Si_3O cluster: excited properties under external electric field and oxygen-deficient defect models*

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This paper investigates the excited states of Si_3O molecule by using the single-excitation configuration interaction and density functional theory. It finds that the visible light absorption spectrum of Si_3O molecule comprises the yellow and the purple light without external electric field, however all the visible light is included except the green light under the action of external electric field. Oxygen-deficient defects, which also can be found in Si_3O molecule, have been used to explain the luminescence from silicon-based materials but the microstructures of the materials are still uncertain. Our results accord with the experimental values perfectly, this fact suggests that the structure of Si_3O molecule is expected to be one of the main basic structures of the materials, so the oxygen-deficient defect structural model for Si_3O molecule also has been provided to research the structures of materials.

Keywords: Si_3O molecule, excited state, luminescence, oxygen-deficient defects

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1. Introduction

Luminescence from silicon-based materials can take place under the action of external electric field or light field, visible luminescence especially the blue light is crucial to silicon-based semiconductor devices. Photoluminescence (PL) from silicon-rich SiO_2 materials has been studied extensively[1−5] but the reason is still a subject of controversy. At present the oxygen-deficient defects[1,6,7] model is one of the main theories.[8−10] Song and Bao[1] has observed strong PL from silicon-ion-implanted thermal SiO_2 film and the PL spectrum consists of four bands centred at about 470-, 550-, 630- and 730 nm. The oxygen-deficient defects are used to explain the PL by Song *et al.*, however, the microstructure of silicon-based materials is still uncertain. It is known that the properties of materials account for the properties of the molecules. Furthermore, as the implantation of silicon, there must be silicon-rich silicon oxide in the materials.[11] So, it is necessary to study on them at the level of molecules.

Si_3O molecule is one of the important silicon-rich silicon oxides. Wang *et al.*[12−14] have studied its ground state and obtained the ionization potential and electron affinity values from both theory and experiment but the excited state properties are still lacking. It is well known that the excited properties under external electric field are crucial to the study on PL and they have been studied theoretically and experimentally,[15−17] therefore, in this paper the excited properties of Si_3O molecule are investigated. All the calculations are executed by using Gaussian03 program package[18] with single-excitation configuration interaction (SCI)-density function theory (DFT) method whose results are more approximate to the experimental results than the ones by TD-DFT, so here we use the former. Song and Bao[1] considered that PL accounts for oxygen-deficient defects which also exist in Si_3O molecule. According to our results, we also provide a structural model for Si_3O molecule with oxygen-deficient defects to study the materials.

2. Theoretical method

The Hamiltonian of the radiation process is described by[15]

$$\boldsymbol{H} = \boldsymbol{H}_0 + \boldsymbol{H}_{\rm int}, \tag{1}$$

where $\boldsymbol{H}_0$ is the complete molecular Hamiltonian and $\boldsymbol{H}_{\rm int}$ is the interaction Hamiltonian between radiation

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and matter. In the case of dipole approximation, the expression of $\boldsymbol{H}_{\rm int}$ is[19]

$$\boldsymbol{H}_{\rm int} = -\boldsymbol{\mu} \cdot \boldsymbol{F}, \tag{2}$$

where $\boldsymbol{\mu}$ is the transition electric dipole moment. According to the SCI-DFT[20] method the oscillator strength f can be expressed as

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

The oscillator strength $f_{\rm lu}$ also depends on the excitation energy $E_{\rm lu}$ and the transition electric dipole moment, so the following expression can be obtained[21]

$$f_{\rm lu} = \frac{8\pi^2 m}{3h^2 e^2} \times (E_{\rm u} - E_{\rm l}) \times |\mu_{\rm lu}|^2. \tag{4}$$

3. Results and discussion

3.1. Ground state structure and excited properties without external electric field

In the present work, we investigate the ground state of Si_3O molecule whose state is $^1A_1$ with the symmetry C_{2v} using DFT (B3P86) method with 6-311++G** basis set. The optimised geometry parameters are listed in Table 1 and the optimised structure is shown in Fig. 1.

Table 1. Optimised bond length d/nm and angles $\angle$/(°) for the ground state of Si_3O molecule.

methods	d /Si_1–Si_2	d/ Si_1–O_3	d /Si_1–Si_4	$\angle Si_1$–Si_2–Si_4	$\angle Si_1$–O_3–Si_4
MP2[12]	0.230	0.175	—	—	—
MP2[13]	0.227	0.173	0.229	60.5	82.9
B3P86	0.229	0.172	0.229	60.0	83.7

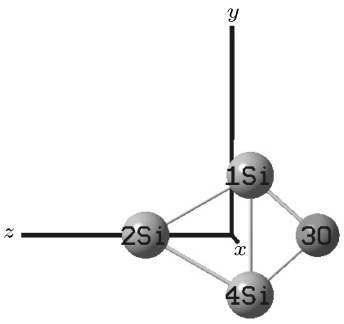


Fig. 1. Optimised structure of the Si_3O molecule.

Boldyrev *et al.*[13] have got the optimised structure of Si_3O molecule from theory at first, then Wang *et al.*[12] also studied the molecule from both theory and experiment and the results are more precise in comparison with the experimental data. Our result d (Si_1–Si_2) is approximate to Ref. [12], the bond d (Si_1–Si_4) and angle ($\angle Si_1$–Si_2–Si_4) are approximate to Ref. [13].

According to the optimised results above, the excited properties without external electric field also have been investigated by using SCI-B3P86 method. As the Si_3O molecule has a singlet ground state, so here we calculate the transitions from the ground state to the first six singlet states. The excited energy $E_{\rm lu}$, excitation wavelength λ, oscillator strength f and transition electric dipole moment μ are listed in Table 2.

Table 2. Excited energy $E_{\rm lu}$, excitation wave length λ/nm, oscillator strength f, and transition electric dipole moment μ of Si_3O molecule.

	excited states					
	1	2	3	4	5	6
state	$^1A_2$	$^1B_2$	$^1B_2$	$^1A_2$	$^1B_1$	$^1A_1$
$E_{\rm lu}$/eV	1.2650	2.1772	2.7923	2.9997	4.1390	4.1508
λ/nm	980.11	569.46	444.02	413.32	299.55	298.70
f	0.0000	0.0009	0.0250	0.0000	0.0034	0.0517
μ	0.0000	0.1280	0.6040	0.0000	0.1844	0.7128

According to the dipole transition selection rule $\Delta S = 0$, we can know that the transitions from ground state to the second, the third, the fifth and the sixth excited states can take place. The excited energy is in the range of 2.1–4.2 eV which is approximate to the absorption spectrum 1.0–3.0 eV obtained in Ref. [22]. Correspondingly, the absorption spectrum consists of three bands which centred at the yellow light, purple light and ultraviolet light regions. Zheng *et al.*[23] also have observed PL 330–600 nm and they considered that the peak about 440 nm derived from the oxygen-deficient defects. From the results, theoretically we consider that the excited states of Si_3O molecule can get back to the ground state with 444.02 nm light-emitting and this just agrees with the experimental data 440 nm.

3.2. Excited properties of Si_3O molecule under different external electric field

Under external electric field, the structural parameters of molecules may change, the molecules can take on new excited properties. In this case, the excited states of Si_3O molecule are investigated on the basis of structural optimisation above. The external electric field F equals to 0.003, 0.006, 0.009, 0.012, 0.015, 0.018 a.u separately and the directions are along x-axis (Fig. 1). All the calculations are carried out by using the SCI-B3P86 method with 6-31++G** basis set. The excitation wave length λ/nm and oscillator strength f are listed in Table 3. The excited energy $E_{\rm lu}$ is shown as Fig. 2 and the transition electric dipole moment μ is shown as Fig. 3.

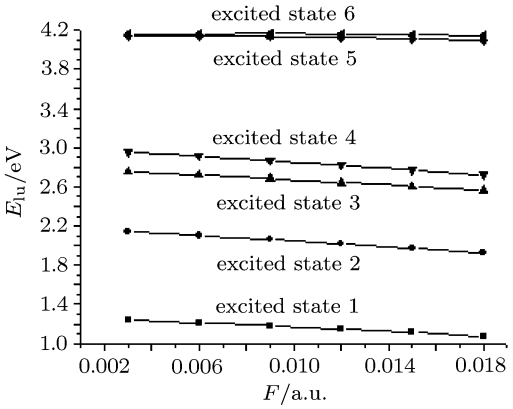


Fig. 2. The excited energy $E_{\rm lu}$ of Si_3O molecule under external electric field.

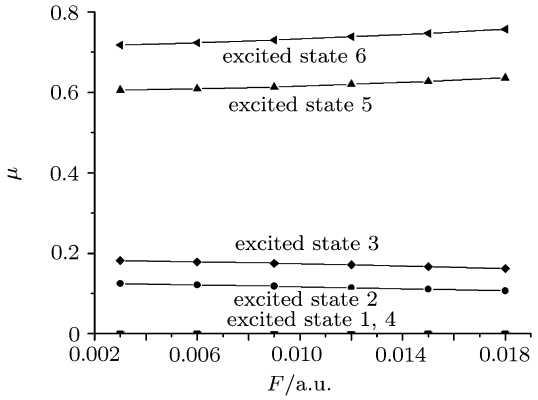


Fig. 3. Transition electric dipole moment μ of Si_3O molecule under external electric field.

Table 3. Excitation wave length λ/nm and oscillator strength f of Si_3O molecule under external electric field.

		excited states					
F/a.u.		1	2	3	4	5	6
	state	$^1A_2$	$^1B_2$	$^1B_2$	$^1A_2$	$^1B_1$	$^1A_1$
0.003	λ/nm	999.16	579.06	449.61	419.22	299.44	298.11
	f	0.0000	0.0008	0.0248	0.0000	0.0034	0.0525
0.006	λ/nm	1021.77	589.83	455.66	425.62	299.57	297.77
	f	0.0000	0.0008	0.0247	0.0000	0.0032	0.0534
0.009	λ/nm	1046.74	601.44	461.95	432.35	299.86	297.55
	f	0.0000	0.0007	0.0247	0.0000	0.0031	0.0544
0.012	λ/nm	1078.79	614.43	468.89	439.41	300.74	298.02
	f	0.0000	0.0006	0.0249	0.0000	0.0030	0.0556
0.015	λ/nm	1113.64	628.48	476.17	446.95	301.69	298.49
	f	0.0000	0.0006	0.0251	0.0000	0.0028	0.0568
0.018	λ/nm	1155.23	644.26	484.19	455.15	302.95	299.26
	f	0.0000	0.0005	0.0254	0.0000	0.0026	0.0582

Notes: Under different external electric field, the electronic states of every excited state are the same, so they are just listed in the first row.

Under external electric field, the states of Si_3O molecule are the same as the ones without external field but the properties make a difference. Transitions from the ground state to the first and the fourth excited states are still forbidden because the oscillator strength f and the electric dipole moment μ all equal zero.

The electric dipole moment μ and the excited energy $E_{\rm lu}$ of the second and the third excited states are both monotonously weakened along with the increase of external electric field. The electric dipole moment μ of the fifth and the sixth excited states increase with the increase of external electric field. The excited state energy $E_{\rm lu}$ of the fifth excited also increases but the sixth increases at first and then decreases with the increase of external electric field.

According to Eq. (4), the oscillator strength f changes complexly because it is affected by the excited energy $E_{\rm l} - E_{\rm u}$ and the square value of the electric dipole moment μ. As shown in Table 3, the oscillator strength f of the third excited state decrease at first and then increases. The second and the fifth decreases but the sixth monotonously increases with the increase of external electric field. As the oscillator strength f shows the electron transition probability from lower state to upper state, the transitions from the ground state to the sixth and the third excited states are more likely to happen.

From the results, the main absorption bands concentrate in ultraviolet region and blue light region, the corresponding wavelengths are 297.55–299.26 nm and 449.61–484.19 nm respectively. The absorption spectra also consist of yellow light and orange light whose wave lengths are 579.06–644.26 nm. According to equation $h\nu = E_{\rm u} - E_{\rm l}$, transitions between upper state and lower state can take place along with light-absorbing or light-emitting. Certainly, the excited states of Si_3O molecule could return to the ground state or the second-level excited states with luminescence theoretically. This is in agreement with the experimental PL value 470-, 550- and 630 nm obtained in Ref. [1] exactly.

3.3. Oxygen-deficient defects model for Si_3O molecule

In order to reveal the microstructure evolution which may be responsible for the observed PL property, the photoelectron spectroscopy experiments have been performed, and the electron paramagnetic resonance and x-ray photo electronic spectra also have been measured.[1,12] The concept of oxygen-deficient defects also has been introduced to explain luminescence and other phenomenon extensively.[1,2,23–25] Two structural models have been proposed for the PL bands, oxygen vacancy and twofold coordinated silicon, which are commonly denoted as $\equiv \mathrm{Si} - \mathrm{Si} \equiv$ and $\mathrm{O} - \ddot{\mathrm{S}}\mathrm{i} - \mathrm{O}$ respectively,[26] furthermore, the structural model $\cdot\mathrm{Si} \equiv \mathrm{Si}_3$ also have been referred in Ref. [1].

Under external electric field, part of the Si–O bands are destroyed and the new structural models of oxygen deficient defects (Si–Si bond) form when the silicon ions are implanted into bulk SiO_2, such as Si_3O molecule which is shown in Fig. 4. Wang *et al.* have studied the models for oxidation of silicon surfaces and defect sites in bulk oxide materials, the oxygen deficient defect structural model of the two-coordinated Si [Si(II)] also has been shown.[12] We think the oxygen-deficient defect structural model of Si_3O molecule can be described as $\mathrm{O} - \dot{\mathrm{S}}\mathrm{i} = \mathrm{Si}$ which is based on the model $\cdot\mathrm{Si} \equiv \mathrm{Si}_3$, however, there is a little difference between the two. It also can be considered as two-coordinated model with –Si–O–Si– which also has been mentioned by Song *et al.* On this basis, we intend to show a compendious description of the microstructures. Some bands in this model constitute the Si_3O molecule structure and the others can be used to make up Si–Si or Si–O bands, every silicon atom forms four bridges with oxygen atoms or silicon atoms planform or tridimensional which are actually the component parts of the microstructures of the materials.

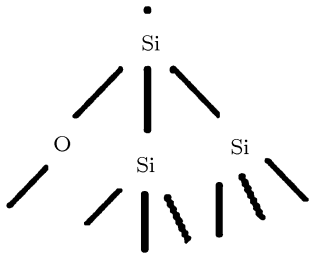


Fig. 4. Simple structural model of Si_3O molecule for oxygen deficient defects.

4. Conclusion

In conclusion we have presented a theoretical study of Si_3O molecule, the geometry of the ground state and excited properties under external electric field have been studied. In theory the Si_3O molecule can absorb yellow and purple visible light when there is no field. However, under the action of external electric field, the absorption spectrum consists of all the

visible light except the green. Our calculation results agree with the experimental values mentioned above perfectly, based on this fact, the structural models of Si_3O molecule also have been described. The presented evidence suggests that Si_3O molecule is expected to be one of the main basic structures of the materials which also show that the oxygen-deficient defects (Si–Si band) are expected to be one of the reasons of the luminescence from silicon-based materials.

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