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The effects of external electric field: creating non-zero first hyperpolarizability for centrosymmetric benzene and strongly enhancing first hyperpolarizability for non-centrosymmetric edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2

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Abstract How to generate a non-zero first hyperpolarizability for a centrosymmetric molecule is a challenging question. In this paper, an external (pump) electric field is used to make a centrosymmetric benzene molecule generate a non-zero value of the electric field induced first hyperpolarizability (β^F). This comes from the centrosymmetry breaking of electron cloud. Two interesting rules are exhibited. (1) β^F is anisotropic for different directional fields (F_i, i=X, Y, Z). (2) The field dependence of β^F is a non-monotonic function, and an optimum external electric field causes the maximum value of β^F. The largest first hyperpolarizability β^F reaches the considerable level of 3.9×10^5 a.u. under $F_Y = 330 \times 10^{-4}$ a.u. for benzene. The external electric field effects on non-centrosymmetric edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2 was also studied in this work. The first hyperpolarizability reaches as much as 2.1×10^7 a.u. under $F_X = 600 \times 10^{-4}$ a.u. for H_2N-(3,3)ZGNR-NO_2. We show that the external electric field can not only create a non-zero first hyperpolarizability for centrosymmetric molecule, but also remarkably enhance the first hyperpolarizability for a non-centrosymmetric molecule.

Abbreviations

β^F	Electric field induced first hyperpolarizability
F_i, i = X, Y, Z	Different directional fields
NLO property	Nonlinear optical property
D-B-A system	Donor-conjugated bridge-acceptor system
NBO charge	Natural bond orbital charge
HOMOs	Highest occupied molecular orbitals
LUMOs	Lowest unoccupied molecular orbitals
β	Inherent first hyperpolarizability

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Introduction

The nonlinear optical (NLO) properties of many kinds of materials, such as inorganic compounds [1–3], organic-metal [4–7], and donor-conjugated bridge-acceptor (D-B-A) systems [8–10], have attracted much attention.

Recently, several kinds of NLO systems with an excess electron have been investigated [11–17]. For nano-molecules, Nakano and co-workers [18–21] clarified the diradical character dependence of the third-order NLO response for open-shell singlet ground state systems. They also proposed a novel molecular design scheme of NLO response.

On the other hand, the effect of an external electric field on a substance is a widely significant research area with many branches, including the area of control and modulation of the electric and magnetic properties of organic conductors [22], carbon nanotubes [23–26], graphene [27, 28], and so on.

While studying the effects of an external (pump) electric field on the NLO response, Nakano and co-workers reported that application of a static external electric field results in a gigantic enhancement of the third-order NLO response in symmetric diradicals [29]. The application of a static external electric field resulting in the enhancement of the second-order NLO response has not been reported in detail.

Kirtman et al. [30] found that the substituent effect on enhancing first hyperpolarizability in a donor-acceptor (D/A) polyene may be simulated by means of a uniform electric field. Considering the effect of external electric field on enhancing first hyperpolarizability, it is expected that the external electric field (F_i, i=X, Y, Z) makes a centrosymmetric non-NLO molecule for second-order NLO response change into the NLO molecule with non-zero first hyperpolarizability, meanwhile remarkably enhances the first hyperpolarizability for non-centrosymmetric molecules.

This investigation was aimed at finding the external (pump) electric field effect on enhancing the static first hyperpolarizability, revealing the anisotropy and the non-monotonic property of the static first hyperpolarizability β^F under different directional fields, and providing a new strategy for enhancing the second-order NLO response by applying an external electric field. It is interesting that an easily polarizable centrosymmetric molecule may become a second-order NLO molecule under an external electric field.

Computational details

For the small benzene molecule, the optimized structures with all real frequencies under a series of external (pump) electric fields (the maximum field is up to an F_Z value of $1,000 \times 10^{-4}$ a.u. to be about 5 V/Å) are obtained at high CCSD/aug-cc-pVDZ levels. The hyperpolarizabilities of a series of benzene structures at different external electric fields were calculated at the CCSD/aug-cc-pVDZ level. The natural bond orbital (NBO) charges were evaluated at the CCSD/aug-cc-pVDZ level. For the large edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2 molecule, the optimized structure was obtained at the feasible B3LYP/6–31g* level and the first hyperpolarizabilities calculated at MP2/6–31g* level under a series of electric fields.

The finite-field method was used to investigate the second order NLO response [31] and third-order NLO response under external electric field in symmetric diradicals [29]. In this work, for second-order NLO response calculations under an external electric field, finite-field theory is used.

The energy of a molecular system in the homogeneous probe electric field can be written as:

$$E = E_0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \cdots \quad (1)$$

where E_0 is the molecular energy without the applied electrostatic field and F_α is a component of the strength on the α direction of applied electrostatic field; μ_α, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ may be called a component of dipole, polarizability, and first hyperpolarizability tensor, respectively.

For a molecule in an external (pump) electric field, F, the first hyperpolarizability tensor, is $\beta^F_{\alpha\beta\gamma}$ from the expansion of Eq. (1) around field F.

The first hyperpolarizability under the pump electric field β^F is defined as

$$\beta^F = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \quad (2)$$

where

$$\beta_x = \frac{3}{5}\left(\beta^F_{xxx} + \beta^F_{xyy} + \beta^F_{xzz}\right)$$

$$\beta_y = \frac{3}{5}\left(\beta^F_{yyy} + \beta^F_{yxx} + \beta^F_{yzz}\right)$$

$$\beta_z = \frac{3}{5}\left(\beta^F_{zzz} + \beta^F_{zxx} + \beta^F_{zyy}\right)$$

All calculations were carried out using the GAUSSIAN 09 program package [32]. The dimensional plots of molecular orbitals were generated with the GaussView program.

Results and discussion

Equilibrium geometries of benzene molecule under external electric fields

The optimized structural parameters of the benzene molecule with all real frequencies under different external electric fields are shown in Fig. 1 and Table 1.

From Table 1, for the D_{6h} structure of the benzene molecule without an electric field, the bond lengths of C–C and C–H are 1.407 and 1.095 Å, respectively. When the external
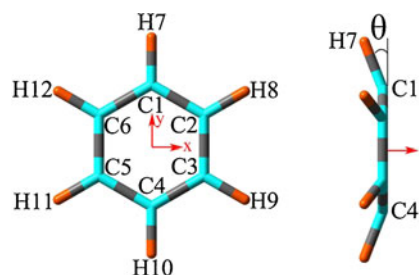
Fig. 1 Structural parameters and coordinate system of benzene

Table 1 Changes in geometric parameters (C–C and C–H in Å, and θ in degree) with electric field F_i (in 10^{-4} a.u.) for benzene

F_X	0	100	200	300	350	360	361
C2-C3	1.407	1.408	1.410	1.413	1.415	1.415	1.415
C5-C6	1.407	1.408	1.409	1.410	1.412	1.412	1.412
C2-H8	1.095	1.097	1.100	1.105	1.108	1.109	1.109
C6-H12	1.095	1.094	1.094	1.096	1.097	1.098	1.098
F_Y	0	100	200	300	320	330	333
C1-C2	1.407	1.408	1.410	1.412	1.413	1.413	1.413
C2-C3	1.407	1.408	1.409	1.411	1.411	1.411	1.411
C3-C4	1.407	1.408	1.409	1.411	1.411	1.411	1.412
C1-H7	1.095	1.097	1.101	1.108	1.109	1.110	1.110
C2-H8	1.095	1.096	1.097	1.099	1.100	1.100	1.100
C4-H10	1.095	1.094	1.095	1.097	1.098	1.098	1.098
F_Z	0	100	200	300	500	700	1000
C-C	1.407	1.408	1.409	1.410	1.416	1.425	1.440
C-H	1.095	1.095	1.095	1.095	1.097	1.100	1.119
θ(°)	0.0	2.23	4.45	6.80	11.66	16.93	17.52

electric field F is applied toward the X and Y direction, the benzene molecule is still a planar structure, the C–C and the C–H bonds are changed slightly with the increasing of F, and small differences in bond lengths (<0.01 Å) are exhibited. Under the F_X and F_Y action, the geometrical centrosymmetry of benzene is slightly broken.

When the F is added to the Z direction, the C–C and C–H bonds are elongated slightly with increasing F_Z (0.018 Å for C–C under F_Z of 700×10^{-4} a.u.). Interestingly, the benzene molecule is out of the planar structure, the C–H bond directions deflect towards the negative direction of the electric field, and the deflection angle θ increases with increasing F_Z. Under F_Z of 700×10^{-4} a.u., the θ value is 16.93° (see Fig. 1). Under the F_Z action, the geometrical centrosymmetry of benzene is broken.

For the geometric effects of different directional electric fields (F_X, F_Y and F_Z) with the same magnitude (for example 300×10^{-4} a.u.), the change in bond lengths were almost the same and small, while for the change in the θ bond angles, F_Z has a very obvious effect compared to the structure under zero electric field. Therefore, F_Z is most effective for molecular structural change. The results also showed that a benzene molecule without broken bonds is stable enough in a high external electric field (see Table 1).

Electric field effects on orbital and charge as well as dipole moment

The interesting evolutions of orbitals under external electric field are shown in Fig. 2, which shows the evolutions of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) under different direction fields (F_X, F_Y and F_Z) for benzene. Under F_X, F_Y, the lobes in the positive direction of electric field are enlarged and the lobes in the negative direction of the field are reduced in HOMOs, indicating that the electric field affects the electron density distribution strongly. In LUMOs, the lobes are pushed powerfully along positive direction of electric field. Under F_Z, lobes in the positive direction of electric field are reduced and lobes in the negative direction of the field are enlarged for HOMOs. In LUMOs, the lobes are powerfully pushed along the positive direction of electric field.

Using the case of electric field F_Y as an example, the electric field dependences on orbital shape and order were determined and are shown in Fig. 3. The lobes of occupied orbitals along the direction of electric field F_Y evolve with the increase of the field. For unoccupied orbitals, not only the lobes, but also the order of the orbitals are changed. For
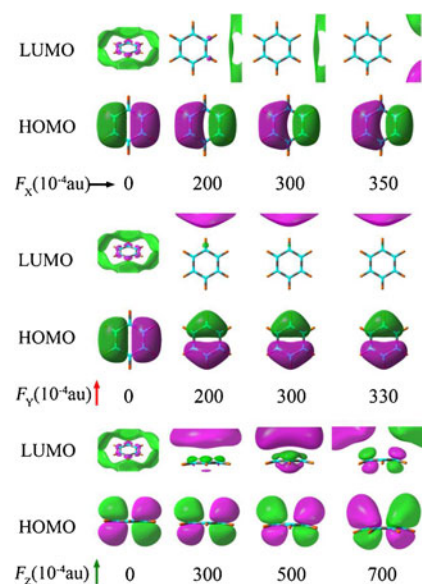
Fig. 2 Evolutions of orbitals with different direction fields
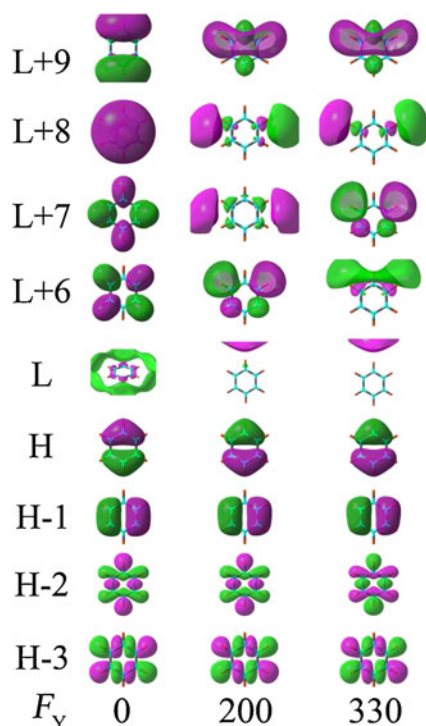
Fig. 3 Dependence on orbital shape and order of electric field F_Y

example, the L+6 orbital under $F_Y = 200 \times 10^{-4}$ a.u. becomes the L+7 orbital under $F_Y = 330 \times 10^{-4}$ a.u.

Therefore, the orbital evolution with electric field affects not only electron density distribution but also the electron transition.

Of course, the orbital changes relate to changes in atomic charges. The NBO charges of benzene under different electric fields at CCSD/aug-cc-pVDZ level are listed in Table 2. From Table 2, q_C and q_H are −0.219 and 0.219, respectively, for benzene without the field. For obvious change of charge, the negative charge of C2 or C1 increases and the positive charge of H8 or H7 decreases with increasing F_X or F_Y. For the Z direction, q_C and q_H both increase with increasing F_Z.

Besides orbital changes, changes in atomic charges also affect the change in electron density distribution.

From Table 2, the inherent dipole moment of benzene molecule is zero due to the centrosymmetries of both molecular geometry and electron density distribution. When the external electric field F is applied, the centrosymmetries of molecular geometry and electron density distribution are broken and a non-zero dipole moment occurs. The induced dipole moment increases with increasing electric field (see Table 2) in the field range used.

External electric field induced first hyperpolarizability for benzene

It is well known that the inherent first hyperpolarizability (β) of centrosymmetric molecule is zero and not a second-order NLO molecule. How to make a centrosymmetric molecule generate a non-zero first hyperpolarizability and become a second-order NLO molecule is a challenging question. An external electric field effect is expected. Benzene is a benchmark aromatic molecule with centrosymmetry and an easily polarizable π-system, so benzene is chosen as a representative exemplar of centrosymmetric molecules in this paper.

When calculating the first hyperpolarizability of a benzene molecule under the external electric field ($F_Y = 300 \times 10^{-4}$ a.u.) using the D_{6h} benzene structure to keep the geometrical centrosymmetry, a non-zero field induced first hyperpolarizability ($\beta^F = 1.0 \times 10^3$ a.u. in second line of Table 3) occurs and benzene becomes a second-order NLO molecule under the field. Here, although the geometrical centrosymmetry of the benzene molecule is retained, the centrosymmetry of the electron density distribution is broken. Hence, a new understanding that it is not the symmetry of electron density distribution but rather the molecular geometry that is the direct factor controlling the second-order NLO response of the molecule is revealed.

Table 2 Effects of electric field F_i (in 10^{-4} a.u.) on the natural bond orbital (NBO) charge for benzene

F_X	0	100	200	300	350	360	361
C2	−0.219	−0.242	−0.265	−0.289	−0.301	−0.303	−0.303
H8	0.219	0.195	0.170	0.144	0.131	0.128	0.128
μ_X	0.0	−2.077	−4.194	−6.399	−7.558	−7.796	−7.820
F_Y	0	100	200	300	320	330	333
C1	−0.219	−0.246	−0.272	−0.300	−0.306	−0.309	−0.310
H7	0.219	0.191	0.162	0.131	0.124	0.120	0.119
μ_Y	0.0	−2.077	−4.194	−6.406	−6.867	−7.100	−7.171
F_Z	0	100	200	300	500	700	1000
C	−0.219	−0.220	−0.224	−0.230	−0.253	−0.282	−0.348
H	0.219	0.220	0.224	0.230	0.252	0.282	0.348
μ_Z	0.0	−1.365	−2.775	−4.301	−8.138	−14.414	−30.046

Table 3 Effects of electric field F_i (in 10^{-4} a.u.) on the electric field induced first hyperpolarizability (β^F in a.u.) of benzene for optimized structures under F_i and the second line values for optimized D_{6h} structure without F_i

F_X	0	100	200	300	350	360	361
β^F	0.0	139.0	327.8	810.1	2.9×10^3	2.9×10^4	6.9×10^4
	0.0	135.3	318.1	773.2			
F_Y	0	100	200	300	320	330	333
β^F	0.0	139.2	331.7	1.1×10^3	1.7×10^4	3.9×10^5	2.5×10^4
	0.0	135.6	321.7	1.0×10^3			
F_Z	0	100	200	300	500	700	1,000
β^F	0.0	156.6	369.4	726.8	2.6×10^3	5.8×10^3	1.9×10^3
	0.0	137.4	325.1	648.8	2.6×10^3		
F_X	0	100	200	300	350	360	361
β^F	0.0	139.0	327.8	810.1	2.9×10^3	2.9×10^4	6.9×10^4
	0.0	135.3	318.1	773.2			
F_Y	0	100	200	300	320	330	333
β^F	0.0	139.2	331.7	1.1×10^3	1.7×10^4	3.9×10^5	2.5×10^4
	0.0	135.6	321.7	1.0×10^3			
F_Z	0	100	200	300	500	700	1000
β^F	0.0	156.6	369.4	726.8	2.6×10^3	5.8×10^3	1.9×10^3
	0.0	137.4	325.1	648.8	2.6×10^3		

Considering the geometric changes under the external field, for benzene structure with noncentrosymmetries of electric field induced electron density distribution and induced geometry, we calculate its first hyperpolarizability using optimized structure under the preponderantly directional field ($F_Y = 300 \times 10^{-4}$ a.u.) and obtained induced first hyperpolarizability to be the β^F of 1.1×10^3 a.u. The β^F of 1.1×10^3 a.u. for the field induced structure is slightly larger than the 1.0×10^3 a.u. for the D_{6h} structure (with noncentrosymmetry of electric field induced

electron density distribution). Obviously, the contribution of induced electron density distribution is the dominating role for small electric fields of $F < 300 \times 10^{-4}$ a.u.

The effects of external electric fields on the first hyperpolarizability (β^F) of benzene and related information are shown in Table 3 and Fig. 4. Three conclusions can be drawn: (1) an external electric field can create a non-zero first hyperpolarizability β^F for the centrosymmetric benzene molecule. For example, the β^F of 1.1×10^3 a.u. under the

Fig. 4 Electric field dependence on β^F value in three electric field directions (F_X, F_Y, F_Z) for optimized benzene geometries under different electric fields
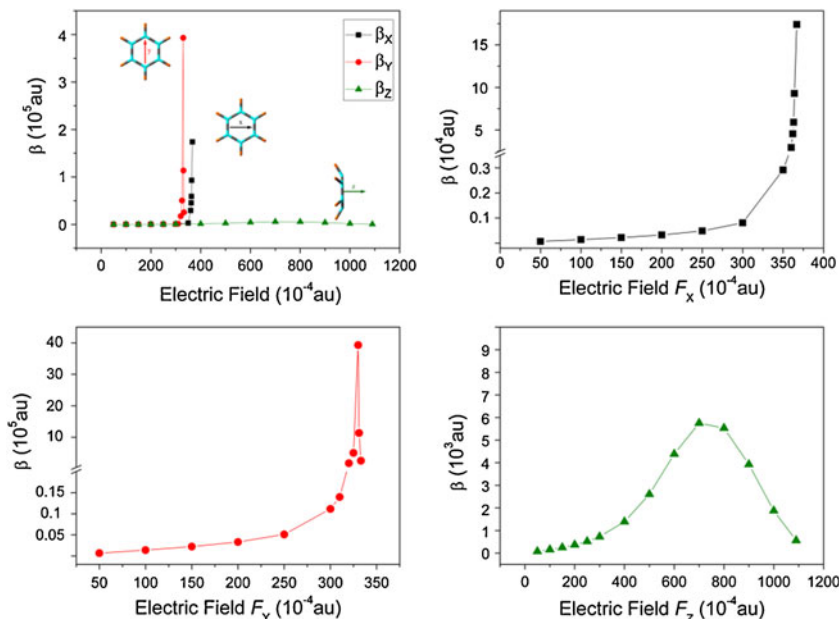
Table 4 Hyperpolarizability (β^F in a.u.), transition energy (ΔE in eV), oscillator strength f_0, dipole moment (μ_i) of ground state, dipole moment of excited state [μ_i(ex)] and the difference in dipole moments ($\Delta\mu$) between ground and excited state (in debye)

F_X	0	100	200	300	350	360	361
β^F	0.0	139.0	327.8	810.1	2.9×10^3	2.9×10^4	6.9×10^4
ΔE	7.70	7.48	6.88	6.19	5.86	5.81	5.80
f_0	0.9394	0.6047	0.2742	0.2133	0.1743	0.1675	0.1668
μ_X	0.0	−2.08	−4.19	−6.40	−7.56	−7.80	−7.82
μ_Z(ex)	0.0	−6.25	−10.64	−14.72	−12.80	−12.79	−12.79
$\Delta\mu$	0.0	4.18	6.45	8.32	5.24	5.00	4.97
F_Y	0	100	200	300	320	330	333
β^F	0.0	139.2	331.7	1.1×10^3	1.7×10^4	3.9×10^5	2.5×10^4
ΔE	7.70	7.63	7.50	7.27	7.21	7.17	7.23
f_0	0.9394	0.6291	0.4038	0.6753	0.5813	0.5871	0.2101
μ_Y	0.0	−2.08	−4.19	−6.41	−6.87	−7.10	−7.17
μ_Y(ex)	0.0	−4.18	−17.13	−9.23	−10.98	−10.89	−13.41
$\Delta\mu$	0.0	2.10	12.93	2.83	4.11	3.79	6.24
F_Z	0	100	200	300	500	700	1,000
β^F	0.0	156.6	369.4	726.8	2.6×10^3	5.8×10^3	1.9×10^3
ΔE	7.70	7.49	7.05	6.53	4.17	3.48	4.70
f_0	0.9394	0.3834	0.3280	0.3231	0.3737	0.6713	0.6708
μ_Z	0.0	−1.36	−2.77	−4.30	−8.14	−14.41	−30.05
μ_Z(ex)	0.0	−5.10	−7.55	−9.62	−13.78	−15.26	−30.56
$\Delta\mu$	0.0	3.73	4.77	5.31	5.64	0.85	0.51

F_Y of 300×10^{-4} a.u. is non-zero. (2) The β^F is anisotropic for different directional fields and the preponderantly directional field (F_Y) exists for the β^F of benzene. Comparing external electric field directional effects on β^F, 1.1×10^3 ($F_Y=300\times10^{-4}$ a.u.)>810.1 ($F_X=300\times10^{-4}$ a.u.)>726.8 ($F_Z=300\times10^{-4}$ a.u.). (3) For each directional field, an optimum electric field value corresponding to the maximum value of first hyperpolarizability (β^F) occurs due to a suitable polarized electron density. The largest β^F of benzene reaches up to 3.9×10^5 a.u. under the optimum field strength of 330×10^{-4} a.u. in the preponderantly directional field F_Y. In this case, benzene changes into a second-order NLO molecule.

In order to further understand the controlling factors of the β^F for benzene molecule, we may find some clues from the two-level model [33, 34]:

$$\beta^F \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3} \qquad (3)$$

In the above expression, β^F is proportional to the difference of dipole moments between the ground and the crucial excited state ($\Delta\mu$) and the oscillator strength (f_0) but is inversely proportional to the third power of the transition energy (ΔE).

For the benzene molecule, the $\Delta\mu$, f_0 and ΔE are estimated by the CIS method with the aug-cc-pVDZ basis set and listed in Table 4. From Table 4, we can see that the $\Delta\mu$ of the centrosymmetric benzene molecule is zero, so its inherent first hyperpolarizability is zero. Under an external electric field, the centrosymmetry of the benzene molecule is broken and a non-zero $\Delta\mu$ occurs, so the non-zero field induced first hyperpolarizability β^F appears. What is the controlling role for the dependence of electric field on β^F? Table 4 shows that the smaller the ΔE, the larger the β^F for each directional field. For example, the largest β^F of 3.9×10^5 a.u. corre-
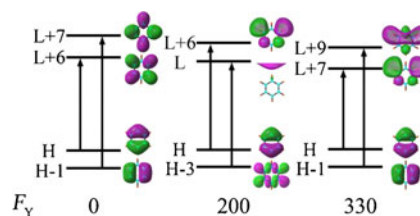
Fig. 5 Electric field dependence on electron transition

Table 5 Hyperpolarizability (β^F in a.u.) at MP2/6–31g* level, transition energy (ΔE in eV), oscillator strength f_0 and difference in dipole moments between the ground and excited state ($\Delta \mu$ in debye) under different electric fields F_X for edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2

F_X	0	150	400	500	600	700	800
β^F	1.7×10^4	1.2×10^4	8.4×10^3	7.9×10^6	2.1×10^7	2.2×10^4	7.0×10^3
ΔE	2.4151	2.4632	2.3800	1.4216	1.4499	2.6608	2.8977
f_0	0.8749	0.8427	0.1248	0.1289	1.31	0.2328	0.2257
Transition	H→L	H→L	H-1→L	H-2→L	H→L	H-1→L+2	H→L+4
$\Delta \mu$	1.17	1.58	12.55	5.44	12.24	6.06	1.61

sponds to the lowest ΔE of 7.17 eV for F_Y field. So besides $\Delta \mu$, the ΔE is also the main controlling factor for the dependence of electric field on β^F.

As above, the external electric field changes not only the shapes and order of molecular orbitals, but also the electron transition and related properties, which relates to the dependence of electric field on β^F (see Fig. 5 and Table 4).

External electric field induced hyperpolarizability for edge modified graphene ribbon

As above, for a centrosymmetric benzene molecule, by using an external electric field, the large non-zero electric field induced first hyperpolarizability β^F is created. Then, for a noncentrosymmetric NLO molecule, the question is whether the electric field can enhance the first hyperpolarizability? Graphene has attracted much attention because of its extraordinary structure and properties [35], such as its high surface area, high Young's modulus, and excellent electric and thermal properties. Regarding optical properties, edge-modified graphene ribbon has a considerable second-order NLO response [10] and becomes a non-centrosymmetric molecule

with a large NLO response, so an edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2 was chosen as a representative exemplar of a non-centrosymmetric molecule in this paper.

The first hyperpolarizability values (β^F) under different electric field values of the preponderantly directional field F_x are shown in Table 5 and Fig. 6. The dependence of the electric field on β^F shows that for the NLO molecule, an electric field of 600×10^{-4} a.u. brings the largest β^F of 2.1×10^7 a.u., which is 1,200 times that of 1.7×10^4 a.u. under the zero field for edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2 molecule [10]. The largest β^F corresponds to the largest f_0, next largest $\Delta \mu$ and next lowest ΔE (see Table 5). The β^F is decided mainly by the three factors $\Delta \mu$, f_0 and ΔE under the electric field.

Conclusions

This work revealed the external electric field effects on structure and first hyperpolarizability. With increasing external field F_Z, the benzene molecule evolves from a planar hexagonal shape into a frustum of hexagonal pyramids. The nonpolar benzene molecule is still stable enough in high external electric field (up to about 5 V/Å, $1,000 \times 10^{-4}$ a.u.), as it is difficult to break the bonds of benzene. Three characteristics of external electric field effect on first hyperpolarizability are revealed. (1) An external electric field remarkably enhances the first hyperpolarizability, due mainly to the change of electron density for a molecule. Therefore, under the external electric field, benzene may become a second-order NLO molecule. The first hyperpolarizability in the external field (β^F) may theoretically reach up to the considerable value of 3.9×10^5 for benzene. And β^F may reach up to 2.1×10^7 a.u. for edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2, which is 1,200 times the value of 1.7×10^4 a.u. obtained under zero field. (2) The β^F is anisotropic for different directional fields. The preponderant directional field is F_Y for the β^F of
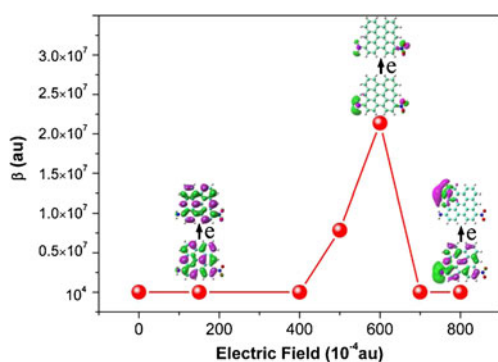
Fig. 6 Electric field dependence on β value and the crucial transitions for edge-modified graphene ribbon H_2N-(3,3)ZGNR-NO_2

benzene and F_X for the β^F of the edge-modified graphene ribbon. (3) The field dependence of β^F is a non-monotonic function. An optimum, preponderantly directional, electric field value corresponds to the maximum value of β^F for a molecule.

Thus, the application of an external electric field may be a new strategy of enhancing a second-order NLO response.

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