



Vibrational frequencies and structural determinations of tetraethynylsilane

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Received 9 September 2002; accepted 15 October 2002

Abstract

The normal mode frequencies and corresponding vibrational assignments of $\text{Si}(\text{CCH})_4$ are examined theoretically using the GAUSSIAN 98 set of quantum chemistry codes. Each of the vibrational modes was assigned to one of six types of motion predicted by a group theoretical analysis (Si–C stretch, C=C stretch, C–H stretch, C=C–H bend, Si–C=C bend, and C–Si–C bend) utilizing the T_d symmetry of the molecule. A set of uniform scaling factors was derived for each type of motion. Predicted infrared and Raman intensities are reported.

Published by Elsevier Science B.V.

Keywords: Vibrations; Normal mode frequencies; Infrared spectra; Raman spectra

1. Introduction

Tetraethynylsilane ($\text{Si}(\text{CCH})_4$) was first reported in the literature in the early 1960s [1–4], and number of methods of preparation have appeared in the literature [1–6]. $\text{Si}(\text{CCH})_4$ is used industrially in the chemical vapor deposition of thin films [7–11] of silicon and silicon carbide. $\text{Si}(\text{CCH})_4$ has also proven to be a useful laboratory reagent [12,13]. The infrared and Raman spectra [1,4,14,15] of $\text{Si}(\text{CCH})_4$ have been reported. The tetrahedral (T_d) symmetry of $\text{Si}(\text{CCH})_4$ (see Fig. 1) is reflected in the relatively small number of normal mode vibrational frequencies of this molecule. Several theoretical studies [16,17] have also been performed on this interesting molecule.

Interpretation of an experimental infrared or Raman spectra of a complex molecule is a difficult task. An empirical set of rules often gets built up over a period of time [18,19]. For organic molecules these empirical rules are well established and have been an aid to scientists for decades. For inorganic compounds with much more variety in bonding types, etc., the rules are far less established. Due to its high symmetry and unusual bonding, tetraethynylsilane is an ideal candidate for a quantum chemical normal mode study. Also high quality experimental data on the vibrational spectra [1,4,14,15] of $\text{Si}(\text{CCH})_4$ exists in the literature.

Quantum chemical methods of normal mode analysis will be used to examine available experimental data in detail. In this study the infrared and Raman spectra of $\text{Si}(\text{CCH})_4$ are examined using the GAUSSIAN 98 suite of quantum chemical codes [20]. A detailed quantum chemical study will aid in making

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definitive assignments to the fundamental normal modes of $\text{Si}(\text{CCH})_4$ and in clarifying the experimental data [1,4,14,15] available for this molecule.

2. Computational methods

The vibrational frequencies of $\text{Si}(\text{CCH})_4$ were calculated at the Hartree–Fock, DFT (B3LYP) [21, 22] and MP2 [23] levels of theory using the standard 6-31G* basis set. The calculations utilized the T_d symmetry of the $\text{Si}(\text{CCH})_4$ molecule (see Fig. 1). The computations were performed using the GAUSSIAN 98 program Package [20]. Each of the vibrational modes was assigned to one of six types of motion (Si–C stretch, C≡C stretch, C–H stretch, C≡C–H bend, Si–C≡C bend, and C–Si–C bend) by means of visual inspection using the Gaussview program [24]. The choice of internal coordinates is always somewhat arbitrary. However, the above set is complete and matches well the observed motion.

The symmetry of the $\text{Si}(\text{CCH})_4$ molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using standard procedures [25] of decomposing the traces of the symmetry operations into the irreducible representations of the T_d group. The symmetry analysis for the vibrational modes of $\text{Si}(\text{CCH})_4$ is

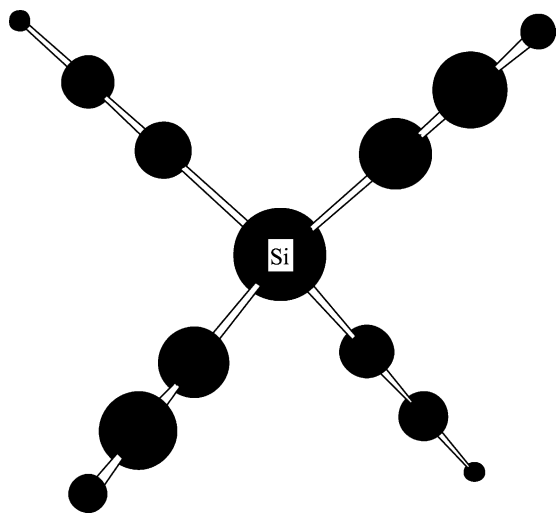


Fig. 1. Structure of tetraethynylsilane.

presented in some detail in order to better describe the basis for the assignments.

For the C≡C stretching modes, the C_3 operator has a trace of one and the σ_d operator has a trace of two. All other operators except E have a trace of zero. Thus, the four C≡C stretching modes possess the symmetries A_1 and T_2 . For the C–H stretching modes, the C_3 operator has a trace of one and the σ_d operator has a trace of two. All other operators except E have a trace of zero. Thus, the four C–H stretching modes possess the symmetries A_1 and T_2 . For the Si–C stretching modes, the C_3 operator has a trace of one and the σ_d operator has a trace of two. All other operators except E have a trace of zero. Thus, the four Si–C symmetric stretching modes possess the symmetries A_1 and T_2 .

For the eight C≡C–H bending modes the C_3 operator has a trace of minus one ($2 \cos(2\pi/3)$). All other operators except E have a trace of zero. Thus, the eight C≡C–H bending modes possess the symmetries E , T_1 , and T_2 . For the eight Si–C≡C bending modes the C_3 operator has a trace of minus one. All other operators except E have a trace of zero. Thus, the eight Si–C≡C bending modes possess the symmetries E , T_1 , and T_2 .

For the C–Si–C bending modes the Si–C wagging motion was used as a basis. The C_3 operator has a trace of minus one ($2 \cos(2\pi/3)$). All other operators except E have a trace of zero. Thus, the eight Si–C wagging modes possess symmetries E , T_1 , and T_2 . However, the molecular rotations (T_1) are also included in the Si–C wagging modes. When the three molecular rotations are subtracted out, it is seen that the five C–Si–C bending modes possess symmetries E and T_2 . By combining the results of the Gaussview program [24] with the symmetry considerations, vibrational frequency assignments were made with a high degree of confidence.

3. Results and discussion

Tables 1–3 contain the calculated vibrational frequencies for $\text{Si}(\text{CCH})_4$ calculated at the Hartree–Fock, B3LYP and MP2 levels of theory, respectively. A set of correction factors for the different types of vibrational modes was calculated, following a procedure that was previously proposed [26].

Table 1
Fundamental normal modes of Si(CCH)₄ calculated at the Hartree–Fock level of theory using the standard 6-31G* basis set

| Symmetry | Normal mode | Calculated frequency | IR ^a intensity | Raman ^b activity | Assignment | Experimental frequency [15] | Corrected ^c frequency |
|-----------------------|-------------|----------------------|---------------------------|-----------------------------|--------------|-----------------------------|----------------------------------|
| <i>A</i> ₁ | ν_1 | 3654 | IR inactive | 75 | C–H stretch | 3298 | 3298 |
| | ν_2 | 2341 | | 128 | C≡C stretch | 2054 | 2053 |
| | ν_3 | 527 | | 9 | Si–C stretch | 530 | 518 |
| <i>E</i> | ν_4 | 847 | IR inactive | 6 | C–H bend | 679 | 679 |
| | ν_5 | 409 | | 24 | Si–C≡C bend | 357 | 359 |
| | ν_6 | 92 | | 17 | C–Si–C bend | 102 | 95 |
| <i>T</i> ₁ | ν_7 | 846 | IR inactive | Raman inactive | C–H bend | 679 | 678 |
| | ν_8 | 269 | | | Si–C≡C bend | – | 236 |
| <i>T</i> ₂ | ν_9 | 3654 | 45 | 26 | C–H stretch | 3298 | 3298 |
| | ν_{10} | 2343 | 18 | 114 | C≡C stretch | 2054 | 2055 |
| | ν_{11} | 735 | 277 | 3 | Si–C stretch | 707 | 723 |
| | ν_{12} | 848 | 128 | 3 | C–H bend | 679 | 680 |
| | ν_{13} | 443 | 69 | 2 | Si–C≡C bend | 392 | 389 |
| | ν_{14} | 120 | 1 | 9 | C–Si–C bend | 115 | 124 |

^a Units of IR intensity are km/mol.

^b Units of Raman scattering activity are Å⁴/amu.

^c Raw calculated frequencies multiplied by the correction factors in Table 4.

Table 2
Fundamental normal modes of Si(CCH)₄ calculated at the DFT (B3LYP) level of theory using the standard 6-31G* basis set

| Symmetry | Normal mode | Calculated frequency | IR ^a intensity | Raman ^b activity | Assignment | Experimental frequency [15] | Corrected ^c frequency |
|-----------------------|-------------|----------------------|---------------------------|-----------------------------|--------------|-----------------------------|----------------------------------|
| <i>A</i> ₁ | ν_1 | 3479 | IR inactive | 99 | C–H stretch | 3298 | 3298 |
| | ν_2 | 2167 | | 347 | C≡C stretch | 2054 | 2054 |
| | ν_3 | 506 | | 11 | Si–C stretch | 530 | 517 |
| <i>E</i> | ν_4 | 688 | IR inactive | 1 | C–H bend | 679 | 682 |
| | ν_5 | 373 | | 18 | Si–C≡C bend | 357 | 359 |
| | ν_6 | 84 | | 17 | C–Si–C bend | 102 | 95 |
| <i>T</i> ₁ | ν_7 | 685 | IR inactive | Raman inactive | C–H bend | 679 | 679 |
| | ν_8 | 245 | | | Si–C≡C bend | – | 236 |
| <i>T</i> ₂ | ν_9 | 3479 | 50 | 38 | C–H stretch | 3298 | 3298 |
| | ν_{10} | 2168 | 89 | 98 | C≡C stretch | 2054 | 2054 |
| | ν_{11} | 711 | 329 | 1 | Si–C stretch | 707 | 726 |
| | ν_{12} | 682 | 4 | 3 | C–H bend | 679 | 676 |
| | ν_{13} | 406 | 46 | 2 | Si–C≡C bend | 392 | 390 |
| | ν_{14} | 110 | 1 | 9 | C–Si–C bend | 115 | 124 |

^a Units of IR intensity are km/mol.

^b Units of Raman scattering activity are Å⁴/amu.

^c Raw calculated frequencies multiplied by the correction factors in Table 4.

Table 3

Fundamental normal modes of Si(CCH)₄ calculated at the MP2 level of theory using the standard 6-31G* basis set

| Symmetry | Normal mode | Calculated frequency | IR ^a intensity | Raman ^b activity | Assignment | Experimental frequency [15] | Corrected ^c frequency |
|-----------------------|-------------|----------------------|---------------------------|-----------------------------|--------------|-----------------------------|----------------------------------|
| <i>A</i> ₁ | ν_1 | 3499 | IR inactive | 131 | C–H stretch | 3298 | 3298 |
| | ν_2 | 2060 | | 284 | C≡C stretch | 2054 | 2053 |
| | ν_3 | 512 | | 11 | Si–C stretch | 530 | 516 |
| <i>E</i> | ν_4 | 603 | IR inactive | 0 | C–H bend | 679 | 682 |
| | ν_5 | 344 | | 14 | Si–C≡C bend | 357 | 356 |
| | ν_6 | 75 | | 17 | C–Si–C bend | 102 | 97 |
| <i>T</i> ₁ | ν_7 | 598 | IR inactive | Raman inactive | C–H bend | 679 | 677 |
| | ν_8 | 198 | | | Si–C≡C bend | – | 205 |
| <i>T</i> ₂ | ν_9 | 3499 | 56 | 46 | C–H stretch | 3298 | 3298 |
| | ν_{10} | 2063 | 93 | 46 | C≡C stretch | 2054 | 2055 |
| | ν_{11} | 721 | 284 | 2 | Si–C stretch | 707 | 727 |
| | ν_{12} | 599 | 77 | 0 | C–H bend | 679 | 678 |
| | ν_{13} | 380 | 36 | 1 | Si–C≡C bend | 392 | 393 |
| | ν_{14} | 94 | 1 | 9 | C–Si–C bend | 115 | 121 |

^a Units of IR intensity are km/mol.^b Units of Raman scattering activity are Å⁴/amu.^c Raw calculated frequencies multiplied by the correction factors in Table 4.

The correction factors are obtained by taking the average of the ratios between the computed and experimental frequencies for a particular type of motion. There is very little variation in the ratios for all of the modes within a motion type. Also the three methods, Hartree–Fock, B3LYP, and MP2 produce consistent results. This indicates that the procedure should lead to reliable predictions. The computed correction factors calculated at the Hartree–Fock, B3LYP and MP2 levels of theory are presented in Table 4. These correction factors were used to generate the predicted frequencies in the last column of Tables 1–3.

Fig. 2 presents a view of the normal modes of Si(CCH)₄ using the NCAPLOT utility in SPIROVIB [27]. The corrected DFT frequencies of Si(CCH)₄ are presented also. The choice of internal coordinates for a normal mode analysis is always somewhat arbitrary. However, the above set is complete and matches well with the motions observed using the Gaussview program. The assignment of the normal modes in Si(CCH)₄ was straightforward and relatively unambiguous.

Table 5 contains the bond length parameters for Si(CCH)₄. Due to the high symmetry of this

molecule (*T_d*) the geometry is completely specified by three bond lengths. Experimental values were not available for comparison. Fig. 3 presents selected molecular orbitals from the Hartree–Fock generated using the Chem3D [28] software package. For brevity, the atomic core orbitals have been omitted. The π-bonding of the C≡C groups is very evident in orbitals 26–33. The π-bonding contributes two bonds to each of the C≡C groups. The fact that each C≡C group gets a single σ-bond from orbitals 17–25 is more difficult to see from Fig. 3. The bondlengths are consistent with a triple

Table 4

Correction factors for Si(C≡C–H)₄ using standard 6-31G* basis set

| | Hartree–Fock | DFT (B3LYP) | MP2 |
|--------------|--------------|-------------|--------|
| C–H stretch | 0.9026 | 0.9480 | 0.9426 |
| C≡C stretch | 0.8770 | 0.9476 | 0.9964 |
| Si–C stretch | 0.9838 | 1.0209 | 1.0079 |
| C–H bend | 0.8017 | 0.9913 | 1.1317 |
| Si–C≡C bend | 0.8789 | 0.9613 | 1.0347 |
| C–Si–C bend | 1.0335 | 1.1299 | 1.2917 |

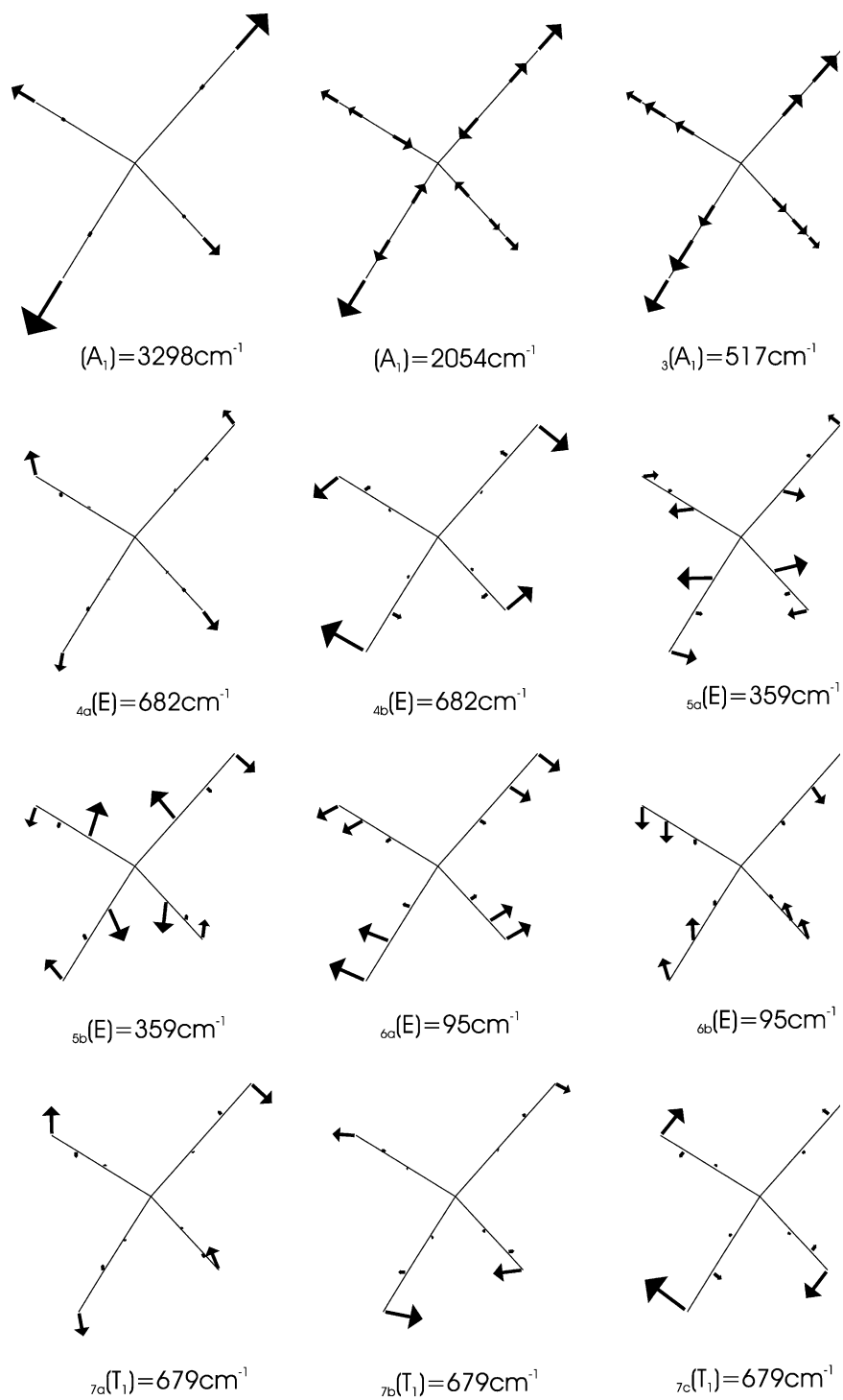


Fig. 2. Normal modes of Si(CCH)₄.

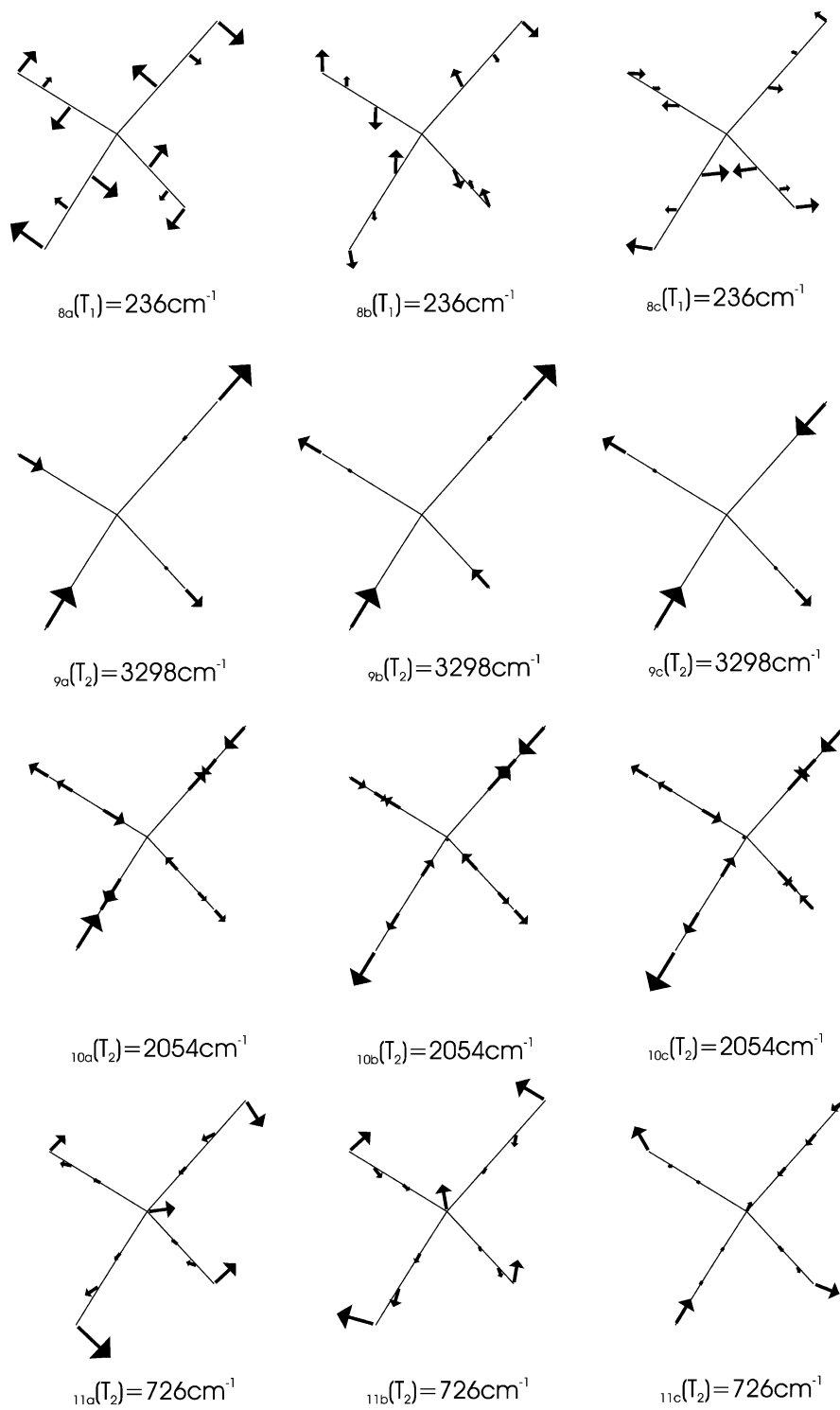


Fig. 2 (continued)

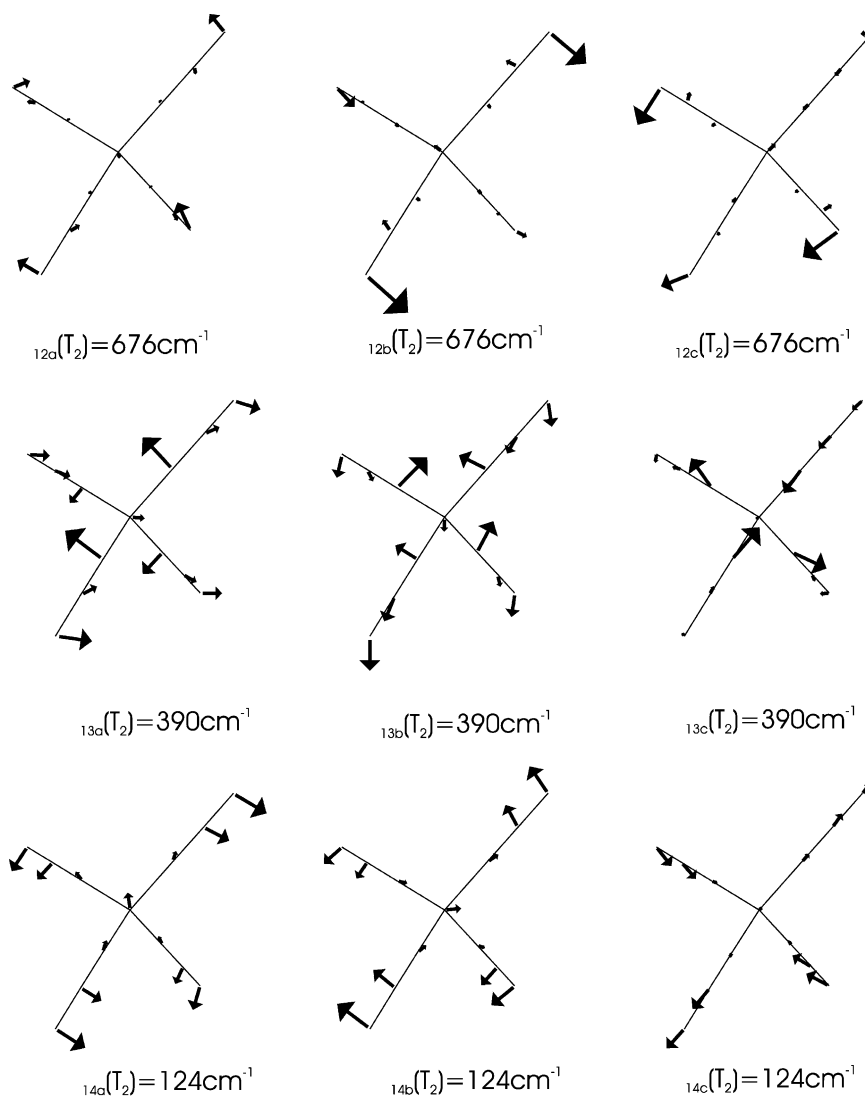


Fig. 2 (continued)

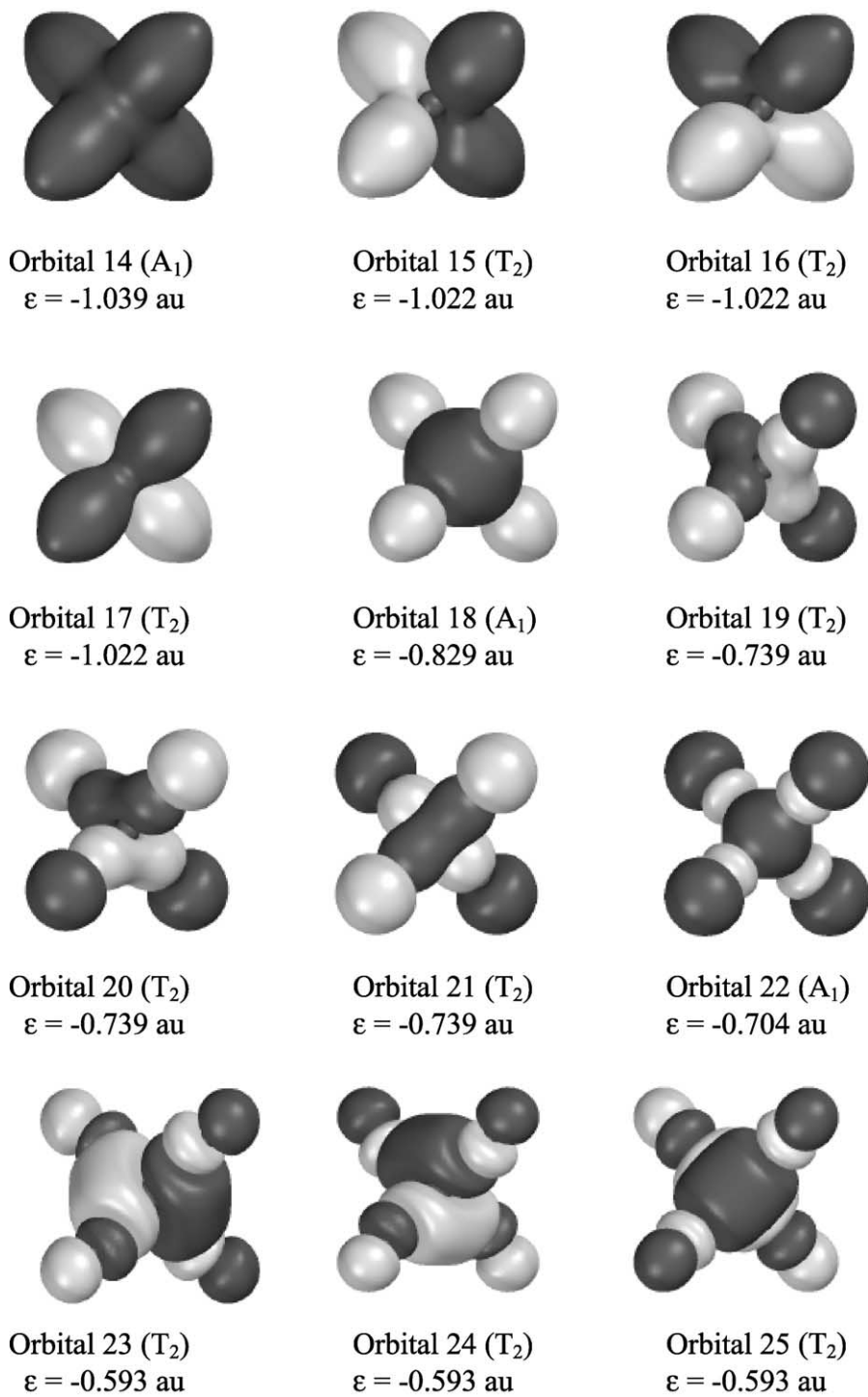
bond between the two carbons in the $\text{C}\equiv\text{C}$ group and single bonds everywhere else.

Table 5
Geometric parameters for $\text{Si}(\text{CCH})_4$. Distances are presented in pm

| | Hartree–Fock | DFT(B3LYP) | MP2 |
|--------------------------|--------------|------------|-------|
| Si–C | 182.9 | 182.4 | 182.0 |
| $\text{C}\equiv\text{C}$ | 119.3 | 121.4 | 122.9 |
| C–H | 105.8 | 106.8 | 106.9 |

4. Summary and conclusions

A normal mode analysis of $\text{Si}(\text{CCH})_4$ was completed with good results. Normal modes were calculated using the Hartree–Fock, DFT (B3LYP) and MP2 methods using the standard 6-31G* basis. Computed vibrational modes were compared against

Fig. 3. Selected molecular orbitals of $\text{Si}(\text{CCH})_4$.

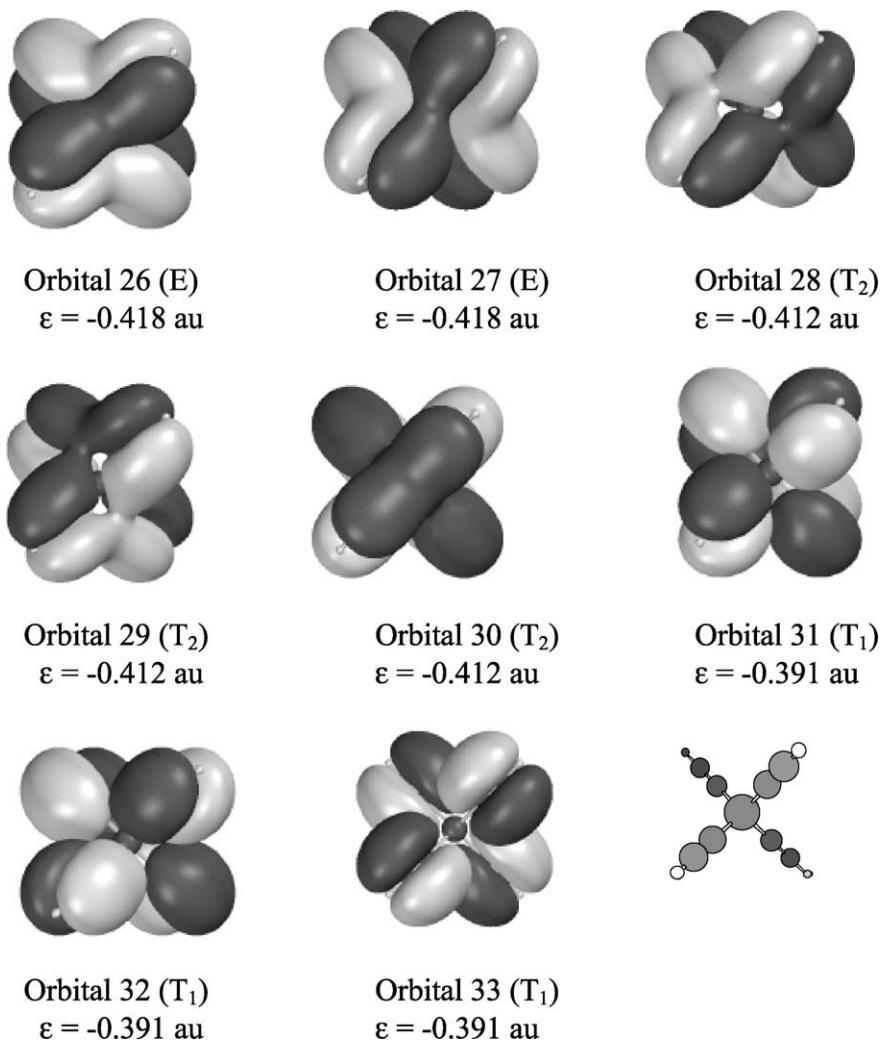


Fig. 3 (continued)

available experimental information that exists in the literature. All normal modes were successfully assigned to one of six types of motion (Si–C stretch, C≡C stretch, C–H stretch, C≡C–H bend, Si–C≡C bend, and C–Si–C bend) predicted by a group theoretical analysis. Infrared and Raman intensities calculated and reported.

Acknowledgements

The author would like to express appreciation to the Joint Science and Technology Panel for Chemical

and Biological Defense (JSTPCBD), for support of this work as part of the Chemical Imaging Sensor program.

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