Si_2O_2 molecule: structure of ground state and the excited properties under different external electric fields*

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(Received 2 February 2010; revised manuscript received 3 April 2010)

Geometry and vibrational frequencies of the ground state of Si_2O_2 molecule are studied using density function theory (DFT) at the level of cc-pvtz and 6-311++G**. It is found that the optimizing value by B3lyp/cc-pvtz is closer to the experimental data. The excited properties under different external electric fields are also investigated by the time-dependent-DFT method. Transitions from the ground state of Si_2O_2 molecule to the first singlet state under different external electric fields can take place more easily. The corresponding absorption spectral line is about 360 nm in wavelength and the excitation energy is about 3.4 eV.

Keywords: Si_2O_2 molecule, excited properties, external electric field, time-dependent density function theory

PACC: 3120A, 3620K, 7970, 3150

1. Introduction

Porous silicon and nanoscale silicon particles embeded oxidised silicon are very promising silicon-based luminescence materials and they have been researched extensively.[1,2] Guo *et al.*,[2] have observed luminescence from silicon-based materials at room temperature and the photoluminescence (PL) spectrum peaks are at 360 nm, 430 nm and 835 nm separately. Silicon-based luminescence materials consist of a great number of nanoscal particles, which are surrounded by an oxidised silicon layer.[3] Si_2O_2, as one of the silicon-rich oxidised silicon clusters, must play an important role so it is meaningful to research it at the level of molecule.

The excited states under an external electric field are critical to the study on luminescence and it is also one of the important topics today.[4−6] Anderson and Ogden[7] and Khanna *et al.*[8] have investigated the Si_2O_2 molecule by infrared analysis. Schnockel *et al.*[9] have calculated the Si_2O_2 dissociation, and Pimentel *et al.*[10] have obtained the rate coefficient for the reaction SiO+ Si_2O_2. However, the excited properties under an external electric field are still lacking. In order to research luminescence of Si_2O_2 in theory we calculate the excited properties under an external electric field using Gaussian 03[11] program package with the time-dependent density function theory (TD-DFT) method.

2. Theoretical method

Under an external electric field, the Hamiltonian H is written as follows:[12]

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

where H_0 is the Hamiltonian under no external electric field and $H_{\rm int}$ is the Hamiltonian of molecule system under an external electric field. In the dipole approximation, the expression of the interaction between a molecule system and an external electric field is[13]

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

where μ is the transition electric dipole moment. Using the single-excitation configuration interaction (CIS-DFT)[14,15] method the oscillator strength f is expressed as

$$g_{\rm l} f_{\rm lu} = \frac{8\pi^2 mca_0^2\sigma}{3h} S = 3.03966 \times 10^{-6}\sigma S, \tag{3}$$

*Project supported by the National Natural Science Foundation of China (Grant No. 10774039), the Natural Science Foundation of Henan Province, China (Grant No. 092300410249), the Natural Science Foundation of the Education Bureau of Henan Province, China (Grant No. 2010A140008), and the Foundation for University Young Core Instructors of Henan Province, China (Grant No. 2009GGJS-044).

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and the line strength S is defined as

$$S = |\langle a\Lambda \| er \| a'\Lambda' \rangle|^2 . \quad (4)$$

The oscillator strength $f_{\rm lu}$ also depends on the difference between energy levels ($E_{\rm u}-E_{\rm l}$) and the transition electric dipole momen, and it can be expressed as[16]

$$f_{\rm lu} = \frac{8\pi^2 m}{3h^2e^2} \times (E_{\rm u} - E_{\rm l}) \times |\mu_{\rm lu}|^2 . \quad (5)$$

3. Results and discussion

3.1. Geometry and vibrational frequencies for ground state of Si_2O_2 molecule

Bond length R, bond angle A and vibrational frequency ω are investigated by the B3lyp and B3p86 methods with the cc-pvtz and 6-311++G** basis sets respectively. However, only the values obtained from the B3lyp/cc-pvtz method are closer to the experimental results. The geometry and frequency calculations are listed in Table 1 and the optimised structure is of symmetry D_{2h} as shown in Fig. 1.

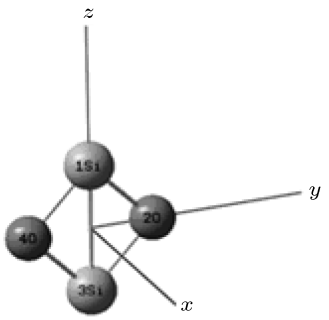


Fig. 1. Optimized structure of the Si_2O_2 molecule by B3lyp method with cc-pvtz basis set.

Table 1. Values of bond length R/nm, angle A/(°), and vibrational frequencies ω/cm^{-1} for the Si_2O_2 molecule, with the ground state being $^1A_{\rm g}$, and the molecule structure being of symmetry D_{2h}.

method	R/Si–O	A/O–Si–O	$\omega_1(B_{3u})$	$\omega_2(B_{3g})$	$\omega_3(A_{\rm g})$	$\omega_4(B_{2u})$	$\omega_5(B_{1u})$	$\omega_6(A_{\rm g})$
B3lyp								
6/311++G**	0.1717	86.3	203.7	513.6	535.3	739.6	788.6	826.9
cc-pvtz	0.1707	87.2	225.1	545.4	549.9	763.9	805.9	840.7
B3p86								
6/311++G**	0.1710	86.7	195.8	532.4	537.6	756.7	801.4	838.4
cc-pvtz	0.1701	87.5	219.5	551.3	562.9	778.7	817.0	850.5
experiment	0.171[a]	87[a]	252[a]			765.5[a]	804.4[a]	
						766.3[b]	804.7[b]	

[a] Anderson and Ogden;[7] [b] Khanna *et al.*[8]

According to Table 1, bond length R vibrational frequencies ω_4 and ω_5 are obtained by the B3lyp/cc-pvtz method to be 0.1707 nm, 763.9 cm^{-1} and 805.9 cm^{-1} respectively. They are even more accurate than the values given in Ref. [10]. A comparison between the results obtained from the B3lyp/cc-pvtz method and the experimental data[7,8] shows that the B3lyp method with cc-pvtz basis set is more suited to optimizing the ground state of Si_2O_2 molecule.

3.2. Excited properties of Si_2O_2 molecule under no external electric field

Using the structural parameters obtained above, we can obtain the excited state parameters such as excitation wave length λ, oscillator strength f and transition electric dipole moment μ of Si_2O_2 molecule.

Table 2. Values of excitation wave length λ/nm, oscillator strength f, and transition electric dipole moment μ for the transition from ground state to excited states of Si_2O_2 molecule.

	excited state					
	1	2	3	4	5	6
state	$^3B_{3u}$	$^3B_{2g}$	$^1B_{3u}$	$^3B_{3g}$	$^1B_{2g}$	$^3B_{2g}$
E/eV	2.1456	2.9289	3.4464	4.2781	4.3470	4.7431
λ/nm	577.86	423.31	359.75	289.81	285.22	261.40
f	0.0000	0.0000	0.0550	0.0000	0.0000	0.0000
μ	0.0000	0.0000	0.8072	0.0000	0.0000	0.0000

All calculations are carried out by the TD-DFT method using Gaussian03 program package. The results are shown in Table 2, and the transition process does not change the symmetry of Si_2O_2 molecule. The symmetry is still D_{2h}.

For the triplet states the transitions are forbidden as they are inconsistent with the dipole transition selection rule $\Delta S = 0$. Oscillator strength f represents the electric dipole transition probabilities, so if f equals zero then the transition is forbidden. The results show that only the transition from the ground state to the third excited state is allowed. The oscillator strength f is 0.0550 and the transition electric dipole moment μ equals 0.8072. Correspondingly, the wave length of the absorption spectrum is 359.75 nm. The PL peaks may be different with the changing of Si atom number in silicon oxidation materials. Zheng *et al.*[17] have observed luminescence from silicon-based SiO_2 film and the wave length ranges from 330 nm to 388 nm. Our result is just in the range.

3.3. Excited properties of Si_2O_2 molecule under different external electric fields

Transitions from the ground state to excited states of molecules can take place under an external electric field. The excited states can return to the ground state or the second-level excited states, accompanied with irradiating luminescence theoretically. Therefore, here we study the excited states of Si_2O_2 molecule under different external electric fields. The values of external electric field F equal 0.001, 0.002, 0.003, 0.004, 0.005, 0.006 a.u and the direction is kept along the x-axis (Fig. 1). All calculations are carried out with the TD-DFT method on the basis of structural optimization under an external electric field as mentioned above. Here we investigate the values of excitation wavelength λ, oscillator strength f of the first six excited states and the results are listed in Table 3. The values of excitation energy E under different external electric fields are shown as Fig. 2. The values of transition electric dipolemoment μ for the third and the fifth excited states are not zero, but for the others they are all equal to zero. The results are described as in Fig. 3.

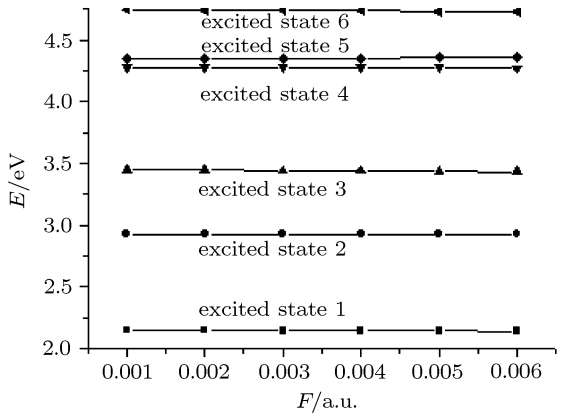


Fig. 2. Excitation energies of Si_2O_2 molecule under external electric fields.

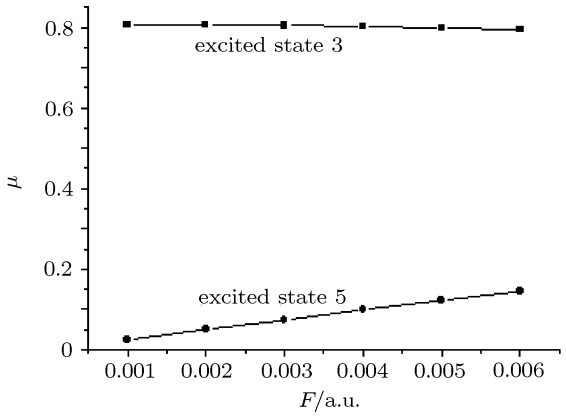


Fig. 3. Transition electric dipolemoments of Si_2O_2 molecule under external electric fields.

According to Table 3, excitation energy E, excitation wave length λ, oscillator strength f and transition electric dipole moment μ under an external electric field are all close to the ones under no external electric field. For the fifth excited state, here, it is different from the one under no external electric field. Neither the oscillator strength f nor the transition electric dipole moment μ is zero.

The results show that the transitions from ground state to the triplet states are forbidden because they are inconsistent with the dipole transition selection rule $\Delta S = 0$. The transitions from ground state to the singlet states are allowed as they satisfy the dipole transition selection rule $\Delta S = 0$ and neither the oscillator strength f nor the transition electric dipole moment μ equals zero.

Table 3. Values of excitation wave length λ/nm and oscillator strength f for transition from ground to excited states of Si_2O_2 molecule under external electric fields.

		excited states					
F/a.u.		1	2	3	4	5	6
	state	$^3A''$	$^3A''$	$^1A''$	$^3A'$	$^1A''$	$^3A''$
0.001	λ/nm	577.85	423.26	359.79	289.83	285.16	261.41
	f	0.0000	0.0000	0.0550	0.0000	0.0001	0.0000
0.002	λ/nm	577.91	423.26	359.93	289.86	285.11	261.50
	f	0.0000	0.0000	0.0548	0.0000	0.0003	0.0000
0.003	λ/nm	578.02	423.26	360.15	289.91	285.03	261.66
	f	0.0000	0.0000	0.0546	0.0000	0.0006	0.0000
0.004	λ/nm	578.18	423.27	360.48	289.99	284.91	261.87
	f	0.0000	0.0000	0.0542	0.0000	0.0010	0.0000
0.005	λ/nm	578.37	423.27	360.89	290.08	284.76	262.14
	f	0.0000	0.0000	0.0538	0.0000	0.0016	0.0000
0.006	λ/nm	578.62	423.28	361.39	290.19	284.58	262.47
	f	0.0000	0.0000	0.0533	0.0000	0.0023	0.0000

Note: Under different external electric fields, the electronic states of each excited state are the same, so they are listed in the first line only.

Under an external electric field the symmetry D_{2h} turns into symmetry C_s. The occupied orbitals from eighteenth to twenty-second are a'', a', a'', a' and a' separately and the occupied orbitals from twenty-third to twenty-sixth are a'', a'', a' and a' separately. For the third excited state, the main electron transition orbit is from $22a'$ to $23a''$. For the fifth excited state, the main electron transition orbit is from $22a'$ to $24a''$. For the symmetry C_s, $A' \times A'' = A''$ belongs to Z symmetry and the contribution comes from Z direction.

For the third excited state, the oscillator strength f and the transition electric dipolemoment μ all become diminishing with the increase of external electric field. However, for the fifth excited state, the oscillator strength f and the transition electric dipolemoment μ all become increasing with the increase of external electric field. Oscillator strength f represents the electric dipole transition probability. By comparison with the two, we can know it is easier to transit from the ground state to the third excited state.

The excitation energy for the fifth excited state increases with the increase of external electric field but the others are quite the contrary. However, the changes are all smooth. This indicates that the increase of external electric field is in favour of electronic excitation overall.

The absorption band of Si_2O_2molecule concentrates in ultraviolet region. For the third excited state, the absorption wave length λ increases from 359.79 nm to 361.39 nm with the increase of external electric field. On the contrary, for the fifth excited state, the absorption wave length λ decreases from 285.16 nm to 284.58 nm.

Theoretically, the high energy level excited states could return to the ground state or the second-level excited states, accompanied with irradiating lminescence. Therefore, Si_2O_2 molecule in the excited state can emit UV-ray whose wavelength is about 360 nm. Liao *et al.*[18] and Song and Bao[19] have observed the visible light emission spectrum. Guo *et al.*[2] also have observed luminescence irradiated from silicon-based materials and the PL spectra peaks are at 360 nm, 430 nm and 835 nm separately. Our result is just in good agreement with the experimental datum, 360 nm.

4. Conclusions

A comparison between the results obtained from the B3lyp method with experimental data shows that the B3lyp method with the cc-pvtz basis set gives the best consistency for the geometry optimization and vibrational frequency calculation of Si_2O_2 molecule.

The transitions from ground state to the third singlet state are allowed both under no external electric field and under external electric field, but for the fifth singlet state the transition is allowed only under external electric field.

Excitation energy E, oscillator strength f, and transition electric dipole moment μ change with the

increase of external electric field. This indicates that the excited properties are correlated with the external electric field strongly.

According to the excitation wave length λ, Si_2O_2 molecule has two main absorption bands. One ranges from 359.79 nm to 361.39 nm and the other from 284.58 nm to 285.16 nm in the ultraviolet region. Theoretically, the excited states of Si_2O_2 molecule could return to the ground state, accompanied with UV-ray emitting, and the wave length is 360 nm mainly.

The oxidation degree of silicon can affect the PL spectral line intensity. Our results are in good agreement with the experimental datum 360 nm, so the material may be comprised of Si_2O_2 cluster element partly. The properties of materials are determined mainly by the properties of molecules, so, it is necessary to research the properties of molecules. This can also be considered as a new way to analyse the luminescence of silicon-based materials at the level of molecule.

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