

The potential energy curves and spectral constants of Si₂N

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Abstract. The equilibrium geometries of Si₂N have been calculated using different quantum chemistry calculation methods. Through a large number of test and research, the method QCISD/6-31G(2d,2p) is the most suitable for the calculation of Si₂N by comparing the experimental equilibrium structure and harmonic frequency data. The force constants have also been calculated. Based on the general principles of microscopic reversibility, the dissociation limits has been deduced. The analytical potential energy function of Si₂N has been obtained based on the many-body expansion theory. The potential surface graphs have been presented. It's found that there is a minimum value of 4.725eV at stable structure of the potential surface and a potential well of 1.7eV correspond to the linear asymmetric structures(²Π). And the reaction of SiN+Si→SiNSi based on the potential energy surface is discussed briefly, which is successfully used for describing molecular reaction dynamics.

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Key words: harmonic frequency; force constants; potential energy function.

1 Introduction

As the Small molecules containing silicon and nitrogen not only were found earlier interstellar molecules but also play an important role in materials science [1,2]. They attract much attention in astrophysics, chemical kinetics, interstellar chemistry and the material chemistry. With an important application of nitrogen and silicon clusters in materials science, much theoretical and experimental researchers are focus on the system of Si₂N molecule. [3-6] The first experimental study of Si₂N was reported for a mass spectroscopic analysis of silicon vaporized from a boron nitride Knudsen cell. It predicted the ionization potential of Si₂N to be 9.4±0.3eV by the vanishing-current method in 1967

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[7]. In 1997, Brugh researched resonant two-photon ionization spectroscopy of the 13-electron triatomic Si₂N [8]. One-color resonant and nonresonant ionization studies of Si₂N and Si₂O have been performed using a pulsed laser vaporization cluster source in conjunction with a time-of-flight mass spectrometer in 2002 [4]. From then on, many technologies and methods of spectroscopy have been applied to experimental research of Si₂N. [5]

To our best knowledge, the potential energy surface of the ground state molecule Si₂N have been constructed in 2006 [9], but the structure constants of Si₂N molecule aren't in agreement with the experimental data [9]. In order to explore the Si₂N molecule intensively, we calculate the equilibrium geometries, harmonic frequency by using different quantum chemistry calculation methods. Through a lot of calculation, we found that the QCISD/6-31G(2d,2p) level is most suitable for calculating the potential energy surface of Si₂N molecule. The dissociation energies and force constants have been further calculated using QCISD/6-31G(2d,2p) method. Based on the results, the analytical potential energy function (APEF) have been obtained according to the many-body expansion theory and the potential energy surface plots of Si₂N molecule are presented. Dynamics results confirmed that we build the potential energy surface accuracy.

2 *Ab initio* calculation of Si₂N (²A₁)

The higher state symmetry of Si₂N belongs to point group C_{2v} with ²A₁. The equilibrium geometries and energy of Si₂N molecule have been optimized with many methods. All calculations are performed by using the Gaussian09 program package. The results are listed in the Table 1.

It can be seen clearly that the calculation of Si₂N molecule by using QCISD/6-31G(2d, 2p) level is in good agreement with experimental result. The values of R_{SiN} , $\angle SiNSi$ deviate from the experimental values only by 0.23%, 1.074% respectively [10]. A series of results of Table 2 are more accurate than experiment value. The bond length of SiN is 0.16911nm and the bond angle is 93.99° with the dissociation energy 4.725eV. The dissociation energy 4.725eV is closer to the experimental value (5.1eV)[10] than the literature value (5.774eV) [9]. In addition, the harmonic frequencies and force constants are determined by using QCISD/6-31G(2d,2p). The results are listed in the Table 2. The results make sufficient preparations for the potential energy function of the triatomic molecule Si₂N.

3 Many-body expansion theory of Si₂N

The many-body expression of the triatomic system can be written as [11]

$$V = \sum V_A^{(1)} + \sum V_{AB}^{(2)} + \sum V_{ABC}^{(3)}(R_{AB}, R_{BC}, R_{CA}) \quad (1)$$

Table 1: The geometry optimization calculations of Si₂N (²A₁).

Computational level	R _{SiN} (nm)	∠SiNSi(°)	Energy (hartree)
QCISD /6-311G(d,P)	0.16801	94.1681	632.2683
QCISD/6-311+G(d,P)	0.16810	94.6840	632.2726
QCISD/6-311+G(2d,2p)	0.16828	95.0207	632.2879
QCISD/6-311+G(3d,3p)	0.16795	95.4071	632.2917
QCISD /6-311G(3d,3P)	0.16791	95.2013	632.2889
QCISD /6-31G(d,P)	0.16912	92.9507	632.2179
QCISD/6-31+G(d,P)	0.16907	93.9093	632.2234
QCISD /6-31G(2d,2P)	0.16911	93.9909	632.2330
QCISD/6-31+G(2d,2P)	0.16926	94.3991	632.2360
QCISD /6-31G(3d,3P)	0.16847	94.8110	632.2397
QCISD/cc-PVTZ	0.16852	93.3600	632.3011
QCISD/cc-PVDZ	0.17143	92.8441	632.2509
QCISD/6-311G(df,pd)	0.16745	93.2306	632.0272
QCISD/6-311G(2df,2pd)	0.16772	93.5782	632.2916
QCISD /6-311G(3df,3pd)	0.16813	94.1364	632.2932
QCISD/6-311+G(2df,2pd)	0.16789	93.8253	632.2949
QCISD/6-311+G(3df,3pd)	0.16756	94.2278	632.2972
reported values [9]	0.16712	94.3862	–
experimental values [10]	0.1695	93.1	–

Table 2: The dissociation energy and force constants of Si₂N molecule.

Equilibrium geometries	Harmonic frequencies	Force constants
R _{SiN} =0.16911nm	ω ₁ =345.8038cm ⁻¹ _(341cm⁻¹[10])	f ₁₁ =f ₂₂ =0.25188 a.u.
∠SiNSi=93.99°	ω ₂ =791.1094cm ⁻¹ _(831cm⁻¹[10])	f ₁₂ =0.04064 a.u.
D _e =4.725eV (5.1eV [10])	ω ₃ =887.5475cm ⁻¹ _(896cm⁻¹[10])	f _{1a} =f _{2a} =-0.01117 a.u. f _{aa} =0.07854 a.u.

If we choose the energy of the ground state of atoms as the reference energy, the $V_A^{(1)}=0$, as for the two-body terms, the Murrell-Sorbie potential energy function (MSPEF) would seem to be a good choice. In general, the three-body term in Eq. (1) isG

$$\sum V_{ABC}^{(3)}(R_{AB}, R_{BC}, R_{CA}) = PT \quad (2)$$

where P is the expression of (R_{AB}, R_{BC}, R_{CA}) , and should meet the requirement of symmetry, T is a range function:

$$T = \Pi(1 - \tanh \gamma_i S_i / 2) \quad (i = 1, 2, 3) \quad (3)$$

where γ_i are parameters, and S_i are symmetrical internal coordinates.

4 The potential energy function of tow-body terms (SiN, SiSi)

A number of functions have been proposed to fit APEF of diatomic molecule. Among them, MSPEF seems to be the best one, because it can accurately reproduce interaction potential energies of neutral and univalent diatomic molecules, and has been used to deduce APEFS for many molecules [12-16] including the ground and excited states. Now, we try to use it to represent the ground states of SiN, SiSi. The M-S function [17] is

$$V = -D_e(1 + \alpha_1\rho + \alpha_2\rho^2 + \alpha_3\rho^3)\exp(-\alpha_1\rho) \quad (4)$$

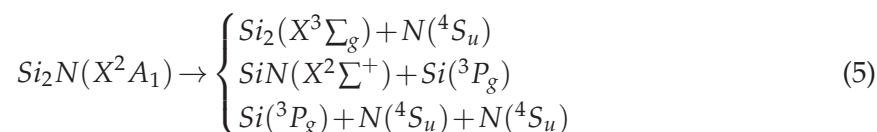
Where $\rho = R - R_e$, R_e is the equilibrium value, D_e is the dissociation energy. The parameters a_1, a_2, a_3 and D_e are determined by fitting. The results are presented in Table 3.

Table 3: Parameters of M-S potential function of SiN, SiSi in ground state.

	R/nm	D/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
SiN [18]	0.15718	5.701	37.32	297.5	1460
SiSi [18]	0.2246	3.242	29.57	230.0	962

5 The analytical potential energy function of Si₂N

Based on the theory and the principle of microscopic reversibility, the dissociation limits of Si₂N have been derived [19]:



The nuclear distances are defined as $R_1 = R_{SiN}$, $R_2 = R_{SiN}$ and $R_3 = R_{SiSi}$. According to the many-body expansion theory, the potential energy function of Si₂N (2A_1) is

$$V = V_{SiN}(R_1) + V_{SiN}(R_2) + V_{SiSi}(R_3) + V_{Si_2N}(R_1, R_2, R_3) \quad (6)$$

The parameters of two-body terms are given in the Table 3. Here, we mainly derived the three-body terms. It is convenient that three-body terms are shown as the functions of symmetrical internal coordinates. We choose C_{2V} symmetry ($R_1^0 = R_2^0 = 0.16911nm$, $R_3^0 = 0.24734nm$) as the reference structure, then the internal coordinates are:

$$\rho_i = R_i - R_i^0 \quad (i = 1, 2, 3) \quad (7)$$

The corresponding symmetry internal coordinates are:

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} \quad (8)$$

Three body terms is:

$$V^{(3)} = PT \quad (9)$$

Where

$$P = C_0 + C_1 S_1 + C_2 S_2^2 + C_3 S_3 + C_4 S_3^2 + C_5 S_1 S_3 + C_6 S_1^2 \quad (10)$$

$$T = [1 - \tanh(\gamma_1 S_1/2)][1 - \tanh(\gamma_3 S_3/2)] \quad (11)$$

The seven linear parameters can be determined by using the equilibrium structure and the force constants (in Table 2). And nonlinear ones γ_1 and γ_3 in the range function, T can be determined by optimizing the potential energy surface. The parameters of the there-body term of Si_2N are calculated and listed in Table 4.

Table 4: Parameters of three-body term of Si_2N (2A_1).

parameters	Si_2N (2A_1)
C_0	9.1756
C_1	-4.9995
C_2	-0.4581
C_3	-0.5735
C_4	-1.3477
C_5	-4.3813
C_6	5.6947
λ_1	0.1
λ_3	0.3

Figs. 1-3 are the contour graphs of the Si_2N (2A_1) potential energy function. These figures reproduce C_{2V} structure and potential energy of Si_2N (2A_1). Fig. 1 is the Si-N bond stretching contours for a fixed angle $\angle \text{SiNSi} = 93.99^\circ$. From this figure, we can see that there is a potential well I (-4.725eV) at (0.16911nm, 0.16911nm). It is in good agreement with the result of optimization. And there is a potential well II (-1.7eV) at (0.2543nm, 0.2543nm) too. We found the dissociation energy of potential well II is smaller than the dissociation energy of potential well I. In document [9], the dissociation energy of asymmetric structures (${}^2\Pi$) is 42.6 kcal/mol (1.848eV). This suggests that the potential well II is corresponding to the linear asymmetric structures (${}^2\Pi$). In addition, we are found that there are two symmetric saddle point at (0.2319nm, 0.1688nm) and (0.1688nm, 0.2319nm), the barrier height which is approximately 3.3eV can be observed. This indicates that Si_2N could be easily formulated when Si atom with the energy surpassing 1.425eV attacks Si-N bond [20-25].

Fig. 2 is the contour lines for Si atom moving around Si-N with the fixed Si-N bond. The Si-N bond is fixed at the X axis, and Y axis is established at the zero by the central point of the Si-N bond. The lowest energy (-4.725eV) is at point (0.0963nm, 0.1687nm). It is of great interest to find that there is a barrier on the reaction channel $\text{Si} + \text{SiN} \rightarrow \text{SiNSi}$. It is in agreement with the result of the Fig. 2.

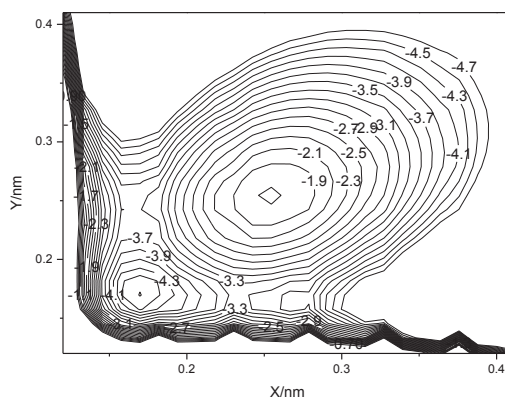
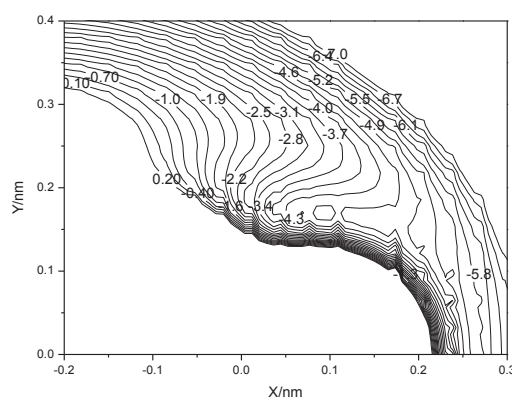
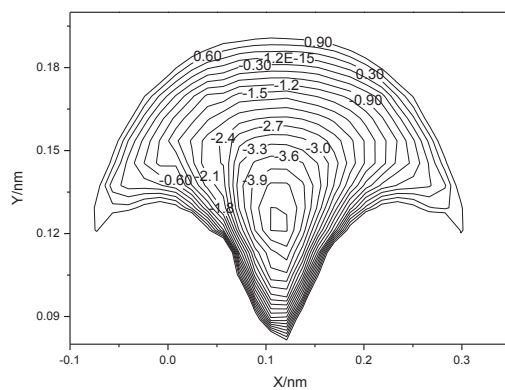
Figure 1: Stretch potential surface of Si_2N (the interval is 0.2eV).Figure 2: Rotation potential surface of Si_2N (the interval is 0.3eV).Figure 3: Rotation potential surface of Si_2N (the interval is 0.3eV).

Fig. 3 is those for N atom moving around Si-Si bond with the bond length 0.2464nm. It shows that when N atom rotated around Si-Si bond, the lower energy is 4.725eV at (0.1232nm, 0.1153nm). It is in agreement with the result of Fig. 1 and Fig. 2.

6 Conclusion

The equilibrium geometry, force constants and harmonic frequencies of Si₂N have been calculated with QCISD/6-31G(2d,2p) method. The geometry and vibration frequencies of them are in good agreement with those in the literature. Based on the group theory and the general principles of microscopic reversibility, the reasonable dissociation limit of Si₂N is determined. For the first time, we extended the many-body expansion theory to Si₂N, and get satisfactory results. The structure and energy can correctly reappear on the potential surface. The above results are useful for dynamic study of Si₂N.

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References

- [1] D. K. Bohme, *Adv. Gas. Phase, Ion. Chem.* 1 (1992) 225.
- [2] O. Parisel, M. Hanus, Y. J. Ellingery, *Phys. Chem.* 100 (1996) 2926.
- [3] R. Viswana, Jr. R.W. Schmude, K. A. Gingerich, *J. Chem. Thermo.* 27 (1995) 1303.
- [4] S. J. Paukstis, J. L. Gole, *J. Phys. Chem. A.* 106 (2002) 8435.
- [5] Y. H. Zhu, B. X. Li, G. X. Ye, *Comput. Theor. Chem.* 1017 (2013) 162.
- [6] G. Meloni, S. N. Cesaro, N. Sanna, *Chem. Phys. Lett.* 343 (2001) 113.
- [7] K. F. Zmbov, J. L. Margrave, *J. Am. Chem. Soc.* 89 (1967) 2492.
- [8] D. J. Brugh, M. D. Morse, *Chem. Phys. Lett.* 267 (1997) 370.
- [9] Y. F. Liu, L. J. Jiang, X. Q. Han, *J. Atom. Mol. Phys.* 23 (2006) 938.
- [10] R. O. Fernando, I. Suehiro, *J. Phys. Chem.* 100 (1996) 10919.
- [11] S. J. Sato, *J. Chem. Phys.* 23 (1955) 2465.
- [12] R. Wang; Z. H. Zhu; C. L. Yang, *J. Mol. Struc. (Theochem).* 571 (2001) 133.
- [13] A. A. Zavitsas, *J. Mol. Spectrosc.* 221 (2003) 67.
- [14] L. H. Chen, R. C. Shang, *J. Mol. Struc. (Theochem).* 629 (2003) 37.
- [15] C. L. Yang, X. Zhang, K. L. Han, *J. Mol. Struc. (Theochem).* 678 (2004) 183.
- [16] F. H. Wang, C. L. Yang, Z. H. Zhu, F. Q. Jing, *Chin. Phys.* 14 (2005) 0317.
- [17] J. N. Murrell, S. C. Farantons, P. Huxley, *Molecular Potential Energy Functions.* (Wiley press, New York, 1984).
- [18] Z. H. Zhu, H. G. Yu, *Molecular Structure and Potential Energy Function* (Science Press, Chinese, 1997).
- [19] Herzberg. *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold ptrss, New York, 1979).
- [20] D. H. Shi, Y. F. Liu, J. F. Sun, X. D. Yang, Z. L. Zhu, *Chin. Phys.* 15 (2006) 2928.
- [21] Z. D. Geng, Y. S. Zhang, X. W. Fan, *Chin. Phys.* 15 (2006) 1257.
- [22] H. Y. Wang, Z. H. Zhu, D. Q. Meng, X. L. Wang, *Chin. Phys.* 12 (2003) 0154.
- [23] Y. F. Liu, L. J. Jiang, H. Ma, J. F. Sun, *Chin. Phys. B.* 17 (2007) 2085.
- [24] Z. Q. Wang, C. Z. Zhang, H. J. Yu, J. M. DU, J. G. Ma, *Chin. Phys. B.* 20 (2011) 033107.
- [25] H. J. Chen, H. Y. Tang, X. L. Cheng, Q. W. Wang, *Acta. Phys. Chim. Sin.* 26 (2010) 740.