Properties of a Si_2N molecule under an external electric field*

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(Received 9 July 2011; revised manuscript received 22 August 2011)

In the present work, we adopt the ccsd/6-31g(d) method to optimize the ground state structure and calculate the vibrational frequency of the Si_2N molecule. The calculated frequencies accord satisfactorily with the experimental values, which helps confirm the ground state structure of the molecule. In order to find how the external electric field affects the Si_2N molecule, we use the density functional method B3P86/6-31g(d) to optimize the ground state structure and the time-dependent density functional theory TDDFT/6-31g(d) to study the absorption spectra, the excitation energies, the oscillator strengths, and the dipole moments of the Si_2N molecule under different external electric fields. It is found that the absorption spectra, the excitation energies, the oscillator strengths, and the dipole moments of the Si_2N molecule are affected by the external electric field. One of the valuable results is that the absorption spectra of the yellow and the blue-violet light of the Si_2N molecule each have a red shift under the electric field. The luminescence mechanism in the visible light region of the Si_2N molecule is also investigated and compared with the experimental data.

Keywords: external electric field, excited properties

PACS: 31.15.–p, 31.15.ag, 31.50.Df **DOI:** 10.1088/1674-1056/21/5/053101

1. Introduction

In recent years, with the development of photoelectric integrated circuits, the investigation of silicon-based materials for optoelectronic devices has become a major research field. As typical silicon-based materials, silicon nitride materials have many good properties, such as excellent insulation, high density, good stability, and cheap price. In addition, as very promising silicon-based luminescence materials, they have been investigated extensively.[1,2] Some investigations on their preparation and optical properties are in progress,[3,4] but some problems, such as the luminescence mechanism and the relationship between the optical property and the structure, have not been thoroughly studied up to now. So, further careful research needs to be done. The material characteristics may change greatly when the electron is transited from the ground state to the excited states under an external electric field. The luminescence is caused by the transition of electron between different excited states or between the excited state and the ground state. So the excited states play a very important role in studying the luminescence mechanism of a material. The study of the characteristics of a molecule under external electric fields has become important in many fields.[5–8]

As is well known, the Si_2N molecule is a part of silicon nitride material, so studying it would be a good introduction to systematically understanding this kind of luminescence material. Because the properties of a material interrelate closely with the molecule properties, the study of the molecule properties will play an important guiding role in exploring the material properties. In past years, there have been abundant studies of the Si_2N molecule. Meloni *et al.*[9] have observed its vibrational frequency in experiment and calculated the frequency by using the *ab initio* method, the two results are in good agreement with each other. Ornellas and Iwata[10] optimized the ground state structures of three possible isomers and calculated the frequency of the Si_2N molecule by using many methods. Brugh and Morse[11] found transition $\tilde{X}^2\Pi_{g,1/2} \rightarrow {}^2\Sigma_u^+$ of Si_2N in experiment and determined that the geometric structure is linear and centrosymmetric in both the ground and the excited

*Project supported by the Foundation for University Young Core Instructors of Henan Province, China (Grant No. 2009GGJS-044), the Natural Science Foundation of the Education Bureau of Henan Province, China (Grant No. 2010A140008), and the Cultivating Fund of Henan Normal University, China (Grant No. 2010PL02).

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states. Other studies of the Si_2N molecule also have been carried out.[12−17] However there is no study on the luminescence properties of the Si_2N molecule under external electric fields. A description of the geometric structure contributes to the knowledge of the properties and the understanding of the mechanism of luminescence of the Si_2N molecule. Based on the geometric structure of the Si_2N molecule under no electric field, in this work, we use the B3P86/6-31g(d) method to optimize the ground state structure and the time-dependent density functional theory TDDFT/6-31g(d) to study the absorption spectra, the excitation energies, the oscillator strengths, and the dipole moments of the first seven excited states of the Si_2N molecule under different external electric fields.

2. Theoretical method

The Hamiltonian of the radiation process is given as

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

where H_0 is the complete molecular Hamiltonian, $H_{\rm int}$ is the interaction Hamiltonian between the electron field and the molecular. Under the dipole approximation, $H_{\rm int}$ is given as

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

where $\boldsymbol{F}$ is the radiation field, and $\boldsymbol{\mu}$ is the dipole moment. The electronic transition can occur only between different states of the molecule with the same spin degree, so in the present work only this type of transition is considered.

3. Results and discussion

3.1. Geometry and vibration frequencies for the ground state structure

In the present work, the ground state structure of the Si_2N molecule is calculated by using different methods and basis sets. Our calculations confirm that Si_2N has a symmetric linear structure (SiNSi) in the $^2\Pi_g$ ground state. The optimized geometric parameters including the bond length and the vibrational frequency are listed in Table 1.

According to Table 1, the vibrational frequency 914 cm^{-1} obtained by the ccsd/6-31g(d) method is closer to the experimental data than the values given in Refs. [9] and [10] and obtained by using different methods. It is shown that the ccsd method with the 6-31g(d) basis set is more superior to the others in optimizing the structure and calculating the frequency of the Si_2N molecule, and the optimized structure is shown in Fig. 1.

Table 1. Optimized Si–N bond length R, angle ∠Si–N–Si, and vibrational frequency ω for ground state of Si_2N molecule obtained with different methods.

Method	Basis set	R/nm	∠Si–N–Si/(°)	$\omega_1(\Pi)$/cm^1	$\omega_2(\Pi)$/cm^1	$\omega_3(\Sigma)$/cm^1	$\omega_4(\Sigma)$/cm^1
ccsd	cc-pvtz	0.16382	180	142	244	622	882
ccsd	6-31g(d)	0.16435	180	181	216	618	914
ccsd	6-31+g(d,p)	0.16453	180	168	243	613	880
ccsd	6-311+g(d)	0.16400	180	133	223	620	893
ccsd	6-311+g(d,p)	0.16400	180	133	223	620	893
qcisd[9]	cc-pvtz	0.1641	180	192	–	615	886
ccsd(t)[10]	cc-pvtz	0.1644	180	–	341	831	896
qcisd	6-31g(d)	0.16466	180	179	262	609	919
qcisd	6-31g(d,p)	0.16477	180	164	240	606	883
qcisd	6-311g(d)	0.16430	180	132	221	612	896
qcisd	6-311+g(d,p)	0.16430	180	132	221	612	896
B3P86	cc-pvtz	0.1638	180	145	242	622	1085
B3P86	6-31g(d)	0.16400	180	204	276	617	1071
B3P86	6-311+g(d)	0.16373	180	168	254	264	1086
B3P86	6-31g+(d,p)	0.16400	180	204	276	617	1071
B3P86	6-311g(d,p)	0.16430	180	174	257	619	1076
Exp.[9]	–	–	–	–	–	–	910

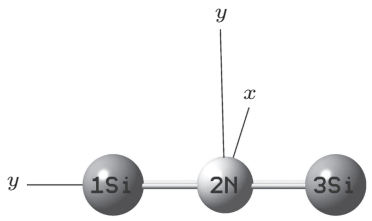


Fig. 1. Optimized ground state structure of Si_2N molecule.

3.2. Excitation properties of the Si_2N molecule without any external electric field

On the basis of the optimization results above, the excitation properties of the Si_2N molecule without any external electric field have been investigated using the TDDFT method. The first seven excited states are calculated, and the parameters, such as excitation energy E, excitation wave length λ, oscillator strength f, and transition electric dipole moment μ of the Si_2N molecule, are listed in Table 2.

Oscillator strength f and transition electric dipole moment μ represent the capacity of the electric dipole transition, so if f equals zero, then the transition is forbidden. According to Table 2, the transitions from the ground state to the third, the fourth, and the seventh excited states are allowed, while the transitions from the ground state to the other four excited states are forbidden. The absorption spectrum in the visible light is very important for studying the luminescence mechanism for the silicon nitride material. When the transitions from the ground state to the third, the fourth, and the seventh states occur, the electron should absorb the photons with the energies of 2.2385 eV, 2.9809 eV, and 4.1498 eV, respectively. Correspondingly, the absorption wave lengths of the Si_2N molecule are 553 nm, 416 nm, and 298 nm in theory. Our results are well consistent with the photon luminescence peaks at 553 nm and 420 nm, which have been observed in experiment.[3,4] Especially, the transition between the ground state and the seventh excited state $\tilde{X}^2\Pi_{g,1/2} \rightarrow^2 \Sigma_u^+$ with the excitation energy of 4.1498 eV (33470 cm^{-1}) of the Si_2N molecule accords well with the experimental result.[11] On the other hand, the electrons at the excited states of the Si_2N molecule can return to the ground state or the second excited states. According to the group theory, for the $D_{\infty h}$ molecule, $\Sigma^+ \times \Sigma^+ = \Sigma^+$, $\Pi \times \Sigma^+ = \Psi$ According to the transition selection rule of $\Delta S = 0$, these transitions occur between the seventh excited state and the third or the second excited state and between the sixth excited state and the third or the second excited state with luminescence spectrum peaks at 1.91 eV, 2.14 eV, 1.82 eV, and 2.05 eV, respectively, which accord with the experimental results exactly.[18]

Table 2. Excitation energy E, excitation wave length λ, oscillator strength f, and transition electric dipole moment μ for the transition from ground state to excited states of the Si_2N molecule.

Excited state	1	2	3	4	5	6	7
S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
E/eV	0.0094	2.0081	2.2385	2.9809	3.9413	4.0622	4.1498
λ/nm	131356	617.42	553.88	415.93	314.58	305.22	298.77
f	0.0000	0.0000	0.1138	0.0002	0.0000	0.0000	0.0020
μ	0.0000	0.0000	1.4404	0.0473	0.0000	0.0000	0.1403

3.3. Effect of external electric fields on orbital energy

Under external electric fields, the structural parameters of the molecule may change, so the molecule can take on new properties. The geometry parameters of the ground state for the Si_2N molecule under external electric fields are investigated. The external electric fields F are equal to 0.018 a.u., 0.021 a.u., 0.024 a.u., 0.027 a.u., 0.030 a.u., and 0.033 a.u., and their directions are all along the z axis (Fig. 1), where a.u. stands for arb. units. All the calculations are performed by using the B3P86 method with the 6-31g(d) basis set. It is well known that many properties of a molecule are determined by the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO). The HOMO and the LUMO of the Si_2N molecule are obtained on the basis of the optimized molecular structure, and the HOMO energy E_H, the LUMO energy E_L, and the energy gap E_{HLG} between them are shown in Table 3.

Table 3. Total energies $E_{\rm tol}$, $E_{\rm H}$, $E_{\rm L}$, and $E_{\rm HLG}$ of Si_2N molecule under different electric fields.

F/a.u.	$E_{\rm tol}$/a.u.	$E_{\rm H}$/a.u.	$E_{\rm L}$/a.u.	$E_{\rm HLG}$/eV
0.000	–634.3897245	–0.17969	–0.12762	1.416304
0.018	–634.3917956	–0.17996	–0.12790	1.416032
0.021	–634.3917900	–0.18007	–0.12800	1.413584
0.024	–634.39176227	–0.18017	–0.12812	1.415760
0.027	–643.9716894	–0.18029	–0.12826	1.415216
0.030	–634.3901841	–0.18066	–0.12818	1.400256
0.033	–634.3897245	–0.18093	–0.12836	1.402704

From Table 3, we know that $E_{\rm H}$ and $E_{\rm L}$ both decrease with the increase of the external electric field. The change of $E_{\rm HLG}$ is complicated, but the value is smaller than that under zero electric field. It suggests that the transition from the HOMO to the LUMO can take place more easily under the external electric fields.

3.4. Effect of external electric fields on excited properties

The excited properties are affected by the external electric fields, and there will be some new properties. Therefore, we study the first seven excited states of the Si_2N molecule under different external electric fields. All the calculations are carried out with the TDDFT method on the basis of the optimized structures under the external electric fields mentioned above. The excitation properties under the external electric fields are shown in Table 4, which shows excitation wave length λ, oscillator strength f, and transition electric dipole moment μ. At the same time, the excitation energies of the first seven excited states under the external electric fields are shown in Fig. 2.

Table 4. Excitation wave length λ, oscillator strength f, and transition electric dipole moment μ of the first seven excited states of Si_2N molecule under different external electric fields.

F/a.u. \ Excited state		1	2	3	4	5	6	7
0.018	S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
	λ/nm	81956	658.82	586.34	422.11	325.95	316.89	301.04
	f	0.0000	0.0000	0.1265	0.0001	0.0000	0.0000	0.0322
	μ	0.0000	0.0000	1.5624	0.0405	0.0097	0.0002	0.5651
0.021	S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
	λ/nm	81956	659.73	587.17	422.12	325.84	317.11	301.06
	f	0.0000	0.0000	0.1260	0.0001	0.0000	0.0000	0.0013
	μ	0.0000	0.0000	1.5606	0.0403	0.0081	0.0000	0.5650
0.024	S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
	λ/nm	81956.14	660.77	588.14	422.14	325.71	317.37	301.09
	f	0.000	0.0000	0.1254	0.0001	0.0000	0.0000	0.0322
	μ	0.0000	0.0000	1.5585	0.0400	0.0057	0.0001	0.5650
0.027	S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
	λ/nm	81850.80	661.91	589.25	422.16	325.55	317.70	301.13
	f	0.0000	0.0000	0.1247	0.0001	0.0000	0.0000	0.0322
	μ	0.0000	0.0000	1.5556	0.0397	0.0028	0.0001	0.5648
0.030	S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
	λ/nm	81065.78	650.38	584.11	422.78	324.82	317.90	301.60
	f	0.0000	0.0000	0.1215	0.0001	0.0001	0.0000	0.0304
	μ	0.0000	0.0000	1.5287	0.0404	0.0385	0.0019	0.5495
0.033	S	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Pi$	$^2\Pi$	$^2\Pi$	$^2\Sigma^+$
	λ/nm	80804	649.19	584.45	422.95	324.42	318.49	301.79
	f	0.0000	0.0000	0.1197	0.0001	0.0002	0.0000	0.0299
	μ	0.0000	0.0000	1.5179	0.0401	0.0432	0.0035	0.5454

According to Table 2 and Fig. 2, the excitation energy does not change with the molecule group and the electron state for the first seven excited states under different electronic fields. The excitation energy of the first excited state is always 0.0151 eV when the external electric fields are 0.018 a.u., 0.021 a.u., 0.024 a.u., and 0.027 a.u., it changes to 0.0153 eV when the electric field increases to 0.030 a.u. and 0.033 a.u. The excitation energy of the second excited state decreases gently before the external field reaches 0.027 a.u., and then increases gently with the increase of the electric field. The excitation energy of the third excited state also decreases gently before the external field reaches 0.027 a.u., then increases until the external field reaches 0.030 a.u., and then decreases again with the increase of the electric field. The excitation energies of the fourth, the sixth, and the seventh excited states all decrease slowly with the increase of the electric field. On the contrary, the energy of the fifth excited state increases slowly with the increase of the electric field. In a word, the excitation energies of the first seven excited states all change gently with the variation of the external electric field.

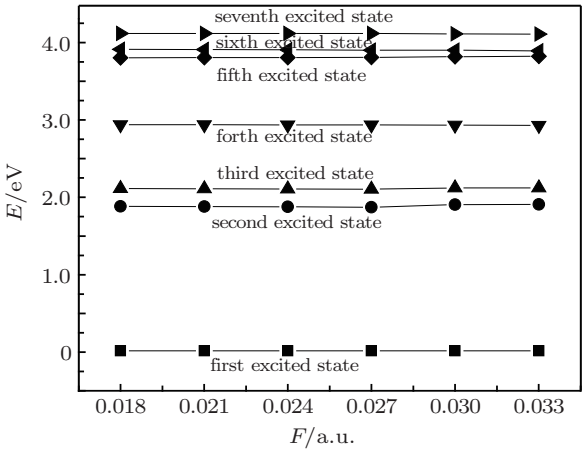


Fig. 2. Excitation energy E of the Si_2N molecule under external electric fields.

The transition electric dipole moments from the ground state to the first and the third excited states are zero, and the one to the sixth excited state is very small. The transition electric moments of the third and the fourth excited states increase gently before the external field reaches 0.027 a.u., and then they decrease gently with the increase of the external electric field. And the transition electric dipole moment for the seventh excited state decreases with the increase of the electric field.

The oscillator strength reflects the ability of the transition. The results above show that the absorption spectra of the Si_2N molecule exist in the region from the ultraviolet to the yellow light. Although a part of the oscillator strength equals to zero, the transition electric dipole is not zero. The relationship between the oscillator strength and the transition electric dipole moment is very complicated and is described in Ref. [19].

According to the results, the change of the absorption spectrum is also complicated under the external electric field. The absorption wavelength of the second excited state increases gently before the external field reaches 0.027 a.u., and then it decreases gently with the increase of the electric field. The absorption wavelength of the third excited state increases gently before the external field reaches 0.027 a.u. However, it decreases before the external field reaches 0.030 a.u., and then increases again with the increase of the electric field. The absorption wavelengths of the fourth, the sixth, and the seventh excited states increase gently with the increase of the electric field. However, the absorption wavelength of the fifth excited state decreases slowly with the increase of the electric field. The red shift of the absorption wavelength may take place and new absorption can appear compared with the case without any electric field. The absorption wavelength is equal to the luminescence wavelength in theory. According to the fact that f is not zero, we can observe the luminescence spectrum at 420–590 nm in the region between the blue-violet and the yellow light, which is exactly in the experimental region.[20] On the other hand, the electrons at the excited states of the Si_2N molecule can return to the ground state or the second excited states. According to the group theory, for the $D_{\infty h}$ molecule, $\Sigma^+ \times \Sigma^+ = \Sigma^+$, $\Pi \times \Sigma^+ = \Pi$ with the transition selection rule of $\Delta S = 0$, these transitions occur between the seventh excited state and the third or the second excited state, and between the sixth excited state and the second excited state, the luminescence spectrum is at 564–668 nm, which is also in the experimental region.[20]

4. Conclusion

We investigate theoretically the parameters of the Si_2N molecule in detail, such as the geometry, the vibrational frequency, the HOMO energy, and the LUMO energy of the ground state and the properties of the excited states under different electric fields. All the calculations are executed by using Gaussian03 program packages.[21] We find that the external electric fields each have a complicated effect on the excited properties of the Si_2N molecule. The orbital energy changes and the transitions occur more easily under

the electric fields. In theory, the Si_2N molecule has a rich absorption spectrum in the ultraviolet and the yellow-green light regions, and the absorption spectrum is weak in the purple light region no matter whether the electric fields exist or not. However, the external fields can induce the red shift of the absorption spectrum of the Si_2N molecule in the visible light region, so we can vary the electric field to obtain the absorption spectrum needed. In addition, there is a wide range of the luminescence spectrum in the visible light, which accords well with the observed results. It is very important to study the emission spectrum of luminescent material. Therefore the present work can be a guide for exploring the luminescence properties of silicon nitride materials in future.

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