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Vibrational Zero-Point Energy of Organosilicon Compounds

Mahmoud Rahal and Abdeslam El Hajbi

Abstract

In this chapter, the calculation of vibrational zero-point energies (ZPEs) of organosilicon compounds is reported. An empirical formula is used. This relationship was determined by relating vibrational zero-point energy to the nature and type of bonds forming the molecule. The calculated vibrational zero-point energies for several organosilicon derivatives belonging to different categories of compounds correlate well with the reported available values. In addition, the comparison of these results with the scaled values obtained using methods of quantum chemistry (AM1, ab initio, and by a similar empirical approach) indicates the reliability of our empirical model to reproduce vibrational zero-point energy of organosilicon compounds.

Keywords: zero-point energy (ZPE), empirical ZPE, organosilicon compounds, theory-experiment correlation

1. Introduction

In the formulas of statistical mechanics, the vibrational zero-point energy (ZPE) constitutes the most significant term for the correction of the total energy of the molecules. ZPE (**Figure 1**) is a positive, additive, collective internal property and can be approximated by the harmonic formula:

$$ZPE = \frac{R}{2} \sum_{i=1}^{3N-6} \left(\frac{hc}{k} \right) \nu_i \quad (1)$$

where the sum runs for the $3N-6$ normal frequencies (ν_i) in the case of a nonlinear molecule of N atoms, R is the gas constant, k is the Boltzmann constant, c is the speed of light, and h is the Planck constant.

Thus, for a precise calculation of the enthalpies of formation, the use of a reliable method to determine vibrational zero-point energy appears necessary. The experimental determination of the ZPE requires the knowledge of all normal vibration mode frequencies by infrared and Raman method. In certain cases [1, 2], these methods involve experimental difficulties, and they are not feasible because of the existence of overtones and combination frequencies in the molecular spectra. Also, this experimental determination becomes even more difficult for the hazardous [3–6] compounds which may be difficult to handle in air [7–9]. Otherwise, vibrational zero-point energy can be obtained by computing molecular vibrational frequencies with quantum chemistry methods [10–14]. However, such calculations

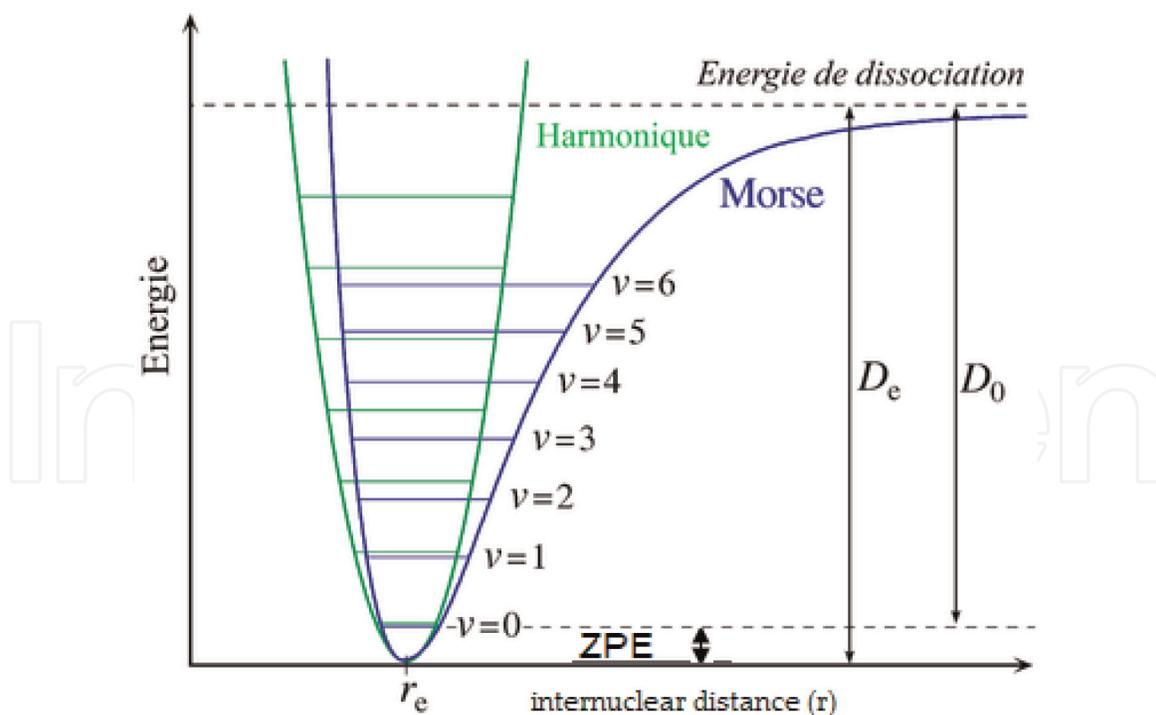


Figure 1.
The Morse potential and harmonic oscillator potential.

can be very demanding in terms of computer time and disk space for large molecules and thus in daily practice; they are not usable by the chemist and technologist. Moreover, the theoretical vibrational frequencies are generally overestimated. The neglect of anharmonicity effects in the theoretical treatment constitutes the major source of this disagreement [15]. To solve this problem, we use an empirical correction factor which depends on the method, the basis set, the property to be determined (ZPE, $H_{\text{vib}}(T)$, $S_{\text{vib}}(T)$, etc.), and sometimes the type of vibrations (low-frequency vibrations, high-frequency vibrations) [16]. For this reason and based on the fact that vibrational zero-point energy (ZPE) can be described with a good approximation by additivity rules [17–19], several researchers have sought to develop empirical rules to determine the vibrational ZPE.

Thus, to estimate ZPEs of molecules without using quantum chemistry methods, several empirical rules [20–24] have been developed in recent years. These additivity rules are classified into two categories: the first methods are based on the atomic contributions, while the second one are based on the contributions of bonds or groupings. The first category takes into account each of the atoms present in a given molecule. Thus, the studied property is evaluated as the sum of the atomic contributions. In the second approach, the molecule is divided into different fragments (bonds or groups). When a fragment is present in one molecule or another, the value of its contribution remains the same.

Using the first approach based on the additivity of atomic contributions, Flanigan et al. [20] have calculated the vibrational zero-point energy (ZPE) of hydrocarbons C_nH_m through the simple empirical relationship:

$$\text{ZPE} = 2n + 7m \text{ (kcal/mol)} \quad (2)$$

In 1985, using the least squares method, Schulman and Disch established a similar empirical relationship [25]. They determined the contributions of carbon and hydrogen atoms to estimate the vibrational zero-point energy of hydrocarbons. The relation thus obtained is written as follows:

$$\text{ZPE} = 3.88n + 7.12m - 6.19 \text{ (kcal/mol)} \quad (3)$$

Then, this last formula has been extended to polyatomic molecular systems containing nitrogen, oxygen, chlorine, fluorine [26], bromine, sulfur [27], and silicon [28]. More recently, in order to obtain the ZPE of organophosphorus compounds, we have determined the increment of the phosphorus atom [29].

Eq. (3) takes now the form

$$\text{ZPE} = \sum_i^N N_i X_i - 6.19 \text{ (kcal/mol)} \quad (4)$$

where N is the number of kinds of atom in the molecule; N_i is the number of atoms of type i; X_i is the increment of the atom i.

In this context, Grice and Politzer [1] have also developed a simple linear relationship between the ZPE and molecular stoichiometry for several organic compounds.

In 2003, Ruzsinszky et al. [30] examined the relationship between ZPE values and partial charges calculated at the functional density theory (DFT) level. The results show that atomic partial charges can be used to estimate ZPEs with high accuracy. However, this method still requires to quantum chemical calculations to estimate the ZPE of the molecules.

The sum $\text{ZPE} + H(T) - H(0)$ was studied by Fliszar et al. [13]. They found that this quantity obeyed to certain additivity rules, and they proved its correlation with the structural characteristics of the molecule, more precisely the number of atoms and the degree of branching in the case of hydrocarbons.

For the approach based on the contributions of bonds or groupings, Pitzer [31] was interested in the computation of the thermodynamic functions for gaseous hydrocarbons; he attributed an empirical value to each mode of vibration. In an n-paraffin study, Cottrell [32] found that the ZPE increases gradually with successive additions of the methylene group (CH_2). Later, Pitzer and Catalano [33] assigned the constant 17.7 kcal/mol per unit of CH_2 to calculate vibrational zero-point energy of these compounds.

The empirical estimation of vibrational zero-point energies of halomethanes, ethylene, haloethylenes, methane isotopes, and benzene has been the subject of several studies by Bernstein [34–36]. He took into consideration the contributions of the internal coordinates and the interactions between them. A few years later, three empirical parameters were determined by Fujimoto and Shingu [37] to calculate the ZPEs of hydrocarbons with a precision similar to that of Bernstein, which are the contributions of C—C bonds, C—H bonds, and carbon chain.

In 1980, based on a system of harmonic oscillators, Oi and his collaborators published some papers [17–19] which describe the theoretical foundation showing the additivity of ZPE estimates.

Still in the framework of the estimates based on the contributions of the bonds or groupings, we established in 2001 an original empirical relation [38] which makes it possible to calculate the ZPE of the organic compounds. This rule was determined by linking the ZPE to the nature and type of bonds forming the molecular system. The established empirical formula is as follows:

$$\text{ZPE}(\text{emp.}) = \sum_i^P N_i \times BC_i - 2.09 \text{ (kcal/mol)} \quad (5)$$

where P is the number of bonds in the molecule; N_i is the number of bonds of type i; BC_i is the contribution of the bond i to the ZPE.

This established empirical relationship also makes it possible to calculate the vibrational zero-point energies of the aromatic derivatives with accuracy, provided that the empirical values are adjusted by the following equation:

$$\text{ZPE} = 1.08 \cdot \text{ZPE (empirical)} - 1.07(\text{kcal/mol}) \quad (6)$$

This adjustment can be explained by the fact that in aromatic compounds, the bonds in the aromatic nucleus are all identical because of the conjugation, whereas in our model it has been assumed that there are three C—C single bonds and three C=C double bonds.

Eq. (5) was used to calculate the ZPEs of several organic compounds belonging to different classes of compounds (hydrocarbons, oxygen compounds, nitrogen compounds, chlorinated compounds, brominated compounds, fluorinated compounds, sulfur compounds, aromatic compounds, etc.). Thus, the contributions of the bonds C—H, N—H, O—H, S—H, C—O, C—C, C—N, C—S, N—N, C—F, C—Cl, C=C, C=N, C=O, C=S, C≡C, and C≡N have been determined. To extend our model to brominated compounds, we have determined in 2004 the contribution of the C—Br bond [39] and incorporated it into our empirical formula. The calculated vibrational zero-point energies for 38 compounds containing this bond (C—Br) correlate well with experimental values. In addition, we have extended the field of application of this empirical model to organophosphorus compounds (III). The bond contributions of P—F, P—C, P—H, P—Cl, P—S, P—N, and P—O were determined [29]. The results obtained for 101 chemical systems containing these bonds are in good agreement with experimental values. The estimated ZPEs were compared with the results obtained by application of quantum chemistry methods at the level *ab initio* (HF/6-31G^{*}) and DFT(B3LYP/6-31G^{*}), in all cases with satisfactory results.

More recently [40], to calculate vibrational zero-point energies (ZPEs) of organophosphorus compounds (V), we determined the contributions of the bonds P=O and P=S and incorporated them into our empirical formula. Comparison of the results obtained for more than 80 organophosphorus compounds (V) with the reported values and with those obtained by *ab initio* (HF/6-31G^{*}) and DFT(B3LYP/6-31G^{*}) shows the reliability of the empirical approach.

In this chapter, we describe the results obtained in the case of organosilicon compounds. We present the values obtained for the contributions of the Si—H, Si—C, Si—Cl, Si—O, and Si—Si bonds which make it possible to calculate the vibrational zero-point energies of the silicon compounds. The results thus obtained are compared firstly with the available experimental values, secondly to the values obtained by the methods of the quantum chemistry at the semiempirical (AM1) and DFT(B3LYP/6-31G^{*}) level, and finally to the results derived from a similar approach based on simple atom additivity.

2. Computational methods

The theoretical calculations were performed at the semiempirical [41] and density functional theory [42, 43] levels using, respectively, the AM1 method and B3LYP [44–46] with 6-31G^{*} basis set which were implemented in the Gaussian03W program [47, 48]. The molecular geometries were optimized without any symmetry constraints, and the harmonic frequencies were calculated to ensure that the structures really corresponded to a true local minimum energy on the potential energy surface in the first time and to determine the vibrational zero-point energies in the second time.

3. Results and discussion

3.1 Estimation based on simple bond additivity

Using the least squares method, we have determined the contributions of the Si—H, Si—C, Si—Cl, Si—O, and Si—Si bond by correlating, for a population of molecules, the values of the vibrational zero-point energies obtained experimentally and those obtained by Eq. (5). The values of the contributions obtained for the studied bonds and those already established [29, 38–40, 49] are given in **Table 1**.

To test the reliability of the extended empirical model, we applied it to 91 silicon compounds different from those used in the compilation of contributions. This group of molecules contains different classes such as silanes, siloxanes, chlorosilanes, silyl ethers, silanols, silyl chlorides, cyclic organosilicon, and aromatic organosilicon.

The ZPEs obtained are recorded in **Table 2**. These results show a very good agreement between the calculated and the experimental values. Indeed, the average error is of the order of 1.51 kcal/mol for the 91 molecular systems for which experimental or ab initio (HF/6-31G^{*}) data are available. However, the ZPEs calculated for 3-phenyl-1,3-thiasilacyclohexane, 1-phenyl-1-silacyclohexane, 3-methyl-3-phenyl-1,3-thiasilacyclohexane, 1-methyl-1-phenyl-1-silacyclohexane, and (C₆H₅)₃SiOH are underestimated.

This is due to the presence of the aromatic ring in these organosilicon compounds [29, 38–40]. Nevertheless, the adjustment of empirical ZPE values by Eq. (6) leads to a decrease of the mean error which becomes 1.02 kcal/mol (i.e., 1.98%).

The curve of correlation between the experimental and empirical values (**Figure 2**) appears very satisfactory, the slope is close to unity (0.99), the correlation coefficient is equal to 0.9994, and standard deviation is 1.2. The statistical data concerning the regression curves $ZPE_{\text{exp}} = aZPE_{\text{theor}} + b$ and $ZPE_{\text{exp}} = aZPE_{\text{theor}}$ are summarized in **Table 3**. The use of this data for the adjustment of the empirical values of vibrational zero-point energies (ZPEs) reduces the mean error to 0.9 kcal/mol.

3.2 Estimation based on simple atom additivity

In order to be able to compare the results obtained by the application of the empirical formula based on bond contribution additivity (Eq. (5)) to those obtained by the approach based on atomic contribution additivity, we have grouped in **Table 2** the values of vibrational zero-point energies computed with the extended rule of Schulman and Disch (Eq. (4)). The increment of the silicon atom was calculated by AbdulHussain and Fleifel [28]. The value of this increment is shown in **Table 4**, with those previously published [25–29] for the atoms H, C, O, N, Cl, F, Br, S, and P. Note that the formula of Schulman and Disch was established on the basis that the structural isomers of organic compounds have almost the same value of ZPE. However, the difference can reach 4 kcal/mol [9]. The results obtained by the method based on the additivity of the atomic contributions show, for the 91 silicon compounds, an average error of 2.53 (6.9%). The correlation between the experimental and calculated values by the Schulman-Disch extended formula is shown in **Figure 3**. The statistical parameters obtained in this case are a correlation coefficient of 0.9972, a slope of 0.95, and a standard deviation of 2.45. Using the regression curves (**Table 3**) for adjusting the calculated values permits to reduce the

| Bond | Bond contribution (BC _i) | Ref. |
|-------|--------------------------------------|------|
| C—H | 7.5877 | [38] |
| N—H | 7.2013 | [38] |
| O—H | 7.2964 | [38] |
| S—H | 5.6921 | [38] |
| C—O | 2.6985 | [38] |
| C—C | 2.0751 | [38] |
| C—N | 4.1409 | [38] |
| C—S | 1.4403 | [38] |
| N—N | 6.8372 | [38] |
| C—F | 3.3078 | [38] |
| C—Cl | 2.2051 | [38] |
| C=C | 2.6501 | [38] |
| C=N | 3.8852 | [38] |
| C=O | 3.9343 | [38] |
| C=S | 2.7319 | [38] |
| C≡C | 4.4125 | [38] |
| C≡N | 4.8169 | [38] |
| C—Br | 1.9837 | [39] |
| Si—H | 5.8011 | [49] |
| Si—C | 0.3593 | [49] |
| Si—Cl | 1.7690 | [49] |
| Si—O | 1.3335 | [49] |
| Si—Si | -1.4548 | [49] |
| P—H | 6.6486 | [29] |
| P—C | 1.4190 | [29] |
| P—O | 1.8406 | [29] |
| P—Cl | 1.6717 | [29] |
| P—N | 0.9873 | [29] |
| P—F | 2.1507 | [29] |
| P—S | 1.5424 | [29] |
| P=O | 2.4032 | [40] |
| P=S | 0.6131 | [40] |

Table 1.
Bond contributions to ZPE (in kcal/mol).

mean error to 1.68 (4.0%) if the intercept is different from 0 ($b \neq 0$) to 2.28 (7.0%) if $b = 0$. These results are slightly less good than those obtained by our approach.

3.3 Quantum chemical calculations

To compare the results obtained by our empirical relationship with those obtained by quantum chemistry methods, we have calculated vibrational zero-point

| Compound | ZPE (kcal/mol) | | | | | Ref. |
|------------------------------------------------------------------------------------------------------|----------------|----------------------|------------------|------------------------------|----------------------|------|
| | Exp. | Eq. (5) ^a | AM1 ^b | B3LYP/ 6-31G ^c | Eq. (4) ^d | |
| SiHCl ₃ | 9.29 | 9.02 | 7.26 | 8.54 | 4.08 | [50] |
| SiH ₃ Cl | 17.01 | 17.08 | 14.50 | 15.88 | 13.88 | [51] |
| SiH ₂ Cl ₂ | 13.31 | 13.05 | 11.00 | 12.42 | 8.98 | [51] |
| SiH ₄ | 19.90 | 21.11 | 17.71 | 18.87 | 18.78 | [52] |
| C ₄ H ₁₂ Si (diethylsilane) | 90.68 | 90.26 | 87.36 | 89.65 | 91.26 | [52] |
| C ₆ H ₁₆ Si (triethylsilane) | 125.98 | 124.83 | 121.78 | 124.68 | 127.50 | [52] |
| C ₈ H ₂₀ Si (tetraethylsilane) | 161.23 | 159.40 | 156.08 | 159.52 | 163.74 | [52] |
| CH ₄ SiCl ₂ (dichloromethylsilane) | 27.09 | 27.67 | 25.27 | 26.67 | 27.10 | [53] |
| CH ₃ SiCl (chloromethylsilane) | 32.48 | 34.40 | 30.62 | 33.60 | 32.00 | [53] |
| CH ₆ Si (methyl silane) | 37.21 | 38.44 | 35.51 | 36.99 | 36.90 | [54] |
| C ₃ H ₆ Si (1-silylpropyne) | 43.96 | 42.85 | 42.71 | 43.64 | 44.66 | [55] |
| CH ₂ Br(CH ₃) ₂ SiH (bromomethyl dimethyl silane) | 66.33 | 67.47 | 64.75 | 66.89 | 67.62 | [56] |
| H ₃ SiSiH ₃ | 30.08 | 31.26 | 27.27 | 29.69 | 29.51 | [57] |
| C ₁₁ H ₁₆ Si (1-phenyl-1-silacyclohexane) | 151.56 | 151.30 ^e | 144.93 | 145.51 | 146.90 | [58] |
| C ₁₀ H ₁₄ SiS (3-phenyl-1,3-thiasilacyclohexane) | 134.31 | 133.54 ^e | 127.60 | 137.91 | 130.65 | [58] |
| C ₁₂ H ₁₈ Si (1-methyl-1-phenyl-1-silacyclohexane) | 169.58 | 170.00 ^e | 161.97 | 162.84 | 165.02 | [58] |
| C ₁₁ H ₁₆ SiS (3-methyl-3-phenyl-1,3-thiasilacyclohexane) | 152.32 | 152.24 ^e | 144.66 | 146.27 | 148.77 | [58] |
| H ₂ ClSiSiH ₃ | 27.48 | 27.23 | 23.89 | 26.34 | 24.61 | [59] |
| HCl ₂ SiSiH ₃ | 23.63 | 23.20 | 20.29 | 22.63 | 19.71 | [59] |
| H ₂ ClSiSiH ₂ Cl | 23.94 | 23.20 | 20.64 | 22.93 | 19.71 | [59] |
| Cl ₃ SiSiH ₃ | 19.47 | 19.17 | 16.53 | 18.62 | 14.81 | [59] |
| HCl ₂ SiSiHCl ₂ | 16.09 | 15.13 | 13.29 | 15.43 | 9.91 | [59] |
| Cl ₃ SiSiH ₂ Cl | 15.90 | 15.13 | 13.14 | 15.18 | 9.91 | [59] |
| Cl ₃ SiSiHCl ₂ | 11.95 | 11.10 | 9.56 | 11.37 | 5.01 | [59] |
| Cl ₃ SiSiCl ₃ | 7.77 | 7.07 | 5.85 | 7.31 | 0.11 | [59] |
| Si ₄ H ₁₀ (n-butasilane) | 50.50 | 51.56 | 46.54 | 50.82 | 50.97 | [60] |
| Si ₅ H ₁₂ (n-pentasilane) | 60.93 | 61.70 | 56.14 | 61.23 | 61.70 | [60] |
| Si ₆ H ₁₄ (n-hexasilane) | 71.39 | 71.85 | 65.80 | 71.85 | 72.43 | [60] |
| Si ₇ H ₁₆ (n-heptasilane) | 81.85 | 82.00 | 81.57 | 82.43 | 83.16 | [60] |
| Si ₈ H ₁₈ (n-octasilane) | 92.54 | 92.15 | 85.11 | 92.90 | 93.89 | [60] |
| Si ₉ H ₂₀ (n-nonasilane) | 102.75 | 102.29 | 94.71 | 103.47 | 104.62 | [60] |
| Si ₁₀ H ₂₂ (n-decasilane) | 113.33 | 112.44 | 104.26 | 114.00 | 115.35 | [60] |
| C ₂ H ₅ SiCl (gauche vinyl silyl chloride) | 37.31 | 37.05 | 35.75 | 37.14 | 35.88 | [61] |
| C ₂ H ₅ SiCl (cis vinyl silyl chloride) | 37.31 | 35.70 | 34.19 | 37.14 | 35.88 | [61] |
| C ₂ H ₆ SiCl ₂ (2-chloroethylsilyl chloride C-gauche-Si-trans (Gt)) | 46.71 | 46.27 | 43.99 | 46.00 | 45.22 | [62] |
| C ₂ H ₆ SiCl ₂ (2-chloroethylsilyl chloride C-trans-Si-trans (Tt)) | 46.62 | 46.27 | 44.01 | 46.03 | 45.22 | [62] |

| Compound | ZPE (kcal/mol) | | | | | Ref. |
|---------------------------------------------------------------------------------------------------------|----------------|----------------------|------------------|------------------------------|----------------------|------|
| | Exp. | Eq. (5) ^a | AM1 ^b | B3LYP/ 6-31G ^c | Eq. (4) ^d | |
| C ₂ H ₆ SiCl ₂ (2-chloroethylsilyl chloride C-trans-Si-gauche (Tg)) | 46.46 | 46.27 | 44.30 | 46.07 | 45.22 | [61] |
| C ₂ H ₇ SiCl (1-chloroethylsilane) | 49.70 | 50.30 | 47.41 | 49.27 | 50.12 | [63] |
| C ₂ H ₇ SiCl (gauche ethyl chlorosilane) | 51.38 | 51.65 | 49.18 | 51.11 | 50.12 | [64] |
| C ₂ H ₇ SiCl (trans ethyl chlorosilane) | 51.42 | 51.65 | 49.19 | 51.10 | 50.12 | [65] |
| H ₃ SiOH | 24.21 | 23.94 | 21.77 | 23.22 | 22.18 | [66] |
| C ₃ H ₆ Cl ₂ Si (1,1-dichlorosilacyclobutane) | 49.65 | 51.84 | 51.55 | 52.36 | 49.10 | [67] |
| C ₂ H ₈ Si (ethylsilane) | 54.79 | 55.69 | 52.75 | 54.54 | 55.02 | [68] |
| C ₃ H ₉ SiCl (chlorotrimethylsilane) | 68.16 | 69.05 | 66.13 | 67.91 | 68.24 | [69] |
| C ₃ H ₁₀ Si (trimethylsilane) | 71.95 | 73.08 | 70.20 | 71.86 | 73.14 | [69] |
| C ₄ H ₁₂ OSi (methoxytrimethylsilane) | 93.41 | 94.07 | 90.81 | 92.94 | 94.66 | [69] |
| (CH ₃) ₃ SiOH (trimethylsilanol) | 75.35 | 75.91 | 73.33 | 75.47 | 73.14 | [69] |
| C ₃ H ₁₀ Si (gauche-n-propylsilane) | 72.29 | 72.94 | 70.00 | 71.89 | 73.14 | [70] |
| C ₃ H ₁₀ Si (anti-n-propylsilane) | 72.07 | 72.94 | 70.00 | 71.78 | 73.14 | [70] |
| C ₃ H ₁₀ Si (trans ethylmethylsilane) | 72.14 | 73.01 | 70.21 | 72.07 | 73.14 | [71] |
| C ₃ H ₁₀ Si (gauche ethylmethylsilane) | 72.27 | 73.01 | 70.30 | 72.20 | 73.14 | [71] |
| C ₄ H ₁₀ Si (cis methylsilylcyclopropane) | 76.81 | 77.09 | 74.07 | 75.51 | 77.02 | [72] |
| C ₄ H ₁₀ Si (gauche methylsilylcyclopropane) | 76.44 | 77.09 | 74.10 | 75.45 | 77.02 | [72] |
| C ₃ H ₁₂ Si ₂ (1,1,1-trimethyldisilane) | 82.56 | 83.23 | 79.69 | 82.38 | 83.87 | [73] |
| C ₅ H ₁₂ Si (cyclopentylsilane) | 94.60 | 94.34 | 93.21 | 94.05 | 95.14 | [74] |
| C ₆ H ₁₄ Si (cyclohexyl silane (chair- equatorial)) | 112.15 | 111.59 | 110.54 | 111.83 | 113.26 | [75] |
| C ₆ H ₁₄ Si (cyclohexyl silane (chair-axial)) | 112.93 | 111.59 | 110.54 | 112.00 | 113.26 | [75] |
| C ₃ H ₈ Si (allylsilane) | 57.75 | 58.34 | 56.22 | 57.51 | 58.90 | [76] |
| C ₃ H ₈ SiCl ₂ (anti dichloromethyldimethyl silane) | 62.42 | 62.31 | 59.76 | 61.78 | 63.34 | [77] |
| C ₃ H ₈ SiCl ₂ (gauche dichloromethyldimethyl silane) | 61.73 | 62.31 | 59.78 | 61.75 | 63.34 | [77] |
| C ₃ H ₇ SiCl (methylvinyl silyl chloride) | 54.48 | 54.38 | 52.92 | 54.55 | 54.00 | [78] |
| (H ₃ Si) ₂ CCH ₂ | 49.65 | 51.26 | 47.92 | 57.01 | 51.51 | ** |
| ((CH ₃) ₃ Si) ₂ CCH ₂ | 152.56 | 155.19 | 151.46 | 155.08 | 160.23 | ** |
| C ₅ H ₁₂ Si (1,1-dimethyl-1-silacyclobutane) | 93.33 | 94.55 | 93.48 | 94.57 | 95.14 | ** |
| C ₃ H ₈ Si (silacyclobutane) | 59.06 | 59.91 | 59.25 | 59.71 | 58.90 | ** |
| C ₄ H ₁₀ Si (1-methyl-silacyclobutane) | 76.38 | 77.23 | 76.50 | 77.18 | 77.02 | ** |
| Cl ₃ SiCH ₃ | 25.44 | 26.34 | 24.28 | 25.83 | 22.20 | ** |
| Cl ₂ Si(CH ₃) ₂ | 46.36 | 47.69 | 45.17 | 47.17 | 45.22 | ** |
| (CH ₃) ₃ SiCN | 71.85 | 72.45 | 70.99 | 72.59 | 73.95 | ** |
| SiH ₃ CN | 19.27 | 20.49 | 19.36 | 19.98 | 19.59 | ** |
| Si(OH) ₄ | 34.56 | 32.43 | 32.10 | 34.64 | 32.38 | ** |
| HSi(OH) ₃ | 30.79 | 29.60 | 28.85 | 30.88 | 28.98 | ** |

| Compound | ZPE (kcal/mol) | | | | | Ref. |
|------------------------------------------------------------------------------------------|----------------|----------------------|------------------|-------------------------------|----------------------|------|
| | Exp. | Eq. (5) ^a | AM1 ^b | B3LYP/ 6-31G ^{*c} | Eq. (4) ^d | |
| H ₃ SiOSiH ₃ | 32.90 | 35.38 | 30.93 | 33.16 | 32.91 | ** |
| Si(OH) ₃ -O-Si(OH) ₃ | 55.86 | 52.36 | 51.11 | 56.39 | 53.31 | ** |
| C ₂ Si ₂ H ₈ O (1-oxa-2,5-disilacyclopentane) | 56.90 | 56.93 | 55.41 | 57.43 | 54.91 | ** |
| (H ₂ SiO) ₃ (cyclotrisiloxane) | 41.40 | 40.72 | 38.12 | 41.43 | 36.20 | ** |
| (H ₂ SiO) ₄ (cyclotetrasiloxane) | 54.91 | 54.99 | 51.19 | 55.05 | 50.33 | ** |
| (C ₂ H ₅ O) ₄ Si | 171.18 | 174.09 | 170.16 | 172.95 | 177.34 | ** |
| CH ₃ SiH ₂ SiH ₂ CH ₃ | 63.83 | 65.90 | 62.65 | 65.31 | 65.75 | ** |
| H ₃ SiSiH ₂ SiH ₃ | 39.94 | 41.41 | 36.92 | 40.19 | 40.24 | ** |
| (Me ₃ Si) ₂ SiH ₂ | 143.61 | 145.34 | 141.84 | 145.47 | 148.96 | ** |
| ((CH ₃) ₃ Si) ₃ SiH | 205.33 | 207.45 | 204.16 | 208.86 | 214.05 | ** |
| CH ₃ OSi(CH ₃) ₃ | 91.48 | 94.07 | 90.79 | 92.94 | 94.66 | ** |
| Et ₃ SiOH | 126.18 | 127.66 | 125.19 | 128.10 | 130.90 | ** |
| Ph ₃ SiOH | 172.20 | 176.01 ^e | 174.18 | 173.66 | 177.46 | ** |
| nbutyl ₃ SiOH | 228.34 | 231.16 | 228.10 | 231.39 | 239.62 | ** |
| (CH ₃) ₃ SiOSi(CH ₃) ₃ | 134.88 | 139.31 | 133.95 | 137.52 | 141.63 | ** |
| (CH ₃) ₃ SiOCOCH ₃ | 97.34 | 97.38 | 97.00 | 98.80 | 101.94 | ** |
| C ₈ H ₁₆ SiO ₂ (4-trimethylsiloxy-3-penten-2-one) | 134.19 | 137.23 | 134.29 | 135.98 | 142.06 | ** |
| (CH ₃) ₃ SiOCOCH ₃ (trimethylsilyltrifluoroacetate) | 84.22 | 85.17 | 84.27 | 84.87 | 90.39 | ** |
| C ₃ H ₇ SiCl (cis-cyclopropylchlorosilane) | 55.47 | 55.80 | 53.87 | 55.03 | 54.00 | [79] |

^aValues determined by our model.

^bValues scaled by 0.95 [80].

^cValues scaled by 0.96 [80].

^dValues computed by Schulman-Disch extended empirical formula.

^eValues adjusted by Eq. (6).

**Values calculated with HF/6-31G^{*} and scaled by 0.89 [80].

Table 2.

Comparison of computed (empirical Eq. (5), AM1, B3LYP/6-31G^{*}, empirical Eq. (4)) zero-point energy with experimental values.

energies for the same organosilicon compounds using semiempirical (AM1) and DFT(B3LYP/6-31G^{*}) methods. Results are summarized in **Table 2**. To correct calculated ZPEs, the scaling factors of Scott and Radom [80] are used.

Based on these results, the values calculated at the DFT(B3LYP/6-31G^{*}) level are closer to the experimental data than those obtained at the semiempirical (AM1) level. The mean error is 2.50 (5.45%) for AM1, compared to 1.08 (1.86%) for DFT (B3LYP/6-31G^{*}). The correlations obtained between the experimental values and those calculated by using AM1 and DFT methods are represented, respectively, in **Figure 4a** and **b**. Examination of this correlations shows that these methods are able to calculate accurately the zero-point vibration energies of the organosilicon compounds with a small advantage for the DFT method. For the adjustment of calculated ZPEs, the use of the regression line of the form $ZPE_{\text{exp}} = aZPE_{\text{theor}}$ (**Table 3**) permits to reduce the mean error of 2.5–1.83 kcal/mol for AM1 and from 1.08 to 1.06 kcal/mol for DFT(B3LYP/6-31G^{*}). When the intercept is different from zero,

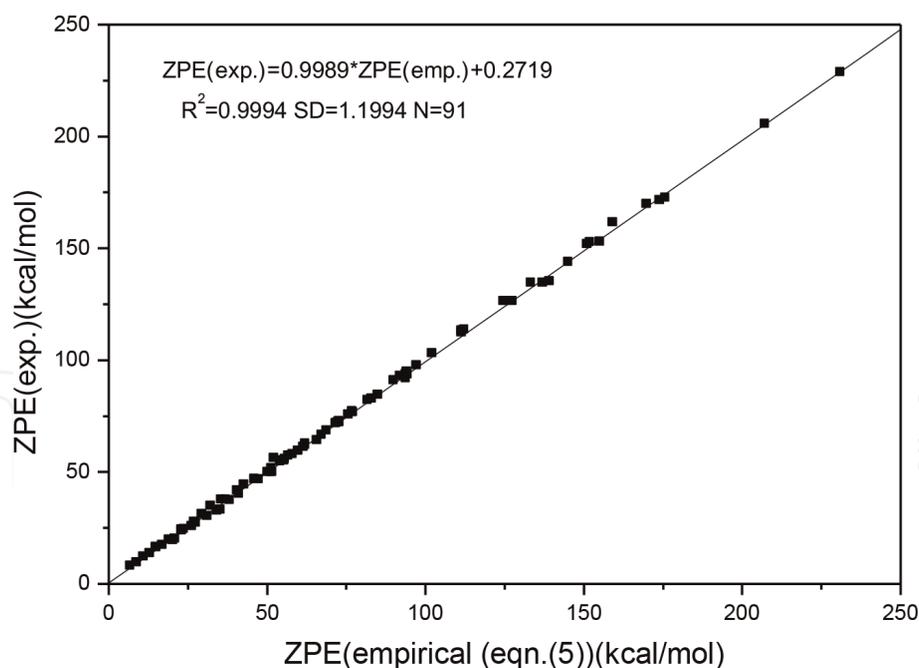


Figure 2.
Correlation between experimental ZPEs and empirical values calculated using Eq. (5).

| Calculation method | Linear model | | | | |
|-----------------------------------------|----------------------------|----------------|--------------------------------|-------|----------------|
| | $ZPE_{exp} = aZPE_{theor}$ | | $ZPE_{exp} = b + aZPE_{theor}$ | | |
| | a | R ² | a | b | R ² |
| Proposed empirical model (Eq. (5)) | 0.993 ± 0.002 | 0.9998 | 0.99 | 0.272 | 0.9994 |
| AM1 | 1.025 ± 0.003 | 0.9992 | 0.95 | 2.212 | 0.9982 |
| DFT (B3LYP/6-31G [*]) | 0.999 ± 0.002 | 0.9996 | 0.95 | 0.304 | 0.9986 |
| Schulman-Disch extended model (Eq. (4)) | 0.984 ± 0.0038 | 0.9986 | 0.95 | 3.545 | 0.9972 |

Table 3.
Coefficients *a*, *b*, and *R*² in equations $ZPE_{exp} = b + aZPE_{theor}$ in both cases $b = 0$ and $b \neq 0$.

| Atom | Increment | Ref. | Atom | Increment | Ref. |
|------|-----------|------|------|-----------|------|
| H | 7120 | [25] | Cl | 2220 | [26] |
| C | 3880 | [25] | S | 1870 | [27] |
| N | 4050 | [26] | Br | 1600 | [27] |
| O | 3400 | [26] | Si | -3510 | [28] |
| F | 3270 | [26] | P | 0.035 | [29] |

Table 4.
Atom contributions to ZPE (in kcal/mol).

the average error decreases from 2.5 to 1.37 kcal/mol for AM1 and from 1.08 to 1.00 for DFT(B3LYP/6-31G^{*}).

As a result, the four estimates of vibrational zero-point energy of the organosilicon compounds (our empirical model, Schulman-Disch extended empirical formula, AM1, and DFT) are correct. But the empirical approaches have the advantage of simplicity and speed. In addition, the approach based on bond contributions additivity has also the advantage of providing different values of ZPE for

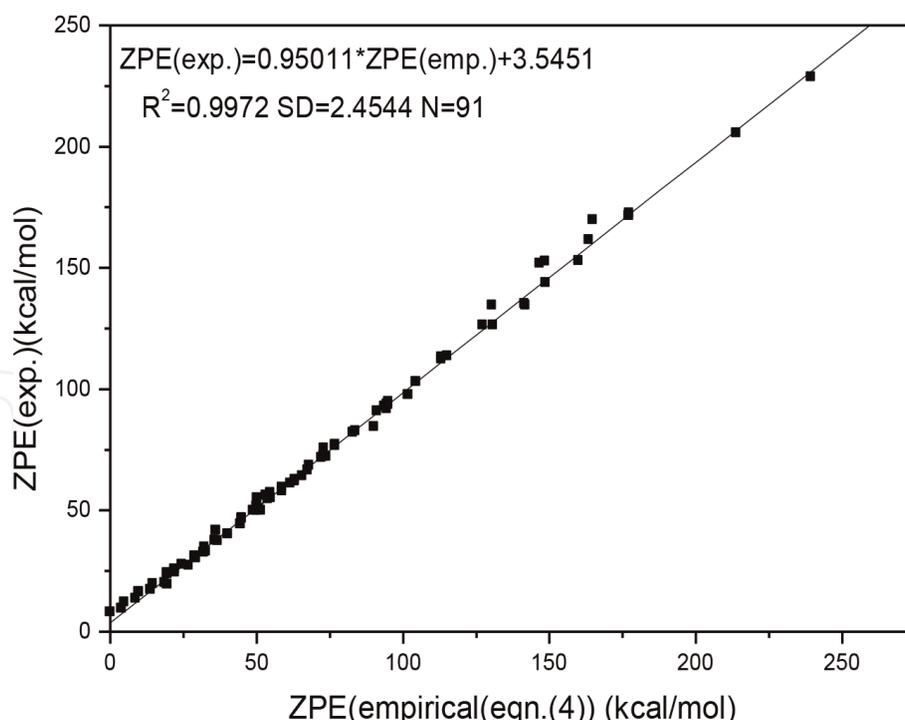


Figure 3.
Correlation between experimental ZPEs and empirical values calculated using Eq. (4).

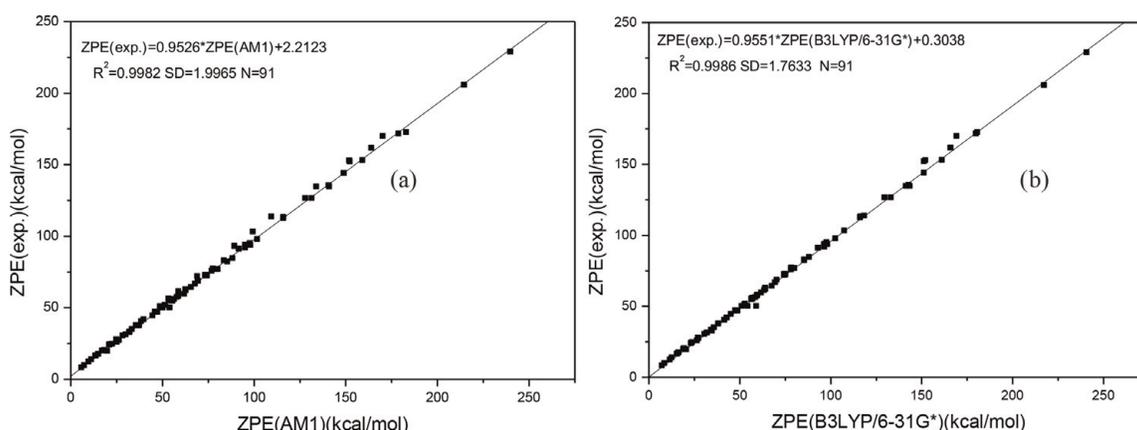


Figure 4.
(a) Correlation between experimental and theoretical (AM1) ZPE and (b) correlation between experimental and theoretical (B3LYP/6-31G^{*}) ZPE.

the function isomers. Furthermore, the adjustment of calculated values, empirically or using quantum methods, with the $ZPE_{\text{exp}} = b + aZPE_{\text{theor}}$ model makes the four estimates comparable.

4. Conclusions and outlook

In this chapter, we reported the extension of our empirical relationship established in 2011 for the computation of zero-point vibrational energies (ZPE) of organosilicon compounds. The bond contributions of Si—H, Si—C, Si—Cl, Si—O, and Si—Si were determined. The application of the proposed empirical model to more than 90 organosilicon shows the reliability of this model. The results derived from this model are compared with those obtained by quantum chemistry methods (semiempirical (AM1) and DFT (B3LYP/6-31G^{*})) on the one hand and to those obtained by similar empirical approach on the other hand. As a result, the empirical

model provides a simple, fast, and accurate way to estimate the vibrational zero-point energies of organosilicon compounds.

Establishing these empirical rules is becoming increasingly important. Indeed, thermodynamic data play an important role in the understanding and design of chemical processes. Experimental methods require appropriate equipment, sufficient product purity, time, and cost of experience. The use of such techniques becomes difficult for toxic compounds. In addition, the large difference between the number of synthesized compounds and the available experimental data continues to increase. In such situation, the practical approach is to use predictive models to estimate the properties of compounds from the molecular structures. In this outlook, we propose to extend the field of application of the proposed empirical model to other compounds such as organoborons, organomagnesiums, etc., and to establish similar approaches to estimate other thermodynamic quantities such as enthalpy of formation (ΔH^0_f), entropy (S^0), and heat capacity (C).

List of abbreviations

| | |
|---------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| ZPE | zero-point vibrational energy |
| AM1 | Austin model 1 (developed by Michael Dewar and collaborators in 1985) |
| $H_{\text{vib}}(T)$ | vibrational enthalpy of the molecule |
| $S_{\text{vib}}(T)$ | entropy due to vibrational motion |
| $H(T) - H(0)$ | thermal correction |
| HF/6-31G* | Hartree-Fock theory in combination with the 6-31G(d) basis set |
| DFT | density functional theory |
| B3LYP/6-31G* | Becke's three parameter exchange function (B3) with Lee-Yang-Parr correlation function (LYP) functional coupled with 6-31G basis set |
| Eqn | equation |

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