Study of the excitation properties of the Si_3O_2 cluster under an external electric field*

Yao Dong-Yong(姚东永)[a)b)], Xu Guo-Liang(徐国亮)[a)], Liu Xue-Feng(刘雪峰)[a)†]
Zhang Xian-Zhou(张现周)[a)], and Liu Yu-Fang(刘玉芳)[a)]

[a)] *College of Physics & Information Engineering, Henan Normal University, Xinxiang* 453007, *China*
[b)] *Pingdingshan Education Institute, Pingdingshan* 467000, *China*

(Received 12 March 2011; revised manuscript received 12 April 2011)

The structure of the Si_3O_x ($x = 2, 3$) cluster is investigated; we find that the geometry of Si_3O_2 is similar to that of Si_3O_3 except for the oxygen-deficient defect structure (Si–Si band) which exists only in the Si_3O_2 cluster. It is known that oxygen-deficient defects are used to explain visible luminescence (especially blue, purple and ultraviolet light) from silicon-based materials, which are directly bound up with the excited states of the molecules. Therefore the excitation properties of the two clusters are also studied. Our results show that the absorption spectrum of Si_3O_2 is concentrated in the visible light region. In contrast, the absorption spectrum of Si_3O_3 is mainly located in the ultraviolet light region. The calculations are perfectly consistent with experimental data and also support the theory of oxygen-deficient defects.

Keywords: Si_3O_2 and Si_3O_3 molecules, excited state, oxygen-deficient defect, single-excitation configurations with density functional theory

PACS: 31.15.–p, 31.15.ag **DOI:** 10.1088/1674-1056/20/10/103101

1. Introduction

It is well known that bulk silicon and silicon dioxide cannot emit visible luminescence but the photoluminescence (PL) spectrum from silicon-ion-implanted thermal SiO_2 film can be clearly observed.[1−6] At present the reason for the PL remains a controversial subject. Quantum confinement theory,[7,8] luminescence centre theory,[9] and oxygen-deficient defect theory[2,10] have been proposed to explain this phenomenon. Qin[11] considered that the PL arose as a result of differences in experimental conditions. However, oxidized silicon clusters play an important role in silicon-based materials. As one of the silicon-rich oxidized silicon molecules, Si_3O_2 may aid theoretical research.

Wang *et al.*[12] have researched its ground state and obtained the ionization potential (IP) and electron affinity (EA) values from both theory and experiment but the excited state properties are still lacking. It is known that the excitation properties under an external electric field are crucial to the study on PL,[13,14] so the properties of the Si_3O_2 molecule are studied in this paper. The geometry of Si_3O_2 is similar to that of Si_3O_3 except for the oxygen-deficient defect structure (Si–Si band) which exists only in the Si_3O_2 cluster. However, their excited states under an external electric field are obviously different. We investigate the properties of the Si_3O_3 molecule[15] and find that its absorption spectrum is mainly located in the ultraviolet region. In order to probe the effect of the oxygen-deficient defect, the properties of the Si_3O_2 molecule are also studied. All the calculations are carried out using the Gaussian 03 program package.[16]

2. Theoretical method

The Hamiltonian of the radiation process is described by[17]

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

where H_0 is the complete molecular Hamiltonian and $H_{\rm int}$ is the interaction between radiation and matter. In the dipole approximation, the expression of $H_{\rm int}$

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

†Corresponding author. E-mail: lxfeng23@sohu.com

© 2011 Chinese Physical Society and IOP Publishing Ltd

is[18]

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

where μ is the transition electric dipole moment. According to the CIS-DFT[19] 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 $f_{\rm lu}$ depends on the excitation energy $E_{\rm u} - E_{\rm l}$ and the transition electric dipole moment $\mu_{\rm lu}$, so the following expression can be obtained:[20]

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

3. Results and discussion

3.1. Ground state structure of the Si_3O_2 molecule and excitation properties under no external electric field

Wang *et al.*[12] have researched the IP and EA values of the Si_3O_3 and Si_3O_2 molecules using an approach that combines both experiment and theory. Anderson and Ogden,[21] and Khanna *et al.*[22] have investigated the Si_3O_3 molecule using infrared analysis. However, experimental structure data on the Si_3O_2 molecule are still lacking. In order to investigate the properties of Si_3O_2 molecule, we first perform an optimization using the B3P86 method with the cc-pvtz basis set. The optimized structures of Si_3O_2 and Si_3O_3 molecules are given in Fig. 1 and Fig. 2 respectively. The optimized bond lengths and angles of the two molecules are listed in Table 1.

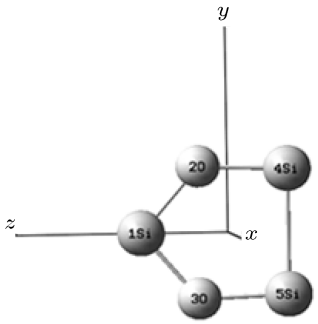


Fig. 1. Optimized structure of the Si_3O_2 molecule.

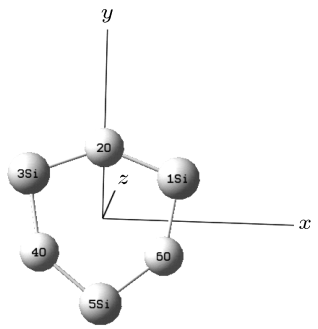


Fig. 2. Optimized structure of the Si_3O_3 molecule.

Table 1. Optimized bond lengths (d/nm) and angles ($\angle$/(°)) for the ground states of the Si_3O_2 and Si_3O_3 molecules.

Molecule	Method	d/Si_1–O_2	d/Si_4–O_2	$\angle Si_1$–O_2–Si_4	$\angle O_2$–Si_1–O_3
Si_3O_2	MP2[21]	0.167	0.167	–	–
	B3P86	0.168	0.168	130.0	99.7
Si_3O_3	expt.[22]	0.17	0.17	140	100
	MP2[21]	0.169	0.169	–	–

The results show that the structure of Si_3O_2 is similar to that of Si_3O_3. The Si–O bond lengths of both molecules are about 0.17 nm and the O–Si–O angles are about 100°. All the bands are Si–O bands in the Si_3O_3 molecule but there is an Si–Si band apart from the Si–O band in the Si_3O_2 molecule. As is well known, the absorption spectrum of the SiO molecule is located in the ultraviolet region and our results show that the spectrum of the Si_3O_3 molecule, about 303.46 nm,[15] exists in the ultraviolet region in the absence of an external electric field.

On the basis of the above optimized results, the excited properties under no action of an external electric field are investigated using the CIS-B3P86 method. The first to the sixth excited states are calculated and parameters such as the excitation wavelength λ, oscillator strength f, and transition electric dipole moment μ are listed in Table 2.

The results in Table 2 suggest that transitions from the ground state to the second and the sixth excited state are forbidden but others are allowed, governed by the dipole transition selection rule $\Delta S =$

0. The oscillator strength f and transition electric dipole moment μ represent the electric dipole transition probabilities. The larger the oscillator strength and transition electric dipole moment, the more the transition probability is possible. According to Table 2, the transition from the ground state to the fourth excited state can take place more easily than others. Correspondingly, the wavelength of the absorption spectrum is 453.89 nm. There are another three absorption spectra and they are at 400.18, 570.21, 473.67 nm. Our calculation accords with the observation of Zheng *et al.*,[23] and the PL spectrum is in the range 330 nm–600 nm.

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

Excited states	1	2	3	4	5	6
State	B_2	A_2	B_1	A_1	A_1	A_2
E/eV	2.1744	2.2900	2.6175	2.7316	3.0982	3.1053
λ/nm	570.21	541.42	473.67	453.89	400.18	399.27
f	0.0042	0.0000	0.0003	0.0214	0.0152	0.0000
μ	0.2794	0.0000	0.0714	0.5653	0.4468	0.0000

3.2. Excitation properties of the Si_3O_2 molecule under different external electric fields

The excitation properties of the molecules can be affected by external fields. In order to investigate the difference in excitation properties between the two molecules, which may be a result of the oxygen-deficient defect (Si–Si band), the excitation properties of the Si_3O_2 molecule under an external electric field are also studied. The values of external electric field F are 0.003, 0.006, 0.009, 0.012, 0.015, 0.018 a.u. and the direction is along the x axis (Fig. 1). All the calculations are performed using the CIS-B3P86 method with the cc-pvtz basis set. Table 3 shows the values of excitation wavelength λ/nm and oscillator strength f under an external field. Figure 3 indicates the excitation energy $E_{\rm lu}$ and the transition electric dipole moment μ is shown in Fig. 4.

Table 3. Values of excitation wavelength λ/nm and oscillator strength f of the Si_3O_2 molecule under an external electric field.

		Excited states					
F/a.u.		1	2	3	4	5	6
0.003	State	A′	A″	A″	A′	A″	A″
	λ/nm	569.85	541.34	472.76	462.82	399.55	396.21
	f	0.0042	0.0000	0.0002	0.0239	0.0000	0.0032
0.006	State	A′	A″	A′	A″	A″	A″
	λ/nm	569.36	541.12	472.17	471.84	400.41	399.64
	f	0.0043	0.0000	0.0262	0.0002	0.0029	0.0000
0.009	State	A′	A″	A″	A′	A″	A″
	λ/nm	563.59	537.00	470.79	460.47	404.14	397.90
	f	0.0027	0.0000	0.0003	0.0257	0.0000	0.0028
0.012	State	A′	A″	A′	A″	A″	A″
	λ/nm	568.92	541.32	493.28	473.88	408.04	399.60
	f	0.0046	0.0000	0.0296	0.0001	0.0025	0.0000
0.015	λ/nm	569.14	541.78	505.32	476.93	410.86	399.18
	f	0.0049	0.0000	0.0312	0.0000	0.0024	0.0000
0.018	λ/nm	569.59	542.43	518.30	481.41	412.72	398.46
	f	0.0053	0.0000	0.0328	0.0000	0.0022	0.0000

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

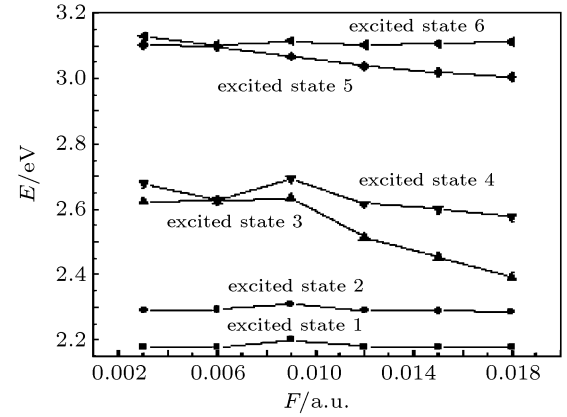


Fig. 3. Excitation energy $E_{\rm lu}$ of the Si_3O_2 molecule under an external electric field.

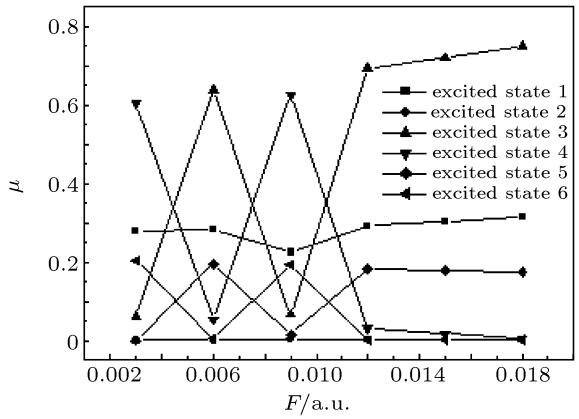


Fig. 4. Transition electric dipole moment μ of the Si_3O_2 molecule under an external electric field.

The symmetric Si_3O_2 molecule turns into C_s from C_{2v} under an external electric field. The third and fourth electronic states A″ and A′ interchange as the external electric field increases from 0.003 a.u. to 0.012 a.u., but they remain the same when the external electric field increases from 0.012 a.u. to 0.018 a.u. The electronic states of the other excited states remain the same when the external electric field changes.

The excitation energy of the fifth excited state decreases gently with the increase of the external electric field. The excitation energy of the third excited state increases from 6.226 eV to 6.335 eV before the external electric field reaches 0.012 a.u., then it diminishes sharply. Although the excitation energies of the other excited states change with external electric field in a complex way, the trendlines change gently. In conclusion, the external electric field has a small effect on the excitation energy of the Si_3O_2 molecule.

The transition electric dipole moments of the first and third excited states both show dentate change with increasing external electric field; when the latter reaches 0.012 a.u., the transition electric dipole moment increases gradually. The curve of the first excited state changes gently but the third changes sharply. The transition electric dipole moment of the fifth excited state shows the same trendline before the external electric field reaches 0.012 a.u., but then decreases gradually. The transition electric dipole moment curve of the fourth excited state is contrary to that of the third excited state. The curve of the sixth excited state is contrary to that of the fifth excited state. The transition electric dipole moment of the second excited state is close to zero and it increases slowly with increasing of external electric field.

The dentate curves of the transition electric dipole moment μ from the third and fourth excited states change sharply, which may be related to the change of the electronic state. The absorption spectrum of the third excited state intersects with the spectrum of the fourth in the region of blue light. Our studies on the above dentate curves indicate that the probability of transition is related to the external electric field.

The oscillator strength f and the transition electric dipole moment μ calculated above show that the absorption spectrum of the Si_3O_2 molecule exists in the light region from purple to yellow. Although part of the oscillator strength in Table 3 is equal to zero, the transition electric dipole moment is not zero. Therefore, all the transitions can take place in theory. According to the result, the main absorption spectrum exists in the regions of green, blue, yellow and purple light in turn. The spectrum of the Si_3O_3 molecule is about 320 nm[15] under an external electric field, which mainly exists in the ultraviolet region.

Song and Bao[2] 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. Guo *et al.*[24] observed luminescence from silicon-based materials and the PL spectrum peaks are 360 nm, 430 nm, and 835 nm. Zheng *et al.*[23] also observed luminescence from silicon-based SiO_2 film and the wavelength ranges from 330 nm to 388 nm. Song and Bao[3] considered that the peaks of blue and purple light derive from oxygen-deficient defects. Our calculation is on the basis of the rigid molecule model of Si_3O_2. Although the emission spectrum can be affected by other factors, our results accord with the experimental values. The excited states of Si_3O_2 could theoretically return to the ground or second-level excited states emitting visible luminescence (except orange and red light). The calculations for Si_3O_3 and

Si_3O_2 are in perfect agreement with the experimental data and the different properties of the two molecules also support the oxygen-deficient defect theory.

4. Conclusions

We presented a theoretical study of the Si_3O_2 molecule, and the geometry of the ground state and the excited state properties under an external electric field were investigated. Despite the fact that the geometry of Si_3O_2 is similar to Si_3O_3 except for the oxygen-deficient defect structure (Si–Si band) which exists only in the Si_3O_2 cluster, the excitation properties of the two molecules are very different. The oscillator strength f and the transition electric dipole moment μ of the Si_3O_2 molecule change regularly with increasing external electric field but those of the Si_3O_2 molecule change in a more complicated manner. The absorption band of the Si_3O_3 molecule is enriched in the ultraviolet region but the absorption spectrum is widely distributed in the region of visible light except orange and red. The differences between the Si_3O_3 and Si_3O_2 molecules support the oxygen-deficient defect theory. Our results also provide a good candidate as a model for the study of PL at the molecular level.

References

[1] Canham L T, Barraclough K G and Robbins D J 1987 *Appl. Phys. Lett.* **51** 1509

[2] Song H Z and Bao X M 1997 *Phys. Rev.* B **55** 6988

[3] Bao X M and Song H Z 1997 *J. Mater. Res.* **11** 601 (in Chinese)

[4] Kanemitsu Y, Suzuki K, Kyushin S and Masumoto H 1995 *Phys. Rev.* B **51** 13103

[5] Ma Z Y, Guo S H, Chen D Y, Wei D Y, Yao Y, Zhou J, Huang R, Li W, Xu J, Xu L, Huang X F, Chen K J and Feng D 2008 *Chin. Phys.* B **17** 303

[6] Liao L S, Bao X M, Zheng X Q, Li N S and Min N B 1996 *Appl. Phys. Lett.* **68** 850

[7] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046

[8] Koch K, Petrova K V, Muschik T, Nikolov A and Gavrilenko V 1993 *MRS Proc.* **283** 197

[9] Augustine B H, Hu Y Z, Irene E A and McNeil L E 1995 *Appl. Phys. Lett.* **67** 3694

[10] Tong S, Liu X N and Bao X M 1995 *Appl. Phys. Lett.* **66** 469

[11] Qin G G 2005 *J. Infrared Millim. Waves* **24** 165 (in Chinese)

[12] Wang L S, Nicholas J B, Dupuis M, Wu H B and Colson S 1997 *Phys. Rev. Lett.* **78** 4450

[13] Zhu Z H, Fu Y B, Gao T, Chen Y L and Chen X J 2003 *J. Atom. Mol. Phys.* **20** 169 (in Chinese)

[14] He J Y, Long Z W, Long C Y and Cai S H 2010 *Acta Phys. Sin.* **59** 1651 (in Chinese)

[15] Xu G L, Liu X F, Xia Y Z, Zhang X Z and Liu Y F 2010 *Journal of Henan Normal University* **38** 69 (in Chinese)

[16] Frisch M J, Trucks G W, Schegel H B, *et al.* 2003 *Gaussian* 03 Revision B03 (Pittsburgh PA: Gaussian Inc)

[17] Ma M Z, Zhu Z H, Chen X J, Xu G L, Zhang Y B, Mao H P and Shen X H 2005 *Chin. Phys.* **14** 1101

[18] Cooper G, Olney T N and Brion C E 1995 *Chem. Phys.* **194** 175

[19] Grimme S 1996 *Chem. Phys. Lett.* **259** 128

[20] Xu G L, Liu X F, Xie H X, Zhang X Z and Liu Y F 2011 *Chin. Phys.* B **20** 013101

[21] Anderson J S and Ogden J S 1969 *J. Chem. Phys.* **51** 4189

[22] Khanna R K, Stranz D D and Donn B 1981 *J. Chem. Phys.* **74** 2108

[23] Zheng X Q, Guo X L, Liao L S and Liu Z G 1998 *J. Semicond.* **19** 21 (in Chinese)

[24] Guo H Q, Lin X X and Wang Q M 2006 *J. Semicond.* **27** 345 (in Chinese)