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Hybrid CIS-DFT method to study electric field effects on electronic excited states of ethylene*

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The present work is devoted to the study of the effects of external dipole electric field on the molecular structure of ethylene using a hybrid method which combines the single-excitation configuration interactions (CIS) with density functional theory (DFT), i.e. CIS-DFT(B3LYP). It is found that the effects of electric dipole field on the molecular geometry (D_{2h}, D_{2d} and C_{2v}), dipole moment, transition dipole moment, polarizability and, particularly, excitation energy of ethylene are remarkable. The advantages of the hybrid CIS-DFT method are that it can determine the symmetry of molecule and the correct order of excitation as well as the Molecular Orbital (MO) electron configuration; thereby the electronic excitation states of ethylene are easily derived, and most of them are in agreement with those obtained in experiments or references. It may be the first time the effects of external electric field on ethylene molecule have been considered. Compared with other *ab initio* methods, the CIS-DFT method is relatively accurate and low cost in computation. We expect that it can be used to study other closed-shell molecules.

Keywords: excited state, hybrid CIS-DFT method, electric dipole field
PACC: 3000, 3150, 3120A, 7115A

1. Introduction

The influences of external electric field on the properties of molecule and its electronic excited states are two active subjects of theoretical and experimental research. The former is to study the properties of ground state of molecule in an external electric field, such as molecular geometry, dipole moment, super polarizability, the electron and proton transfers and nonlinear optical properties of molecules[1−5] mostly by use of the point charge model[6] or the finite field model,[7] while the latter mainly deals with the excited state properties in the field-free case,[8−15] such as excitation energies, transition, radiation, photoabsorption process and oscillator strength, etc. From the theoretical point of view, there are two accurate *ab initio* methods for the excited states: the multireference configuration interaction method (MRCI)[13] and the method based on the complete active space self-consistent field with the second order perturbative theory (CASSCF-PT2).[11] These two methods are either complex or time consuming in computation. A hybrid scheme, which is empirical in nature but has been demonstrated to offer surprisingly high accuracy in computational practice, is the combination of the CIS with the DFT method. This scheme is proposed by Grimme,[16] but has not yet been widely adopted because of its empirical nature.[17]

In recent years, however, the excited states under the action of an external electric field are of more importance in some cases such as the radiolysis and degradation of organic complexes and polymers, and the laser–matter interaction[18−21], etc. All of these are significant for photochemistry and radiation chemistry, and hence have formed a new research field in which recently much work has been done experimentally[22−27] but not theoretically. Zhu Zheng-He[28] studied the external electric field effect on H_2 by calculating the excitation energies, disso-

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ciation energies and oscillation frequencies, etc. Aschi *et al*[5] proposed a method based on a perturbation theory[29] to calculate an electron wavefunction in an external homogeneous electric field but it can only be applied to ground states and the first excited state in a weak field because of its perturbative nature. A new method based on time-dependent density functional theory (TDDFT) using real space grid algorithm[30−34] to treat matter–field interaction by solving directly the time-dependent Schrödinger equation has been developed. Nevertheless, the high cost and time consuming computation restrict its application to large molecular systems.

In this work we extend Grimme's method[16] to the investigation of the electric field effects on the characteristics of excited states of molecule. In order to test it we take an ethylene molecule as an example for it is not only the simplest organic chromophore but also an interesting prototype[35−40] for more complicated molecules. In Section 2 we examine the theoretical foundation and develop a hybrid configuration interaction single-excitation with density functional theory (CIS-DFT) for studying the electric field effect on excited states of molecule. Section 3 gives the computation details. In Section 4 we use the finite field model to study the electronic excited states of C_2H_4 by means of the CIS-B3LYP at 6-311++G(d, p) levels with the GAUSSIAN98 program. The electronic excitation energies, transition dipole moments and oscillator strengths are calculated, and a comparison of the calculations with available experiment data is made as well. Finally, conclusive remarks are presented in Section 5.

2. Theory

The Hamiltonian of the radiation absorption process is described by

$$H = H_0 + H_{\rm int}, \tag{1}$$

where H is the total Hamiltonian of the system, H_0 is the complete molecular Hamiltonian, and $H_{\rm int}$ the interaction between radiation and matter. One of the methods of studying radiation–matter interaction is the second quantization which is based upon the principle of the Bose–Einstein quantum statistics for bosons. But for simplicity, we adopt the semiclassical electromagnetic field theory and perturbation theory[15] to treat the radiation-matter interaction as

$$H_{\rm int} = -\mu \cdot F, \tag{2}$$

where μ is the dipole moment of the molecule, and F the electric field from the point charge model or the finite field model.[2]

For dipole electric field, the polarizability α satisfies

$$\alpha = \frac{\mu}{F}, \tag{3}$$

and the energy increase is

$$\Delta E = -\frac{1}{2}\alpha F^2. \tag{4}$$

Under the action of a time-dependent radiation field the molecule can be excited from lower-lying excited states to upper-lying excited states or vice versa by absorption or radiation of a photon respectively. For L-S or Λ-S coupling, the transition dipole moment from an upper state to a lower state is[28]

$$\mu_{\rm ul} = (-1)^{\Lambda-\Omega} \begin{pmatrix} \Lambda & u & \Lambda' \\ -\Omega & v & \Omega' \end{pmatrix} \langle \alpha\Lambda||\mu||\alpha'\Lambda'\rangle, \tag{5}$$

and the line strength S is defined as

$$S = |\langle \alpha\Lambda||\mu||\alpha'\Lambda'\rangle|^2, \tag{6}$$

where Λ and α represent the principal quantum number and other quantum numbers respectively, and Ω is the component of the total angular moment along the molecular axis or the direction of the external field.

The relations among the spontaneous emission coefficient $A_{\rm ul}$, absorption coefficient $B_{\rm lu}$, the transition electric dipole moment $\mu_{\rm ul}$ and excitation energy $E_{\rm lu}$ are described by[14]

$$\begin{aligned} A_{\rm ul} =& \frac{\hbar\nu_{\rm ul}^3}{\pi^2 C^3} B_{\rm lu} \approx 5.60613 \times 10^{-24} (E_{\rm ul})^2 B_{\rm ul} \\ =& 4.29148 \times 10^3 (\mu_{\rm ul})^2 (E_{\rm lu})^2, \end{aligned} \tag{7}$$

$$B_{\rm lu} = \frac{4\pi^2}{3\hbar^2}\mu_{\rm lu}^2 \approx 7.65498 \times 10^{26} (\mu_{\rm lu})^2, \tag{8}$$

where $E_{\rm lu}$ is in eV, $A_{\rm ul}$ in $\rm s^{-1}$ and $B_{\rm lu}$ in $\rm cm^3 s^{-2} J^{-1}$. The oscillator strength $f_{\rm ul}$ is[28]

$$gf_{\rm ul} = \frac{4\pi mca_0^2\sigma}{3\hbar} S = 3.0396610^{-6}\sigma S, \tag{9}$$

$$gA_{\rm ul} = \frac{8\pi^2 e^2 \sigma^2}{mc} gf_{\rm ul} = 0.667486\sigma^2 gf_{\rm lu}. \tag{10}$$

In this paper the computation of excitation energies is made through a hybrid scheme that is empirical in nature but has been demonstrated to offer surprisingly high accuracy in computational practice. This scheme is the combination of CIS with DFT

method.[16,17] In particular, all Hartree–Fock (HF) orbital energies are replaced by Kohn–Sham equivalents, and the Coulomb integrals and diagonal elements are empirically scaled. In the single-excitation configuration interaction, CI-Hamiltonian matrix elements for singly excited spin-adapted singlet configurations with substitution of an occupied MO $\psi_{\rm a}$ by a virtual MO $\psi_{\rm r}$ where CI stands for configuration interaction, and MO, molecular orbital are

$$\langle\psi_{\rm a}^{\rm r}|\,H-E_0\,|\psi_{\rm a}^{\rm r}\rangle=\varepsilon_{\rm r}^{\rm HF}-\varepsilon_{\rm a}^{\rm HF}-J_{\rm ar}+2K_{\rm ar}, \quad (11)$$

$$\langle\psi_0|\,H\,|\psi_{\rm a}^{\rm r}\rangle=\sqrt{2}\,(\psi_{\rm a}\,|f|\,\psi_{\rm r})\,, \quad (12)$$

$$\langle\psi_{\rm a}^{\rm r}|\,H\,|\psi_{\rm b}^{\rm s}\rangle=(\psi_{\rm r}\,|f|\,\psi_{\rm s})\,\delta_{\rm ab}-(\psi_{\rm a}\,|f|\,\psi_{\rm b})\,\delta_{\rm rs} -(\psi_{\rm a}\psi_{\rm b}\psi_{\rm r}\psi_{\rm s})+(\psi_{\rm a}\psi_{\rm r}\psi_{\rm b}\psi_{\rm s})\,, \quad (13)$$

where ψ_0 is the closed-shell reference determinant with the HF expectation value E_0, and H is the one- and two-electron Hamiltonian, and $\psi_{\rm a}^{\rm r}$ is the single excitation wavefunction. The magnitude of the excitation energy is often dominated by the energy gap of the dominating configurations. The energy gap between the occupied and the virtual orbitals is large if the HF operator is applied (roughly 2–3 times the energy gap), and is mainly reduced by subtraction of the integral $J_{\rm ar}$. In the DFT, on the other hand, the gap between the corresponding eigenvalues of the Kohn–Sham operator is very close to the exact excitation energy. Thus it seems a reasonable approximation to replace the term $\varepsilon_{\rm r}^{\rm HF}-\varepsilon_{\rm a}^{\rm HF}$ in Eq.(11) by $\varepsilon_{\rm r}^{\rm KS}-\varepsilon_{\rm a}^{\rm KS}$.

It should be mentioned that ψ represents an MO from the solution of the Kohn–Sham equation for the closed-shell ground state. These one-electron functions closely resemble HF-MOs in the occupied space but differ substantially in the virtual parts. The virtual KS-MOs are closer to natural orbitals and thus better suited for CI calculations than their HF counterparts. Since we do not want to relax these KS-MOs to HF-MOs through coupling of the $\psi_{\rm a}^{\rm r}$ state functions with the ground state via the Fock matrix elements in Eq.(12), these terms are neglected. Consistently, the off-diagonal Fock matrix elements between the singly excited configurations in Eq.(13) are also discarded so that the modified CI matrix elements in short notation read as follows[16,17]:

$$\langle\psi_{\rm a}^{\rm r}|\,H-E_0\,|\psi_{\rm a}^{\rm r}\rangle=\varepsilon_{\rm r}^{\rm KS}-\varepsilon_{\rm a}^{\rm KS}-J_{\rm ar}+2K_{\rm ar}, \quad (14)$$

where the $\varepsilon_{\rm r}^{\rm KS}$, $\varepsilon_{\rm a}^{\rm KS}$ are the Kohn-Sham orbital energies, and $J_{\rm ar}$, $K_{\rm ar}$ are the Coulomb and exchange integrals, respectively. In Grimme's formula, the Coulomb integrals $J_{\rm ar}$ and diagonal elements are empirically scaled[16,17] by a factor c_1 and an additive term $\Delta=-0.025\varepsilon+c_2\exp(-c_3K^4)$, respectively. In our method, however, the excitation energy is calculated directly from the diagonalization of the perturbed Hamiltonian as shown in Eq.(14).

3. Computation details

The ground state $D_{2h}(\tilde{X}^1{\rm A_g})$ of C_2H_4 molecule is assumed to lie in the yz-plane with the carbon double bond along the z-axis (Fig.1(a)), and the applied electric field is directed parallel to the C–C double bond. To determine the symmetries of the excited states of molecule with respect to a certain field firstly we optimize the ground state geometry under the action of the same field by using the density functional theory B3LYP with basis set 6-311++G(d, p), and secondly, investigate the excited state characteristics with the hybrid CIS-DFT method at 6-311++G(d, p) level. All the computations are made by use of the Gaussian98 package.

4. Results and discussion

4.1. Molecular structure under the action of external electric field

Table 1 lists the calculated results of optimized bond lengths, bond angels and dihedrals for ground state $D_{2h}(\tilde{X}^1{\rm A_g})$ of ethylene with an electric field varying in a range of 0.00–0.05 a.u. For the ground state of ethylene the stable geometries are found when the applied field is parallel to the C–C double bond; in this case introduction of the field lowers the symmetry of the system from D_{2h} to C_{2v}, and the double bond lengthens. The dipole moment, which is zero for the molecule in the field-free case, increases remarkably with the field strength. These results are similar to those found previously by Andre's[1] using an *ab initio* method with a double zeta Huzinga–Dunning basis set, for the same orientation of the field (0.01–0.04 a.u.).

Another stable orientation of ethylene is found for the first excited state $D_{2d}(\tilde{A}^3\ {\rm B_{1u}})$ as shown in Fig.1(c). When the applied field is directed along the C–C bond the symmetry is transformed into $C_{2v}(\tilde{A}^1{\rm A_1})$ under the action of an electric field as shown in Table 2. The bond length of C–C (R_{12}) decreases with electric field. However, all $R_{\rm CH}$ increase gradually, which is consistent with the experimen-

tal results.[6] For the ground state, the bond angles $A_{(3,1,4)}$ and $A_{(5,2,6)}$ are 116.52, whereas for the first excited state, $A_{(5,2,6)}$ decreases as the field increases. The reason for that lies in the transfer of electrons from hydrogens to 2C, and the attraction among 2C and 5H and 6H decreases the bond angle $A_{(5,2,6)}$, i.e. the binding of 5H and 6H to 2C is enhanced. On the contrary, the binding of 3H and 4H to 1C is weakened due to the decrease in the charge population of 1C, 3H and 4H. As the electric field increases from 0.00 to 0.05 a.u., shown in Tables 1 and 2, both geometrical point groups D_{2h} and D_{2d} are changed into C_{2v}, and the dipole moment and polarizability are on the increase. However the total energy decreases, e.g. the energies of $D_{2h}(\tilde{X}^1\mathrm{A_g})$ and $C_{2v}(\tilde{X}^1\mathrm{A_1})$ reduce by 0.05 and 0.038a.u. (1.3606 and 1.034eV) at F=0.05a.u. respectively. We might infer that C_2H_4 molecule under a certain external electric field becomes more stable than under no field.

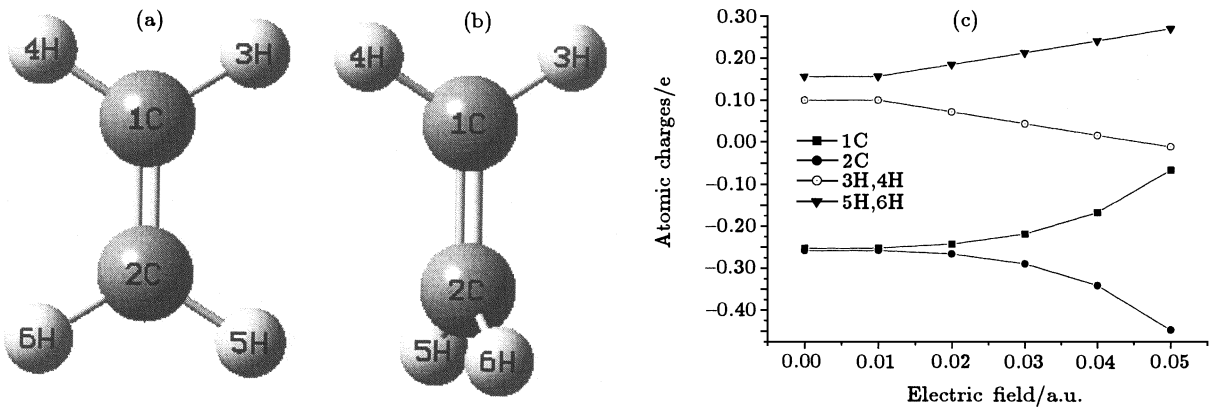


Fig.1. Optimized geometry for ground state $D_{2h}(\tilde{X}^1\mathrm{A_g})$ (a), the first excited state D_{2d} $(\tilde{A}^3\mathrm{B_{1u}})$ (b) of ethylene and Mulliken's charge population as a function of electric field (c).

Table 1. Optimized bond length R, bond angle A, dihedral D, dipole moment μ, total energy E and polarizability α for the ground states $D_{2h}(\tilde{X}^1\mathrm{A_g})$ and $C_{2v}(\tilde{X}^1\mathrm{A_1})$ under the action of an electric field F.

F/a.u.	R_1/nm	R_{13}/nm	R_{25}/nm	A_{314}/D	A_{526}/D	D_{3126}/D	symmetry	μ/D	E/a.u.	$\alpha=\mu/F$ /10^{-24}cm^3	$\alpha=2\Delta E/F^2$ /10^{-24}cm^3
0.00	0.1328	0.1080	0.1080	116.52	116.52	180.0	$D_{2h}(\tilde{X}^1\mathrm{A_g})$	0.000	–78.6155	—	—
0.01	0.1329	0.1086	0.1084	116.70	116.22	180.0	$C_{2v}(\tilde{X}^1\mathrm{A_1})$	0.893	–78.6173	5.2097	5.2826
0.02	0.1331	0.1088	0.1084	116.88	115.74	180.0	$C_{2v}(\tilde{X}^1\mathrm{A_1})$	1.799	–78.6226	5.2476	5.2901
0.03	0.1335	0.1090	0.1085	117.05	114.95	180.0	$C_{2v}(\tilde{X}^1\mathrm{A_1})$	2.733	–78.6316	5.3147	5.3255
0.04	0.1340	0.1094	0.1087	117.03	114.20	180.0	$C_{2v}(\tilde{X}^1\mathrm{A_1})$	3.712	–78.6445	5.4139	5.3828
0.05	0.1347	0.1098	0.1090	116.93	113.35	180.0	$C_{2v}(\tilde{X}^1\mathrm{A_1})$	4.773	–78.6616	5.56915	5.4690

Table 2. Optimized bond length R, bond angle A and dihedral D, dipole moment μ, and energy E for $D_{2d}(\tilde{A}^1\mathrm{B_{1u}})$ and $C_{2v}(\tilde{A}^1\mathrm{A_1})$ under the action of an electric field F.

F/a.u.	R_1/nm	R_{13}/nm	R_{25}/nm	A_{314}/D	A_{526}/D	D_{3126}/D	D_{3126}/D	symmetry	μ/D	E/a.u.
0.00	0.1452	0.1087	0.1087	116.25	116.20	–90.03	89.94	$D_{2d}(\tilde{A}^1\mathrm{B_{1u}})$	0.0009	–78.48801
0.01	0.1452	0.1086	0.1088	116.05	116.26	–89.98	90.01	$C_{2v}(\tilde{A}^1\mathrm{A_1})$	0.7204	–78.49025
0.02	0.1451	0.1086	0.1091	115.48	116.06	–89.99	90.00	$C_{2v}(\tilde{A}^1\mathrm{A_1})$	1.4618	–78.49051
0.03	0.1449	0.1087	0.1096	115.71	115.57	–90.01	89.99	$C_{2v}(\tilde{A}^1\mathrm{A_1})$	2.2495	–78.50127
0.04	0.1445	0.1094	0.1109	115.62	114.74	–90.01	89.99	$C_{2v}(\tilde{A}^1\mathrm{A_1})$	3.1170	–78.51268
0.05	0.1441	0.1094	0.1109	115.07	113.60	–90.01	89.99	$C_{2v}(\tilde{A}^1\mathrm{A_1})$	4.1189	–78.52735

4.2. Vertical electronic excitation energy under the action of an external electric field

The vertical excitation energies are calculated with the hybrid method CIS-B3LYP at 6-311++G(d, p) level. For the field-free case, as shown in Table 3, in which twelve states and their corresponding excitation energies are relative to ground state $D_{2h}(\tilde{X}^1\mathrm{A_g})$, the calculated results are in good agreement with the measurements (in parentheses),[9,14,41] with a mean absolute error of 0.2eV. When the applied field is directed along the z-direction, the excitation energies decrease quickly with the field increasing, as listed in Table 4. The transition wave-lengths increase from about 300nm to 140nm lying in the ultraviolet band. Recent experimental work[35] on the photo-dissociation of ethylene has shown that 193nm and 157nm radiation can excite ethylene to $3p_{x,y,z}$ Rydberg states, the geometries of which are all nearly planar.[30] It should be noted that the introduction of electric field makes the symmetries of the excited states quite different from those in the field-free case because of different geometries from which the excited states are calculated. The vertical excitation energies from $C_{2v}(\tilde{X}^1\mathrm{A_1})$ to $^3\mathrm{B_1}$, $^1\mathrm{B_1}$ and $^1\mathrm{B_2}$ low down dramatically, which implies that the polarizability α of the excited state of molecule is greatly changed by the field.

Table 3. Some quantities related to transitions from ground state $D_{2h}(\tilde{X}^1\mathrm{A_g})$to twelve excited states: vertical excitation energy E_{lu}, transition electric dipole moment element μ_{ul}, oscillator strength f_{lu}, absorption coefficient B_{lu} and spontaneous emission coefficient A_{ul}. The experiment data in parentheses for E_{lu} and f_{lu} are cited from Refs.[9,41] and Ref.[14], respectively.

state	Transition orbitals and coefficients		E_{lu}/eV	μ_{ul}/a.u.	f_{lu}	$B_{\mathrm{lu}}/10^{10}\mathrm{m^3s^{-2}J^{-1}}$	$A_{\mathrm{ul}}/10^6\mathrm{s^{-1}}$
$^3\mathrm{B_{1u}}$	8→9	0.82178	4.129	0.0000	0.0000	0.0000	0.0000
	8→16	–0.20464	(4.36)				
$^3\mathrm{B_{3u}}$	8→10	0.70522	6.9805	0.0000	0.0000	0.0000	0.0000
			(6.98)				
$^1\mathrm{B_{3u}}$	8→10	0.70183	7.1501	–0.8338	0.0569	0.2637	0.59460
			(7.15		(0.04)		
$^3\mathrm{B_{2g}}$	8→11	0.70686	7.4692	0.0000	0.0000	0.0000	0.0000
			(7.79)				
$^1\mathrm{B_{1u}}$	8→9	0.61183	7.4933	–1.349	0.3333	1.3930	3.5197
	8→16	0.16927	(7.66)		(0.34)		
$^3\mathrm{B_{1g}}$	7→9	–0.47639	7.5412	0.0000	0.0000	0.0000	0.0000
	8→12	0.53164	(7.79)				
$^1\mathrm{B_{2g}}$	8→11	0.70489	7.5836	0.0000	0.0000	0.0000	0.0000
			(8.0)				
$^1\mathrm{B_{1g}}$	8→11	0.70489	7.6823	0.0000	0.0000	0.0000	0.0000
			(7.83)				
$^3\mathrm{B_{1g}}$	7→9	0.53277	7.7115	0.0000	0.0000	0.0000	0.0000
	8→12	0.46322					
$^1\mathrm{B_{1g}}$	7→9	0.69242	8.1361	0.0000	0.0000	0.0000	0.0000
$^3\mathrm{A_g}$	8→13	0.71490	8.2056	0.0000	0.0000	0.0000	0.0000
			(8.15)				
$^1\mathrm{A_g}$	8→13	0.69316	8.5858	0.0000	0.0000	0.0000	0.0000
			(8.29)				

The electronic configurations for the ground state of C_2H are
$(a_g)(b_{1u})(a_g)(b_{1u})(b_{2u})(a_g)(b_{3g})$ (b_{3u}) for the occupied MOs $(b_{2g})(a_g)(b_{1u})$ $(b_{2u})(b_{3u})$ (b_{3g}) (b_{1g}) (b_{2g}) for the virtual MOs.

Table 4. The influences of varying electric field on excitation energy E_{lu}, transition electric dipole element μ_{ul} and oscillator strength f_{lu} (only dipole-allowed transitions from $C_{2v}(\tilde{X}^1\mathrm{A_1})$ are listed).

F/a.u.	$1^1\mathrm{B_1}$			$1^1\mathrm{B_1}$			$2^1\mathrm{B_1}$			$1^1\mathrm{B_2}$		
	E_{lu}/eV	μ_{ul}/a.u.	f_{lu}	E_{lu}/eV	μ_{ul}/a.u.	f_{lu}	E_{lu}/eV	μ_{ul}/a.u.	f_{lu}	E_{lu}/eV	μ_{ul}/a.u.	f_{lu}
0.01	6.327	–0.498	0.039	7.358	–1.268	0.290	7.854	–0.782	0.118	8.400	0.312	0.020
0.02	5.058	–0.023	0.019	7.051	–1.090	0.2054	7.343	0.139	0.132	7.228	0.042	0.014
0.03	3.704	–0.349	0.011	6.633	–0.899	0.1316	7.146	–0.844	0.127	6.633	0.250	0.009
0.04	2.320	–0.344	0.006	6.089	–0.368	0.0201	6.939	–0.837	0.119	4.356	0.229	0.006
0.05	0.942	–0.355	0.002	4.882	–0.540	0.0349	6.618	–0.828	0.111	2.855	0.218	0.003

4.3. Influences of electric field on oscillator strength, transition electric dipole moment, absorption coefficient $B_{\rm lu}$, and spontaneous emission coefficient $A_{\rm ul}$

The computation of oscillator strength for electronic transition presents a severe challenge to *ab initio* methods due to electron correlation. Thus, high degrees of electron correlation are necessary in order to evaluate both accurate excitation energies and transition dipole moments.[14] Although the simple method CIS provides less accurate excitation energies and transition electric dipole moments for a number of low-lying excited states, we find that a hybrid CIS-DFT method which combines single excitation configuration interaction with density functional theory can present quite good results to the excitation energies, oscillator strengths and transition dipole moments.[6,17,18] Tables 3 and 4 list the transition dipole moment, oscillator strength, the absorption coefficient $B_{\rm lu}$ and spontaneous emission coefficient $A_{\rm ul}$ calculated from Eq.(7) and Eq.(8) in different fields. As the field increases the transition dipole moment and the corresponding oscillator strength decrease, as shown in Table 4.

The advantages of the CIS-DFT method are that it is able to determine the symmetries of the excited states and determine the MO electron configuration. Eight occupied MOs and eight virtual MOs are listed in Table 3, from which it is easy to derive twelve single-excitation states as indicated in Table 3. The first excited state $^3B_{1u}$ with a vertical excitation energy of 33302.4cm^{-1},or 4.129eV is comparable with an experimental value of 4.36eV, as shown in Table 3, and also approximates $^3B_{1u}$[41] with an excitation energy of 28700cm^{-1}. The third excited state $^1B_{3u}$ with an excitation energy of 57669.1cm^{-1}, or 7.1501eV may be the $^1B_{3u}$.[41] The oscillator strengths $f_{\rm lu}$ of the third ($^1B_{1u}$) and fifth ($^1B_{3u}$) excited states are also comparable with the experimental data 0.04 and 0.03 in parentheses[14] respectively.

It is obvious that the electric dipole transitions from $C_{2v}(\tilde{X}^1A_1)$ to $^3A_1$, $^3B_1$ and $^3A_2$ are forbidden because they do not satisfy the selection rule ΔS=0, whereas the transitions to $^1B_1$, $^1A_1$ and $^1B_2$ states are possible for the transitions induced by the components μ_x, μ_y and μ_z of dipole moment, which are dipole-allowed. The transition from $C_{2v}(\tilde{X}^1A_1)$ to $^1A_2$ is forbidden, for there is no dipole component included in the direct product of $^1A_1\otimes{}^1A_2$, i.e. its integrand is not completely symmetrical irreducible representation of C_{2v}. However, the magnetic dipole Rz or electric quadruple Q_{xy} is allowed. Similarly, we can explain the transition from $D_{2h}(\tilde{X}^1A_g)$ to various excited states in Table 3.

5. Conclusion

In this paper we present a hybrid CIS-DFT method which combines the merits of the single-excitation configuration interaction with those of density functional theory in the study of the external dipole electric field influences on the characteristics of the excited states of ethylene. The calculated results indicate that both the excitation energies and the orbital energies decrease with the external field. The dipole moments are proportional to the external electric field strength. As the field increases the molecular geometry undergoes a transformation from ground state $D_{2h}(\tilde{X}^1A_g)$ to $D_{2d}(\tilde{A}^3B_{1u})$ and $C_{2v}(\tilde{X}^1A_1)$. The advantages of the CIS-DFT method are that it can determine the symmetries of excited states of molecule and the correct order of excitation as well as the MO electron configuration, and thus can be used to calculate various physical quantities of molecules such as the transition dipole moment, oscillator strength absorption and emission coefficients, etc. for both the ground and excited states. The method proposed here proves to be comparatively easy and accurate. We expect it can be used to study larger molecule systems. Further investigation of the radiation field effects involving time-dependent density functional theory will be presented later.

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