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REGULAR ARTICLE

Computation of large systems with an economic basis set: systems in excited states

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Abstract An economic basis set for ab initio calculations of systems in excited states has been studied. The economic basis set, in which the polarization functions are applied only to oxygen (O), while the 6-31G basis set is used for carbon (C) and hydrogen (H), is shown to save considerable computing time and to give reliable geometric and frequency measurements. In addition, the economic basis set has been considered for obtaining reliable excitation energies, with the correction factor, using high-level single-point energy calculations. This study is expected to shed light on basis set selection for computations of large systems in excited states.

Keywords Economic basis set · Excited state · Excitation energy

1 Introduction

With the recent improvement in computation facility, ab initio calculations have achieved satisfactory agreement with experimental data for small and medium-sized molecular systems in terms of structure, energy, spectroscopic properties, and reactivity [1–5]. However, on large systems in the biological or materials science fields, such as nucleic acids, proteins, enzymes, or nano-materials, accurate ab initio calculations are usually difficult to compute. It often takes enormous amounts of computer time, memory, and disk space. In order to solve the problem, much work has and is being done on developing new methods that could yield results of ab initio quality at a lower cost. Successful examples include the well-known hybrid quantum mechanics/molecular mechanics (QM/MM) method [6,7], in which the active site is calculated with quantum mechanics and the rest with molecular mechanics. Recently, the QM/MM method has been successfully used in computations of many large systems [8–11].

In addition to the theory or algorithm, the basis set is an important factor relating to computational cost. In general, the more complicated the basis set is, the higher are the computational resources required and the more accurate are the calculations. Ideally, a cost-effective scheme would be developed for selecting basis sets, so that reliable results could be achieved with a reduced use of computational resources. Recently, the principles of choosing such a basis set for ground-state systems have been discussed extensively by the authors [12–18] and Truhlar et al. [19,20]. Yet, the efficiency of the economic basis set for systems in excited states has not been demonstrated.

Excited states of molecules are common to all photo-induced processes. However, there is a general lack of information on the structural nature of molecules in excited states, even for important small molecules such as formic acid (HCOOH) and acetic acid (CH_3COOH). This is because the excited-state properties are hard to obtain using conventional quantum chemistry methods, which mainly deal with systems in ground state, where the atomic geometry is relaxed to its lowest energy configuration and the electrons are usually paired. With the development of biological and materials sciences, the accurate calculation of open systems has become increasingly necessary. However, excited-state calculations are much more difficult. There are several reasons for this difficulty. Firstly, to describe the structure and properties of a system in excited states correctly, two or more states must be considered and the problem of convergence usually arises. A good solution to the convergence problem is to use the

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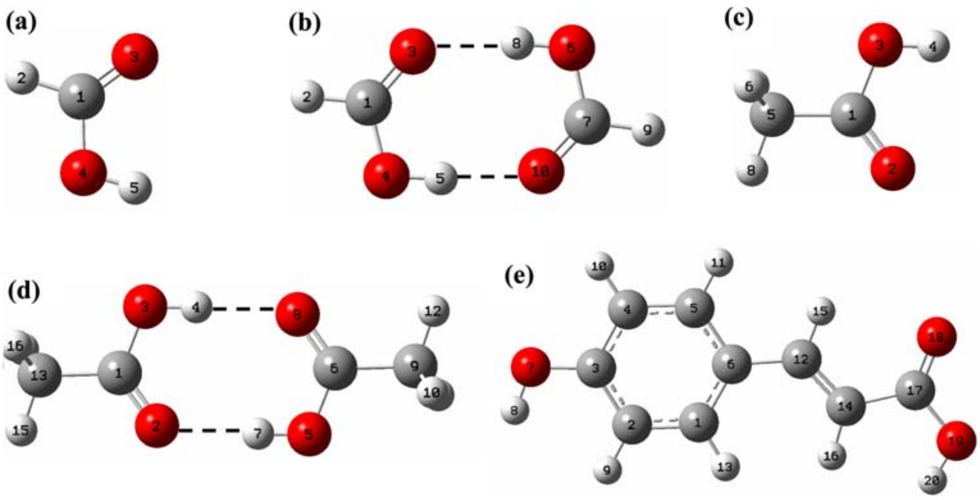

Fig. 1 Structures of molecules investigated in this work. **a** HCOOH, **b** $(HCOOH)_2$, **c** CH_3COOH, **d** $(CH_3COOH)_2$, and **e** *trans-p*-CA

state-averaging method between two or more states [21]. Furthermore, quantitative prediction of the excited-state properties requires calculations that include electron correlation. Unfortunately, both state-average and electron correlation calculations require considerable computational resources. This makes excited-state geometry optimization only possible for very small systems and extensive studies of potential energy surfaces very expensive. Any improvement that can reduce the computational cost thus becomes very desirable.

In this study, ab initio calculations with different basis sets were carried out to investigate the structures and properties of selected molecules in excited states. Emphasis was laid on the comparison of results obtained using an economic basis set and those with standard basis sets. The present work is expected to provide new insights into the basis set selection in computations of large systems in excited states.

2 Basis set selection and computational details

Following the practice of dealing with ground state problems using economic basis sets [12–18], we know that the amount and type of the basis functions are determined according to the real occupation and the behavior of valence electrons in the molecule. In general, the fewer electrons it possesses, the fewer basis functions it may require. Furthermore, if the atom is negatively charged, more basis functions should be used. In contrast, if the atom is positively charged, the use of the basis function could be reduced. The polarization and diffuse functions are correction functions which can describe the deformation and diffusion of the electronic cloud. When atoms form a bond, electron transfer occurs, leading to poor uniformity of the electron cloud and the requirement of the polarization function and/or diffusion functions. When an atom loses an electron, its electron cloud contracts. Such deformation can easily be described without using the polarization function and/or diffusion functions. Therefore, appropriate polarization and diffuse functions should be chosen for the atoms in a molecule, according to the bonding feature there.

In this work, HCOOH,$(HCOOH)_2$,CH_3COOH,$(CH_3COOH)_2$, and *trans-p*-coumaric acid (*trans-p*-CA) were chosen to test the economic basis set. Their structures are shown in Fig. 1. Mulliken charge populations of the above-selected molecules calculated at HF/6-31G* level show that the site of C or H is covered with a positive charge while that of O is covered with a negative charge. According to our previous discussions and experience [12–17], the basis functions used for C and H may be small in size and probably without polarization and diffuse functions, while the basis functions for O should be carefully designed. Consequently, the economic basis set 6-31G$^{\#}$, using 6-31G for C and H, and 6-31G* for O, was designed as an economic basis set for the molecules investigated in this work.

The electronic states considered here are the low-lying electronic states, such as the S_0 and S_1 states for carboxylic acids and the S_0,S_1,T_1,S_2, and T_2 states for *trans-p*-CA. Geometries were obtained by full optimizations using the complete active space self-consistent field (CASSCF) [22] method. The CASSCF wave function has sufficient flexibility to model the large changes in electronic structure that take place during the chemical reactions [23]. Furthermore, the CASSCF method offers an acceptable compromise between accuracy and computational cost.

Selection of the active space is a crucial step in CASSCF calculations because the active space formalism contains a certain amount of ambiguity in terms of which particular electrons and orbitals are chosen for inclusion. In the present work, an active space with 10 electrons in 8 orbitals was employed for calculations of HCOOH, CH_3COOH, and their dimers, referred to as CAS(10, 8) hereafter, which includes

Table 1 Deviations of bond lengths and bond angles from 6-31G* results for selected molecules in S_1 state calculated using various basis sets (where 6-31G$^{\#}$: O: 6-31G*; C, H: 6-31G) in CAS(10,8) calculations

Species	Structural parameters	6-31G*	6-31G	6-31G$^{\#}$	6-31+G*	cc-pVDZ	cc-pVTZ
HCOOH	C1–O3	1.398	0.043	0.012	−0.001	−0.002	−0.005
	C1–O4	1.383	0.029	0.018	0.000	0.000	−0.005
	$\angle$O3C1O4	111.6	1.0	0.6	−0.2	0.0	0.0
	$\angle$C1O4H5	108.8	3.9	−0.7	0.7	−0.6	0.3
$(HCOOH)_2$	C1–O3	1.389	0.034	0.01	−0.003	−0.002	−0.006
	C1–O4	1.340	0.020	0.014	−0.001	−0.001	−0.003
	O3–O6	2.960	−0.055	0.001	0.021	−0.005	0.044
	O4–O10	2.941	−0.063	0.018	0.014	−0.016	0.040
	$\angle$O3C1O4	111.8	0.8	0.6	−0.2	−0.1	0.1
	$\angle$O4H5O10	154.7	−6.3	−0.6	−0.3	1.7	1.0
	$\angle$O3H8O6	165.3	−8.5	1.5	−0.6	0.6	0.6
CH_3COOH	C1–O2	1.380	0.036	0.011	−0.007	−0.001	−0.011
	C1–O3	1.359	0.023	0.014	0.031	−0.001	0.027
	$\angle$O2C1O3	110.8	0.6	0.4	−0.9	−0.1	−0.7
	$\angle$C1O3H4	109.2	4.2	−0.6	−1.4	−0.5	−1.7
$(CH_3COOH)_2$	C1–O2	1.394	0.039	0.010	−0.003	0.000	−0.006
	C6–O8	1.221	0.030	0.009	0.002	0.000	−0.006
	O2–O5	2.962	−0.058	−0.004	0.018	−0.007	0.043
	O3–O8	2.927	−0.057	0.015	0.013	−0.009	0.024
	$\angle$C6O5H7	110.6	5.2	−0.6	0.3	−0.5	0.0
	$\angle$C1O3H4	109.2	4.7	−0.6	0.7	−0.5	0.5
	RMSD	0.000 (0.0)	0.043 (4.7)	0.012 (0.7)	0.013 (0.7)	0.006 (0.7)	0.024 (0.8)

The RMSDs of the bond lengths and angles (in parentheses) are presented as well. Units: length in Å, angle in degree

the C=O π and π^* orbitals, and the non-bonding orbital of oxygen atom in the C=O group. For trans-*p*-CA, the active space contains 12 electrons and 11 orbitals [24], which originate from the five π and five π^* orbitals, and the non-bonding orbital of oxygen atom in the C=O group.

All calculations reported here were carried out using a Gaussian 03 package of programs [25].

3 Results and discussion

3.1 HCOOH, CH_3COOH, and their dimers in the S_1 state

Carboxylic acids are very common and play an important role in many chemical and biological processes. HCOOH and CH_3COOH are the two simplest organic acids and ideal model compounds for spectroscopic and theoretical studies of the carboxylic acids and related organic compounds [26–28]. Furthermore, their cyclic dimers, formed by two intermolecular O–H$\cdots$O=C hydrogen bonds acting as bridges, can undergo double proton transfer and serve as prototypes for DNA base pairs. Numerous experimental [29–39] and theoretical [3,40–42] studies have been devoted to the structures and spectroscopic properties of HCOOH, $(HCOOH)_2$, CH_3COOH, and $(CH_3COOH)_2$.

Table 1 presents the geometric parameters of HCOOH, $(HCOOH)_2$, CH_3COOH, and $(CH_3COOH)_2$ in the S_1 state, along with the labels illustrated in Fig. 1. To make the data easier to read, we also provide the root mean square deviation (RMSD) of the geometries with respect to 6-31G* geometry. According to the deviations of bond lengths and bond angles, the structures described using 6-31G$^{\#}$ are quite similar to those deduced from larger basis sets, such as 6-31G*, 6-31+G*, cc-pVDZ, and cc-pVTZ. The difference in structures between the results with 6-31G* and 6-31G$^{\#}$ is at most 0.018 Å for the distance and 1.5° for the angle. For the structure of HCOOH in the S_1 state, it is well known that ground-state formic acid has a planar structure due to the sp^2 hybridization of the C atom and that the C=O bond length is about 1.2 Å [3]. At CAS(10,8)/6-31G$^{\#}$ level, the C1–O3 bond distance is 1.410 Å in S_1 HCOOH, which is about 0.2 Å longer than that in the ground state. The elongation of the C1–O3 bond exhibits the nature of $n \rightarrow \pi^*$ transition, where the carbonyl group attempts to reduce its π^*-bonding character upon excitation to the S_1 state. In 1974, based on the 2,593 Å band contour analysis [33], the C1–O3 bond length and the

Table 2 Calculated nine lowest frequencies (cm^{-1}) for S_1 state HCOOH, $(HCOOH)_2$, CH_3COOH, and $(CH_3COOH)_2$ at CAS(10,8) level with different basis sets

	HCOOH	$(HCOOH)_2$	CH_3COOH	$(CH_3COOH)_2$
6-31G*	4,070, 3,362, 1,484, 1,319, 1,140, 1,102, 1,002, 459, 387 (0.0)	689, 594, 515, 200, 175, 154, 127, 103, 62 (0.0)	1,282, 1,133, 1,063, 922, 550, 450, 394, 330, 202 (0.0)	398, 206, 142, 132, 119, 110, 86, 60, 40 (0.0)
6-31G	3,979, 3,413, 1,434, 1,290, 1,049, 969, 925, 434, 384 (72.1)	661, 635, 496, 193, 181, 163, 126, 104, 68 (18.3)	1,244, 1,155, 1,049, 889, 532, 441, 393, 335, 184 (21.0)	399, 194, 150, 135, 124, 114, 87, 69, 40 (6.2)
6-31G$^{\#}$	4,046, 3,372, 1,481, 1,307, 1,102, 1,057, 949, 441, 378 (28.9)	668, 580, 502, 199, 173, 153, 125, 102, 59 (9.6)	1,286, 1,152, 1,074, 912, 538, 444, 394, 324, 193 (10.0)	397, 196, 143, 133, 120, 109, 85, 58, 37 (3.6)
6-31+G*	4,065, 3,373, 1,474, 1,308, 1,134, 1,096, 1,002, 463, 387 (7.1)	685, 607, 524, 190, 165, 147, 126, 105, 64 (7.6)	1,255, 1,148, 1,041, 910, 532, 440, 388, 360, 199 (18.1)	399, 208, 135, 124, 115, 109, 81, 61, 38 (4.3)

The RMSDs of the frequencies with respect to 6-31G* results are also presented in parentheses

Table 3 Number of basis functions and CPU time per SCF cycle (second, Intel Pentium 4, 3.0 GHz computer) for S_1 state HCOOH, $(HCOOH)_2$, CH_3COOH and $(CH_3COOH)_2$ at CAS(10,8) level with different basis sets

Species	6-31G*	6-31G	6-31G$^{\#}$	6-31+G*	cc-pVDZ	cc-pVTZ
HCOOH						
No. of basis	49	31	41	61	52	118
CPU time	2.5	2.1	2.4	6.1	2.5	34
$(HCOOH)_2$						
No. of basis	98	62	82	122	104	236
CPU time	11.6	2.4	5.8	32.9	14.3	345.7
CH_3COOH						
No. of basis	68	44	54	84	76	176
CPU time	3.4	2.4	2.5	14.4	5.7	220.4
$(CH_3COOH)_2$						
No. of basis	136	88	108	168	152	352
CPU time	33.9	6.5	15.4	97.6	52.1	1,153.5

O–C–O angle in S_1 HCOOH were derived as 1.407 Å and 114.4°, respectively. At CAS(10,8)/6-31G$^{\#}$ level, our calculated values, 1.410 Å and 112.2°, are in reasonable agreement with the experimental data [33]. However, using the 6-31G basis set produces much poorer results. For instance, the deviations of the angles ∠C1O4H5 in HCOOH, ∠O4H5O10 and ∠O3H8O6 in $(HCOOH)_2$, ∠C1O3H4 in CH_3COOH, and ∠C6O5H7 and ∠C1O3H4 in $(CH_3COOH)_2$, between 6-31G and 6-31G* results, are 3.9°, 6.3°, 8.5°, 4.2°, 5.2°, and 4.7°, respectively. In addition, we can see that the diffuse functions do not play a significant role in predicting the geometrical parameters.

Table 2 lists the calculated nine lowest harmonic frequencies using different basis sets for S_1 state HCOOH, $(HCOOH)_2$, CH_3COOH, and $(CH_3COOH)_2$. The RMSDs of the frequencies with respect to 6-31G* data are also presented for comparison. It is clear that all the vibrational frequencies at CAS(10,8)/6-31G$^{\#}$ level are close to those at CAS(10,8)/6-31+G* and CAS(10,8)/6-31G* levels.

Table 3 lists the number of basis functions and computing time per SCF cycle for S_1 state HCOOH, $(HCOOH)_2$, CH_3COOH, and $(CH_3COOH)_2$ in CASSCF calculations with different basis sets. An Intel Pentium 4, 3.0 GHz computer was used for the calculations. It is clear that the designed economic basis set greatly reduces the number of basis functions and saves much computing time compared with the larger basis set. For example, as far as $(CH_3COOH)_2$ is concerned, the use of the 6-31G$^{\#}$ basis set saved about 20% basis functions and 55% computing time compared with the 6-31G* basis set.

3.2 *Trans*-*p*-CA in low-lying states

As the unique chromophore of photoactive yellow protein (PYP) [43], trans-*p*-CA can absorb a photon and isomerize from the *trans* form to the *cis* form around the C=C bond. An optical signal is converted to mechanical motion on a length scale extending from angstroms to micrometers. Due to its key role in the photo-induced processes of PYP, *trans*-*p*-CA has been widely studied both experimentally [44–46] and theoretically [22,47,48].

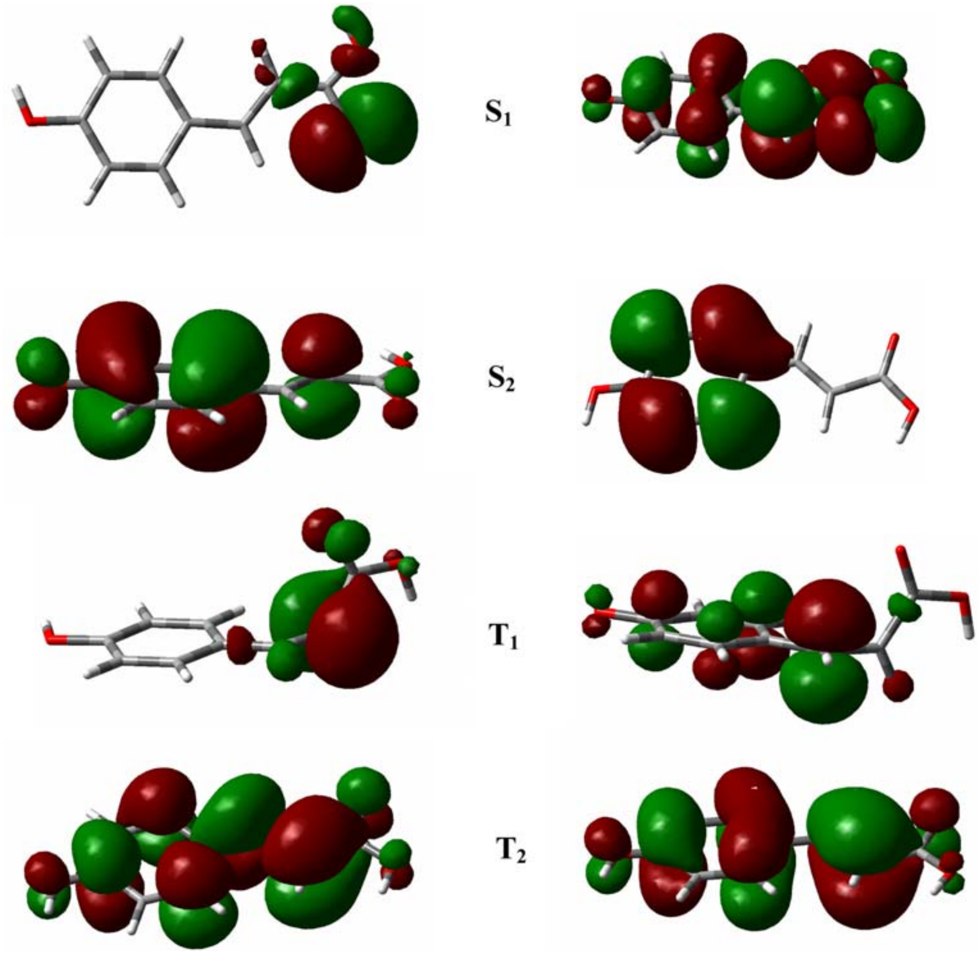

Fig. 2 Singly occupied orbitals of *trans*-*p*-CA in S_1, S_2, T_1 and T_2 states

As mentioned above, the 6-31G$^{\#}$ basis set is economic and reliable in the calculation of geometric parameters and frequencies of HCOOH,$(HCOOH)_2$, CH_3COOH, and $(CH_3COOH)_2$ in the S_1 state. This economic basis set, 6-31G$^{\#}$, has been further used to optimize the structures of *trans*-*p*-CA in low-lying electronic states. The geometric configuration of *trans*-*p*-CA, along with the atom-labeling scheme, is displayed in Fig. 1e. Some selected bond lengths and bond angles, together with the RMSDs with respect to 6-31G* geometry, are listed in Table 4. It can be seen that the difference between the results of the 6-31G* and 6-31G$^{\#}$ basis sets is less than 0.03 Å for the distance and 1.0° for the angle. Natural orbital analysis was carried out on the basis of CAS(12,11)/6-31G$^{\#}$ wave functions. Singly occupied orbitals of *trans*-*p*-CA in the S_1, T_1, S_2, and T_2 states are shown in Fig. 2. The optimized S_1, T_1, S_2, and T_2 states are assigned as $^1n\pi*$, $^3\pi\pi*$, $^1\pi\pi*$, and $^3\pi\pi*$, which is the same as the assignment at CAS(12,11)/6-31G* level in our previous work [24].

Total and relative energies of *trans*-*p*-CA in the S_0, S_1, T_1, S_2, and T_2 states, calculated with different basis sets, are listed in Table 5. Using 6-31G$^{\#}$, the adiabatic excitation energies from ground state to the S_1, T_1, S_2, and T_2 states were predicted to be 103.0, 53.8, 106.4, and 80.6 kcal/mol, respectively. Compared with the corresponding data obtained using the 6-31G* basis set [24], it is clear that the present calculations with the 6-31G$^{\#}$ basis set overestimate the adiabatic excitation energies, especially for the S_1 and T_2 states. Our previous work [15] found that the economic basis set does not guarantee the energy order of silicon oxide clusters, because the silicon atom contains too many electrons compared with oxygen and also the difference in their electronegativities is not significant enough. As far as the excited states are concerned, the electronic excitation could be responsible for the energy deviations shown in the data using different basis sets. Upon absorption of a photon, an electron is excited from the low-energy orbital to the high-energy orbital. The charge is then redistributed throughout the whole molecule and the difference in the electronegativities of C, H, and O becomes less than that in ground state.

Given that the structures predicted by the economic basis set are very similar to those using the 6-31G* basis set,

Table 4 Selected deviations of bond lengths and bond angles for *trans-p*-CA in S_0, S_1, T_1, S_2 and T_2 states calculated using 6-31G$^{\#}$ from the results of 6-31G*

Structural parameters	S_0 6-31G*(6-31G$^{\#}$)	S_1 6-31G*(6-31G$^{\#}$)	T_1 6-31G*(6-31G$^{\#}$)	S_2 6-31G*(6-31G$^{\#}$)	T_2 6-31G*(6-31G$^{\#}$)
C1–C2	1.393 (0.001)	1.392 (0.001)	1.392 (0.003)	1.435 (0.002)	1.383 (0.002)
C2–C3	1.395 (−0.001)	1.395 (−0.019)	1.375 (0.017)	1.418 (0.003)	1.403 (0.002)
C3–C4	1.394 (−0.002)	1.399 (0.004)	1.403 (0.001)	1.415 (0.002)	1.421 (0.000)
C4–C5	1.391 (−0.015)	1.385 (−0.002)	1.379 (−0.014)	1.431 (0.001)	1.368 (0.004)
C5–C6	1.404 (0.002)	1.420 (0.000)	1.422 (0.002)	1.452 (0.002)	1.456 (0.000)
C1–C6	1.403 (−0.002)	1.414 (−0.007)	1.408 (0.006)	1.448 (0.002)	1.453 (0.000)
C6–C12	1.472 (−0.002)	1.433 (0.009)	1.428 (−0.003)	1.423 (0.001)	1.378 (0.004)
C12–C14	1.345 (0.003)	1.433 (−0.008)	1.470 (0.000)	1.370 (0.001)	1.469 (−0.001)
C14–C17	1.487 (−0.006)	1.345 (0.014)	1.468 (−0.005)	1.481 (−0.004)	1.458 (−0.010)
C17–O18	1.193 (0.029)	1.358 (0.007)	1.216 (0.011)	1.194 (0.009)	1.201 (−0.008)
C17–O19	1.343 (0.012)	1.349 (0.010)	1.344 (0.014)	1.344 (0.014)	1.346 (−0.005)
∠C6C12C14	127.6 (−0.1)	126.2 (−0.3)	124.6 (0.2)	127.1 (−0.1)	125.6 (−0.1)
∠C12C14C17	120.6 (0.4)	124.3 (−0.3)	121.9 (0.0)	120.6 (0.2)	120.3 (−0.7)
∠C14C17O18	124.2 (0.1)	123.7 (−0.1)	123.3 (0.2)	124.1 (0.2)	123.3 (0.4)
∠O19C17O18	119.8 (−0.7)	109.0 (−0.5)	119.7 (−0.6)	119.7 (−0.6)	119.4 (0.4)
RMSD	0.011 [0.4]	0.009 [0.3]	0.009 [0.3]	0.005 [0.3]	0.005 [0.5]

The data obtained with 6-31G* are taken from Ref. [24]. The RMSDs of bond lengths and angles (in square brackets) with respect to 6-31G* results are presented as well. Units: length in Å, angle in degree

Table 5 Total energy (hartree) and relative energy (kcal/mol), number of basis functions and CPU time per SCF cycle (min, Intel Pentium 4, 3.0 GHz computer) in CASSCF calculations with different basis sets for *trans-p*-CA in S_0, S_1, T_1, S_2, and T_2 states

	S_0	S_1	T_1	S_2	T_2
6-31G$^{\#}$					
Total energy	−570.03970	−569.87549	−569.95399	−569.87012	−569.91122
Relative energy	0.0	103.0	53.8	106.4	80.6
6-31G* (Ref. [23])					
Total energy	−570.17928	−570.04730	−570.09944	−570.01433	−570.08475
Relative energy	0.0	82.8	50.1	103.5	59.3
6-31G*/6-31G$^{\#}$					
Total energy	−570.17743	−570.04673	−570.09891	−570.01372	−570.08380
Relative energy	0.0	82.0	49.2	102.7	58.7
6-31G*					
No. of basis	196	196	196	196	196
CPU time	4.5	14.7	7.9	7.0	8.4
6-31G$^{\#}$					
No. of basis	139	139	139	139	139
CPU time	3.0	10.4	5.4	5.8	5.4

single-point energy calculations were performed with the 6-31G* basis set, using the optimized structures with the 6-31G$^{\#}$ basis set. Using this method, the adiabatic excitation energies from the ground state to the S_1, T_1, S_2, and T_2 states are very close to those obtained with the 6-31G* basis set, as can clearly be seen in Table 5. The largest deviation in relative energy is less than 1 kcal/mol. Therefore, in order to yield accurate excitation energies, it is necessary to use the single-point energy calculations with higher basis sets on the optimized structures with the economic basis set.

Table 5 also shows the number of basis functions and computing time for each SCF cycle in calculations of *trans-p*-CA with the 6-31G* and 6-31G$^{\#}$ basis sets. It can be seen that, using the 6-31G$^{\#}$ basis set, more than a quarter of the basis functions are decreased and the computing time is reduced by about a third compared with that using the 6-31G* basis set.

4 Conclusions

Our calculations reveal that 6-31G* is such a good basis set that it is hard to improve its performance without significant loss of accuracy. The best that can be done is to selectively remove some polarization functions to obtain modest performance gains. The economic basis set $6\text{-}31G^{\#}$, which applies polarization functions only to O and the 6-31G basis set for C and H, is shown to be advantageous and cost effective for predicting reliable geometric parameters and frequencies for excited-state systems, including HCOOH,$(HCOOH)_2$, CH_3COOH,$(CH_3COOH)_2$, and *trans*-*p*-CA. However, the excitation energies are not accurately reproduced by the economic basis sets. This shortcoming could be overcome by single-point energy calculations using a bigger basis set. This principle for basis set selection can be extended to general ab initio calculations for large systems in excited states.

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