



Rapid estimation of vibrational zero-point energies of silicon compounds



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ABSTRACT

In this paper, we extended the application of our empirical formula for the calculation of vibrational zero-point energies (ZPEs) to silicon compounds. The bond contribution of Si–C, Si–H, S–O, Si–Cl and Si–Si were determined. The results obtained for more than 90 chemical systems containing these bonds are in good agreement with the experimentally available values. The estimated zero-point energies were compared with the results obtained by application of the extended empirical formula of Schulmann and Disch and with the scaled values obtained using the semi-empirical method (AM1) and the DFT method (B3LYP/6-31G*), in all cases with satisfactory results.

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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. The experimental determination of this grandeur ($ZPE = 1/2 \sum h\nu_i$) requires the knowledge of all the frequencies of the normal modes of vibration by IR and Raman spectroscopic methods. In certain cases these methods involve experimental difficulties and are not feasible. Other authors used the methods of quantum chemistry [1–5]. However such methods cannot be applied to all the chemical systems, on the one hand because the parameters of the elements of the periodic table are not all known, and on the other large systems size require an important computing time. This explains the interest of the empirical rules making it possible to determine vibrational zero-point energy. The investigated grandeur can be described with a good approximation by rules of additivity whose theoretical justification was already established [6–8]. Flanigan et al. [6] have used the simple empirical relationship for C_nH_m hydrocarbons:

$$ZPE = 2n + 7m \quad (\text{kcal/mol}) \quad (1)$$

In 1985 Schulman and Disch [9] changed this relationship and used the least squares method to determine the increments of carbon and hydrogen atoms for hydrocarbons. The relationship thus obtained is written:

$$ZPE = 3.88n + 7.12m - 6.19 \quad (\text{kcal/mol}) \quad (2)$$

A year after [10], the application of this relation was extended to other molecules containing the nitrogen, oxygen, chlor and fluor atoms. In 1987, Ibrahim and Fataftah [11] also widened the application of this relation to the thio and bromo compounds. They determined the increments of the bromine and sulfur atoms. Lately, AbdulHussain and Fleifel [12] determined the increment of the silicon atom. The precedent equation takes now the form:

$$\begin{aligned} ZPE = & 7.12N_H + 3.88N_C + 4.05N_N + 3.40N_O + 3.27N_F \\ & + 2.22N_{Cl} + 1.87N_S + 1.60N_{Br} - 3.51N_{Si} \\ & - 6.19 \quad (\text{kcal/mol}) \end{aligned} \quad (3)$$

In 2001 we established an empirical relationship [13] making it possible to calculate the zero-point energies of organic compounds. This relationship was determined by relating ZPE to the nature and type of bonds forming the molecule. The empirical formula found is written as follows:

$$ZPE(\text{emp.}) = \sum_i^P N_i \times BC_i - 2.09 \quad (\text{kcal/mol}) \quad (4)$$

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with P the number of bonds in the molecule, N_i the number of bonds of type i and BC_i the contribution of the bond i to the zero-point energy (ZPE).

This equation makes it possible to calculate the ZPE of compounds containing 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. It has been applied to more than 80 chemical systems belonging to different categories of compounds (alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, ketones, aldehydes, acids, esters, alcohols, ethers, amines, amides, nitriles, thio compounds, chloro compounds, fluoro compounds, aromatics, etc.) The correlation between the experimental and empirical ZPE values is virtually linear for the non-aromatic compounds ($ZPE(\text{exp.}) = 1.00ZPE(\text{emp.}) - 0.2046$, $R = 0.998$).

For aromatic compounds, the empirical values have to be adjusted using the equation:

$$ZPE = 1.08.ZPE(\text{empirical}) - 1.07 \quad (\text{kcal/mol}) \quad (5)$$

This correction is due to the fact that in the aromatic nucleus the CC bonds are identical, while the model supposes the presence of three C–C bonds and three C=C bonds.

In 2004, the contribution of the bond C–Br has been determined [14] and incorporated in our empirical formula to calculate zero-point energies of bromo compounds. The calculated zero-point energies for 38 molecules containing this bond correlate well with experimental values.

Following our anterior work, we are interested in this study to determine the contribution of the Si–C, Si–H, S–O, Si–Cl and Si–Si bond in order to calculate the vibrational zero-point energies of silicon compounds. The results are compared to the experimental values on the one hand, and to the values obtained using AM1, DFT (B3LYP/6-31G*) calculations and with the results deduced from similar approach based on simple atom additivity on the other.

2. Computational details

The semiempirical [15] and density functional theory [16,17] calculations were carried out using respectively the AM1 method and B3LYP [18–20] with 6-31G* basis set which were implemented in the Gaussian03 W program [21]. The geometry of all systems was determined without any symmetry constraints. Harmonic frequencies of each compound were calculated in order to ensure that the optimized geometry really corresponded to a global 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. Empirical estimation of ZPE

We used the least squares method to determine the contribution of the Si–C, Si–H, S–O, Si–Cl and Si–Si bond to zero-point energy (ZPE) by correlating for a population of molecules the values of ZPE obtained experimentally and those obtained using Eq. (4). The contribution of studied bonds and those already established [13,14] are given in Table 1.

In order to test the applicability of the generalized empirical formula, we applied it to a group consisting with 91 silicon compounds belonging to various classes as silanes, chlorosilanes, siloxanes, silanols, silyl ethers, silylchlorides, cyclic organosilicon and aromatic organosilicon. The obtained results given in Table 2 are in very good agreement with the experimental available values. The mean error is of the order of 1.51 kcal/mol for the 91 compounds for which experimental or ab initio (HF/6-31G*) data are

Table 1
Contributions of each bond to ZPE (in kcal/mol).

Bond	Bond contribution (BC _i)	Ref.
C–H	7.5877	[13]
N–H	7.2013	[13]
O–H	7.2964	[13]
S–H	5.6921	[13]
C–O	2.6985	[13]
C–C	2.0751	[13]
C–N	4.1409	[13]
C–S	1.4403	[13]
N–N	6.8372	[13]
C–F	3.3078	[13]
C–Cl	2.2051	[13]
C=C	2.6501	[13]
C=N	3.8852	[13]
C=O	3.9343	[13]
C=S	2.7319	[13]
C≡C	4.4125	[13]
C≡N	4.8169	[13]
C–Br	1.9837	[14]
Si–H	5.8011	This work
Si–C	0.3593	This work
Si–Cl	1.7690	This work
S–O	1.3335	This work
Si–Si	-1.4548	This work

available. However the values calculated for 1-phenyl-1-silacyclohexane, 3-phenyl-1,3-thiasilacyclohexane, 1-methyl-1-phenyl-1-silacyclohexane, 3-methyl-3-phenyl-1,3-thiasilacyclohexane and (C₆H₅)₃SiOH are underestimated. This is due to the presence of the aromatic nucleus in these compounds [13,14]. On the other hand, the use of Eq. (5) to adjust empirical ZPE values leads to a decrease the average absolute error and becomes 1.02 kcal/mol (that is 1.98%).

The correlation between the experimental and empirical values (Fig. 1a) is improved, the slope is close to unity (0.9899), the correlation coefficient is near to 0.9997 and standard deviation is 1.2. The statistical data for the regression lines $ZPE_{\text{exp}} = aZPE_{\text{theor}} + b$ and $ZPE_{\text{exp}} = aZPE_{\text{theor}}$ are grouped in Table 3. The use of these data to adjust the empirical ZPE reduce in the same way the average error to 0.9 kcal/mol.

3.2. Semi-empirical and DFT estimation of ZPE

Next, we have calculated zero-point energies for the same silicon compounds using the semi-empirical (AM1) and DFT (B3LYP/6-31G*) methods. Results are shown in Table 2. Scaling factors of A.P. Scott and L. Radom [51] are used to correct calculated vibrational zero-point energies. We see from these results that the values calculated using DFT (B3LYP/6-31G*) are closer to the experimental data than the semi-empirical values (AM1). The average error is 2.50(5.45%) for AM1, compared to 1.08 (1.86%) for DFT (B3LYP/6-31G*). The examination of the correlation between the experimental values and those calculated using the semi-empirical and DFT methods (Fig. 1b and c) shows that these methods are reliable for the calculation of zero-point energies of silicon compounds with a small advantage for the DFT method. The use of the adjustment equations of the calculated ZPEs (Table 3), makes it possible to reduce the average error from 2.5 to 1.37 kcal/mol for AM1 and 1.08 to 1 kcal/mol for DFT (B3LYP/6-31G*) when the intercept is different from zero. For the regression line of the form $ZPE_{\text{exp}} = -aZPE_{\text{theor}}$, the average error passes from 2.5 to 1.83 kcal/mol for AM1 and from 1.08 to 1.06 for DFT (B3LYP/6-31G*).

3.3. Empirical estimation of ZPE based on simple atom additivity

With the aim of comparing the results derived from the application of our empirical formula (Eq. (4)) with those obtained by a

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