J. At. Mol. Sci.
doi: 10.4208/jams.071215.081615a

Vol. **6**, No. 3, pp. 172-178
September 2015

The potential energy curves and spectral constants of Si_2N

Xiaoqin Han[a,*], and Xiajie Xiao[b]

[a] *Department of Physics, Shangqiu Normal College, Shangqiu 476000, China*
[b] *Henan Quality Polytechnic, Pingdingshan 467000, China*

Received 12 July 2015; Accepted (in revised version) 16 August 2015
Published Online 30 September 2015

Abstract. The equilibrium geometries of Si_2N 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 Si_2N 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 Si_2N 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($^2\Pi$). 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.

PACS: 31.50.Bc

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 Si_2N molecule. [3-6] The first experimental study of Si_2N was reported for a mass spectroscopic analysis of silicon vaporized from a boron nitride Knudsen cell. It predicted the ionization potential of Si_2N to be 9.4±0.3eV by the vanishing-current method in 1967

*Corresponding author. *Email address:* hanxiaoqin88@163.com (X. Q. Han)

[7]. In 1997, Brugh researched resonant two-photon ionization spectroscopy of the 13-electron triatomic Si_2N [8]. One-color resonant and nonresonant ionization studies of Si_2N and Si_2O 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 Si_2N. [5]

To our best knowledge, the potential energy surface of the ground state molecule Si_2N have been constructed in 2006 [9], but the structure constants of Si_2N molecule aren't in agreement with the experimental data [9]. In order to explore the Si_2N 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 Si_2N 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 Si_2N molecule are presented. Dynamics results confirmed that we build the potential energy surface accuracy.

2 *Ab initio* calculation of Si_2N ($^2A_1$)

The higher state symmetry of Si_2N belongs to point group C_{2V} with $^2A_1$. The equilibrium geometries and energy of Si_2N 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 Si_2N 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 Si_2N.

3 Many-body expansion theory of Si_2N

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

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