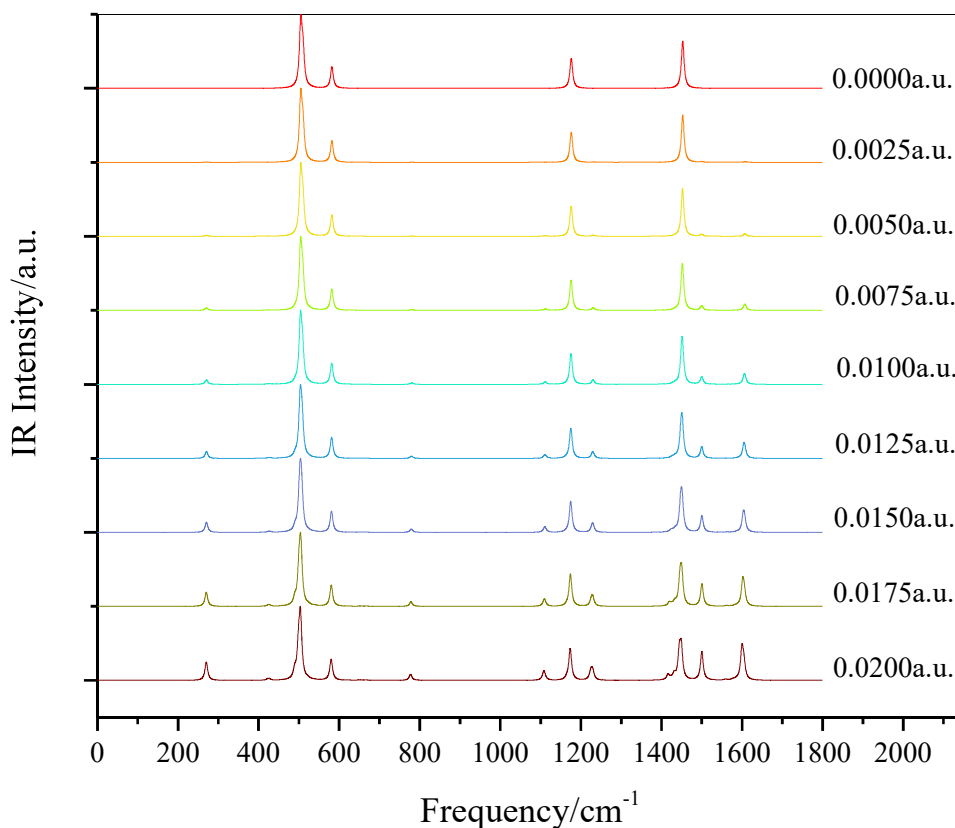
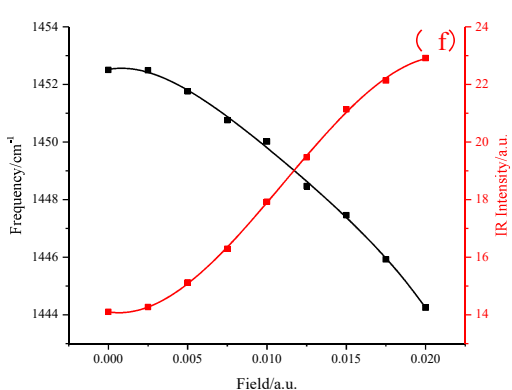
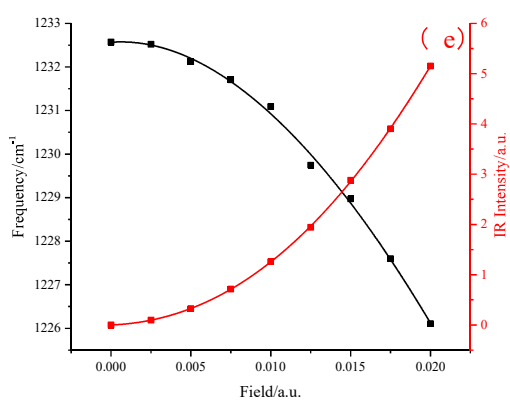
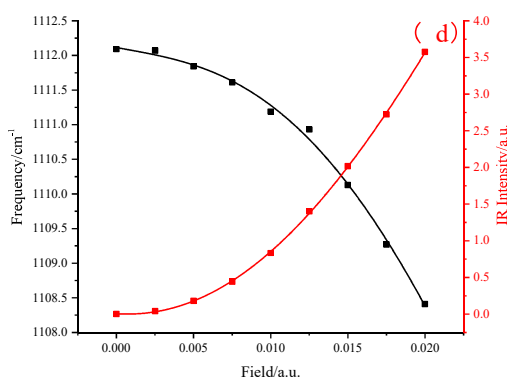
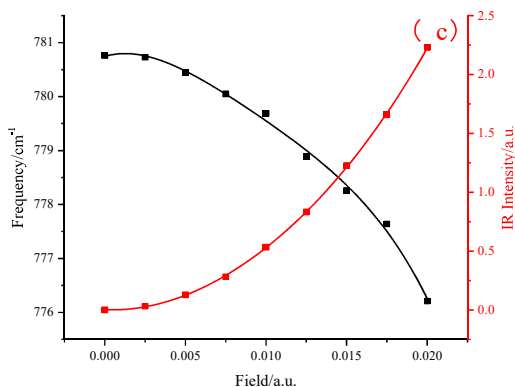
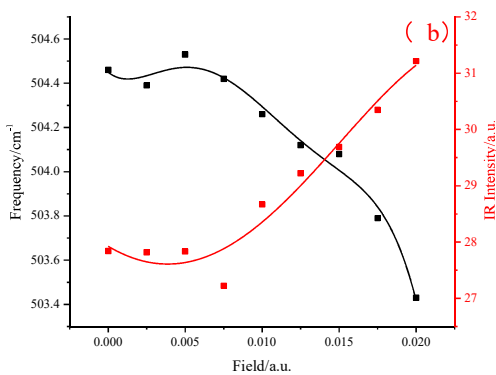
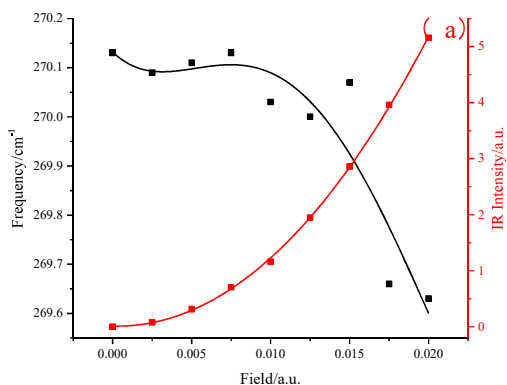


Figure 6. The IR spectrum of endohedral fullerenes  $\text{N@C}_{60}$  under the different EEFs

In the range of  $0\sim 800\text{ cm}^{-1}$ , there exists two absorption peaks in ground states, the frequencies of them are  $504.46\text{ cm}^{-1}$  and  $582.41\text{ cm}^{-1}$ , respectively. With the climbing of the EEF, another two absorption peaks emerge and the frequencies of them are  $270.13\text{ cm}^{-1}$  and  $780.76\text{ cm}^{-1}$  respectively. According to the calculated results, the EEF has a very weak effect on the absorption peak at a frequency of  $582.41\text{ cm}^{-1}$ , while the EEF has an obvious effect

1 on the other three absorption peaks. The strongest modes of these three absorption peaks are  
 2 studied detail and the results are shown in Fig. 7(a), Fig. 7(b) and Fig. 7(c) respectively.  
 3 Under the effect of the EEF, the infrared intensity of the vibrational mode at the frequency of  
 4  $270.13 \text{ cm}^{-1}$  increase from 0 a.u. to 5.1573 a.u., while the infrared intensity of vibrational  
 5 mode at a frequency of  $504.46 \text{ cm}^{-1}$  increases from 27.8415 a.u. to 31.2155 a.u. and the  
 6 infrared intensity of vibration mode at a frequency of  $780.76 \text{ cm}^{-1}$  rise from 0 a.u. to and  
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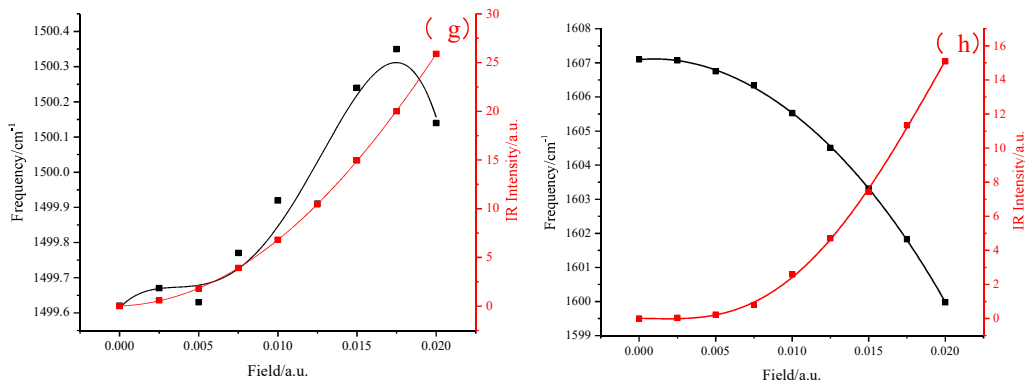


Figure 7. The infrared intensity and frequency of some special modes of endohedral fullerenes N@C<sub>60</sub> under the different EEFs

In the range of 800~1300 cm<sup>-1</sup>, there exists only one absorption peak in ground states and the frequency of absorption peak is 1175.63 cm<sup>-1</sup>. Two absorption peaks at the frequency of 1112.09 cm<sup>-1</sup> and 1232.57 cm<sup>-1</sup> began to emerge with the effect of EEF, and the detail parameter of strongest vibrational mode of them are shown in Fig. 7(d) and Fig. 7(e) respectively. With the climbing of the EEF, the vibration mode at a frequency of 1212.09 cm<sup>-1</sup> becomes active with its infrared intensity rise from 0 a.u. to 3.57 a.u., while the infrared intensity of vibrational mode at a frequency of 1232.57 cm<sup>-1</sup> increase from 0 a.u. to 5.152 a.u.. These two modes, which are activated by the EEF, appear different degrees of redshifts.

In the range of 1300~1800 cm<sup>-1</sup> without EEF, there is only one absorption peak at the frequency of 1452.5 cm<sup>-1</sup>. With the impact of EEF, another two absorption peaks emerge and the frequencies of them in ground states are 1499.62 cm<sup>-1</sup> and 1607.1 cm<sup>-1</sup> respectively. The strongest vibration modes of these absorption peaks are studied in detail and the results are shown in Fig. 7(f), Fig. 7(g) and Fig. (h). The mode at 1452.5 cm<sup>-1</sup> occurs redshift from 1452.5 cm<sup>-1</sup> to 1444.25 cm<sup>-1</sup>, while the IR intensity of this mode increase from 14.0981 a.u. to 22.9179 a.u. under the effect of EEF. The modes at 1499.62 cm<sup>-1</sup> and 1607.1 cm<sup>-1</sup> are activated by the EEF and the IR intensities of them increase to 25.8978 a.u. and 15.0952 respectively.

### 3.3 The Raman spectrum of endohedral fullerenes N@C<sub>60</sub> under the effect of EEF

The Raman spectrum of endohedral fullerenes N@C<sub>60</sub> are studied with DFT at B3LYP/3-21G level. The Raman spectrum of endohedral fullerenes N@C<sub>60</sub> in ground states are obtained. As is shown in Fig. 8, like fullerene C<sub>60</sub> [39], there exist ten distinct absorption

1 peaks without EEF. As is shown in Table 3, it is clearly seen that the calculated results of  
2 Raman spectrum of N@C<sub>60</sub> in ground states is closely to the C<sub>60</sub>'s, which reflects that the  
3 method employed in this work is precise [29-32]. The frequencies of absorption peaks are  
4 marked with red font in Fig. 8. According to the calculated results, the influence of the EEF  
5 on the Raman spectrum is clearly distinct from the infrared spectrum. The most obvious  
6 difference is that no new absorption peak appears in the Raman spectrum under the influence  
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Table 3. The comparison between the absorption peaks of Raman spectrum of N@C<sub>60</sub> in ground states and the calculated and experimental values of absorption peaks of Raman spectrum of C<sub>60</sub> in ground states (frequencies in cm<sup>-1</sup>)

This work	Calculated			Experimental
	Schettino et	Giannozzi et	Schettino et	Menendez et
	al. [39]	al. [40]	al. [41]	al. [42]
270.31	261	259	266	272
429.91	429	425	431	433
491.73	487	495	494	496
673.64	705	711	709	709
781.56	772	783	772	772
1112.64	1104	1120	1095	1099
1232.57	1251	1281	1248	1252
1434.97	1426	1450	1421	1425
1499.62	1474	1504	1468	1470
1607.64	1585	1578	1574	1575

In this work, the strongest vibrational modes of the absorption peaks, which are affected by EEF obviously, are investigated in detail and the results are shown in Figure 9. As is shown in Fig. 9(a), the Raman intensity of the vibration mode at a frequency of 491.73 increase from 113.1994 a.u. to 116.7262 a.u. with the effect of the EEF, while the EEF has a weak influence on its frequency. As is shown in Fig. 9(b), with the increase of the EEF, the vibrational mode at a frequency of 1232.57 occur redshift, while the Raman intensity of this mode increase. In Fig. 9(c), it is clear that the vibrational mode at a frequency of 1499.62 cm<sup>-1</sup>, which is the strongest vibration mode of the Raman spectrum of endohedral fullerenes N@C<sub>60</sub>, are affected by the EEF greatly. With the climbing of the EEF, the Raman intensity of this mode decrease rapidly and the deviation is -68.03 a.u.. It can be seen from Fig. 9(d) that as the electric field strength increases, the Raman intensity of the vibration mode at a frequency of 1067.64 cm decreases from 49.1906 a.u. to 38.7916 a.u..



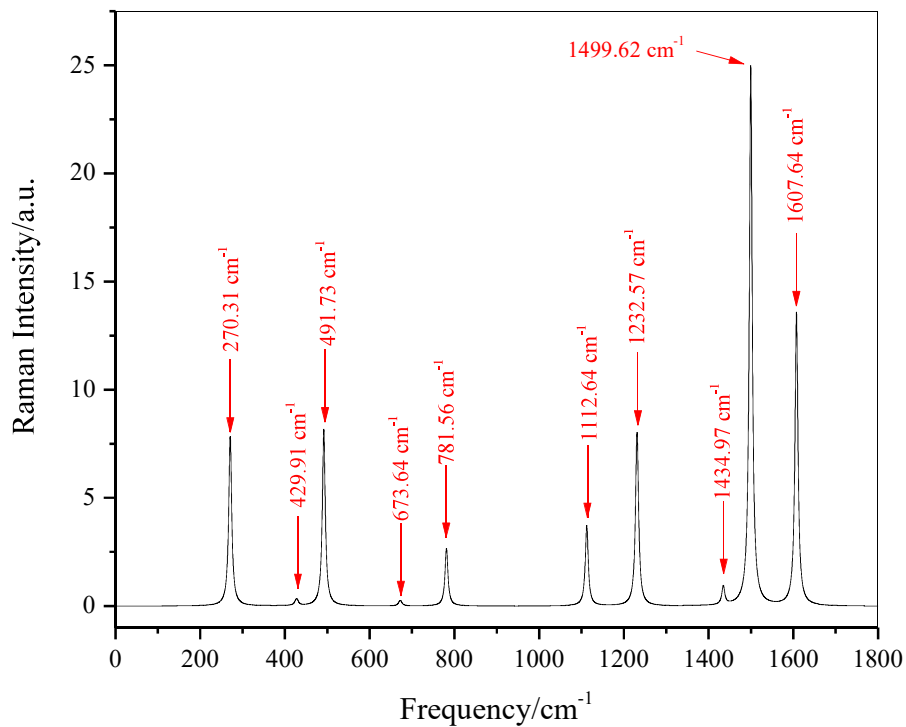


Figure 8. The Raman spectrum of endohedral fullerenes N@C<sub>60</sub> in the ground state

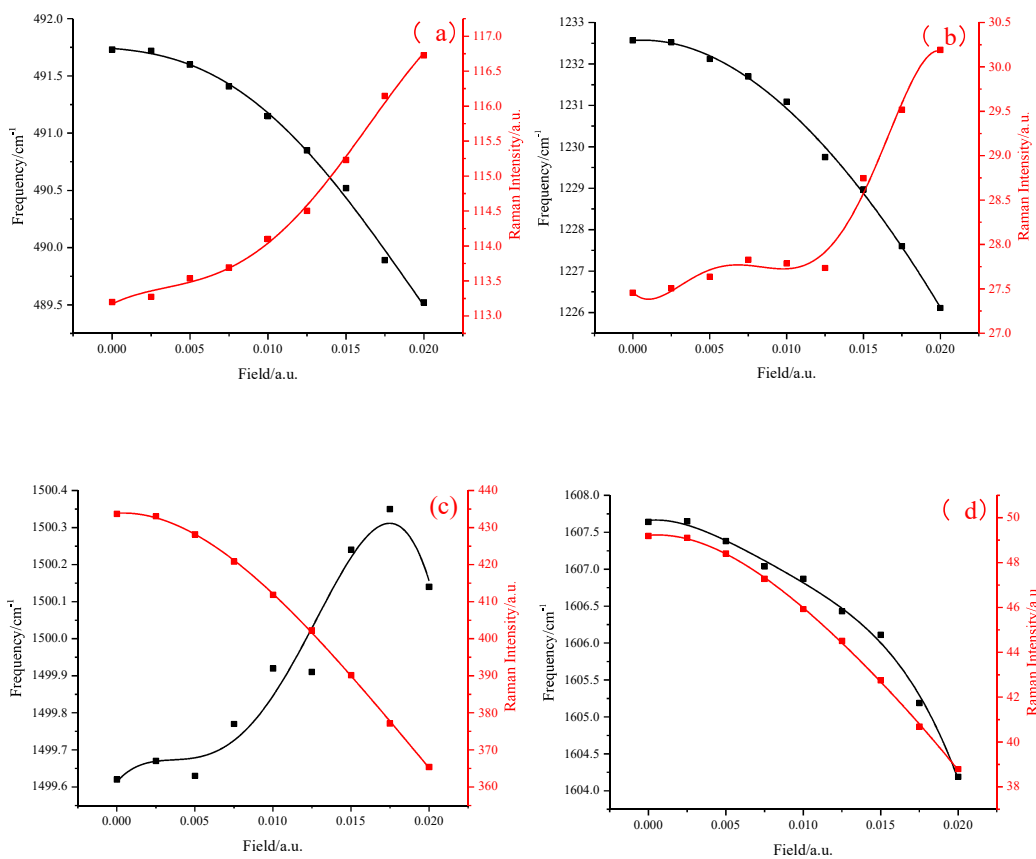


Figure 9. The Raman intensity and frequency of some special modes of endohedral fullerenes

#### 4. Conclusion

In this work, the spectrum and physical properties of endohedral fullerenes N@C<sub>60</sub> are studied by the DFT at the B3LYP/3-21G level, including the total energy, LUMO energy, HOMO energy, energy gap, infrared spectrum and Raman spectrum. With the increase of EEF, the total energy of endohedral fullerenes N@C<sub>60</sub> decreases and the deviation is about -233.16183 kJ/mol. The LUMO energies of the alpha MOs and beta MOs present two different trends under the effect of the EEF, while the HOMO energies of these two MOs have a similar trend. What's more, the E<sub>G</sub> of the alpha MOs and beta MOs decrease in different degree. With the impact of the EEF, six new absorption peaks appear in infrared spectrum due to the excitation of several silent modes. The EEF also have a significant effect on the Raman spectrum and the Raman intensity of the strongest vibration mode of the Raman spectrum decrease from 433.7222 a.u. to 365.3419 a.u.. The results in this work prove that modulation method of the properties of endohedral fullerene based on the EEF is very promising. It can be expected that this modulation method can be widely applied to other endohedral fullerene molecules, and plays a vital role in the process of endohedral fullerene materials towards applications.

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