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Vibrational zero-point energies of non-aromatic silicon compounds

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• Abstract

In this study, the increment of silicon atom has been determined and incorporated in empirical formula to calculate zero-point energies (ZPE) of non-aromatic silicon compounds. The calculated ZPE for 49 molecules containing silicon atom correlates well with the experimental values. The comparison of these results with semiempirical (AM1) ZPE appears very satisfactory.

Keywords: Zero-point energy; Empirical ZPE; silicon compounds.

• Introduction

The zero point energies (ZPE) of polyatomic molecules can be experimentally determined via equation (1):

$$\text{ZPE} = \frac{1}{2} \sum_i^k h \nu_i \quad (1)$$

Where h Planck's constant, ν_i is the frequency of fundamental vibration i , and k the normal modes of vibrations .

Normal vibrations are usually determined by IR and Raman spectroscopy. This method has some difficulties, especially, for large molecules because of the existence of overtones and combination frequencies in their molecular spectra. Ab initio calculations are also used in the determining the frequencies of normal modes of compounds.

This method has several difficulties. Firstly, It overestimates the frequencies by about 10% [1]. Secondly, ab initio calculations require sophisticated computers and need long computing times especially for large molecules.

Several authors [2–5] have tried to determine ZPE (Zero-point energy) by additivity rules whose theoretical justification has already been established [6–8]. Flanigan et al. [9] determined the following simple empirical relationship for C_nH_m hydrocarbons :

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

Where n , m are the numbers of carbon and hydrogen atoms, respectively

In 1985, Schulmann and Disch [10] used the least squares method to determine the

increments of carbon and hydrogen atoms for hydrocarbons. The relationship thus obtained is written :

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

Ibrahim and Abdulhussain [11-13] used Schuman and Disch formula to calculate the ZPE,s of other organic compounds by deriving increment for N, O, Cl, F, S, Br and I atoms. Empirical formula of all atoms increments are developed to reproduce the ZPE values of molecules containing these atoms via :

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

- **Computational details**

The semiempirical calculations were carried out using the (AM1) method [14] implemented in the Hyperchem 8.0.9 program [15] and Pentium IV PC. Zero-point

- **Derivation of increments, results and discussion**

1. **Empirical estimation of ZPE**

The Si increments which has been developed in this work are listed in (table 1) along with the previously published increments [10-13] for the H, C, N, O, F, Cl, S, Br and I atoms. Due to the nature of the equation (4), the value of any atom increment must be greater than -6.19, therefore, the negative value of silicon increment are acceptable. In order to derive each increment, averages of a large set of molecules whose zero-point energies are reliably known were taken.

We used the least squares method to determine the increment of Si atom to ZPE by correlating for a population of molecules the values of ZPE obtained experimentally and those obtained using Eq. (4).

In order to test the reliability of the generalised empirical formula, we applied it to 49 non-aromatic silicon compounds of various classes compounds, including silicon alkanes, silicon alkenes, silicon alkynes, inorganic silicon compounds as well as

where N_i is the number of atom i , X_i

In this study, we determine the increment of silicon atom order to calculate the ZPE of non-aromatic silicon compounds. The results obtained have been compared with experimental values on one hand, and to the values obtained using semi-empirical (AM1) calculations on the other hand.

vibrational energy was calculated after optimising the geometry on the basis of normal vibration frequencies.

compounds containing sulphur, chlorine, fluorine, oxygen, etc. The results (Table 2) show that the calculated values correlate well with the experimental values. The average error is of the order of 0.90 Kcal/mol for the 49 compounds for which experimental data are available. The table shows that there is little difference between the experimental values of ZPE and those calculated empirically, less than 1.6 Kcal in all cases except tetra-Ethhylsilane were the difference is -2.51 kcal/mol.

The correlation between the experimental and empirical values (Fig. 1a) is improved, the slope is close to unity 0.976, the correlation coefficient is 0.9996 and standard deviation is 1.04. This shows that our empirical formula can be used to calculate the ZPE of non-aromatic silicon compounds. The standard deviation, SD and average error will be improved to 0.99 and 0.87 respectively if the tetra-Ethylsilane value is neglected Fig (1b).

2. Semiempirical estimation of ZPE

ZPE for the same silicon compounds are calculated by using the semiempirical (AM1) method. Results are shown in (table 2). Vibrational energies values calculated with (AM1) method are corrected by a factor of 0.96. The correlation between the experimental and AM1 values (Fig.2a) is

3. Comparison of the AM1 method and the empirical model

In order to compare the results calculated by the semiempirical AM1 method with those obtained by applying our empirical model, we considered a group of 49 molecules whose experimental or theoretical (ab initio) ZPEs are known. Results are shown in (table 2). Values calculated by the AM1 method are farther from the experimental values than values obtained with the empirical model. The average error is 1.23 kcal/mol for the AM1 method and 0.90 kcal/mol for the empirical model.

The correlation between the experimental and calculated values for both methods is shown in (Fig. 1 and Fig. 2). The

• Conclusion

ZPE values of 49 non-aromatic silicon compounds were calculated using the increment of the silicon atom determined in this study. The results obtained were compared with the experimental results

the increment of atom i , and p the number of different atoms in the molecule. These improved formula give good predictions for the ZPE for different classes of organic and simple inorganic molecules containing the above mentioned atoms. The standard deviation, SD and average error will be improved to 1.16 and 0.87 respectively if the tetra-Ethylsilane value is neglected Fig (2b).

correlation between experimental and theoretical (AM1) ZPE gives a slope of 0.966, a correlation coefficient of 0.9997, average error of 1.23 and standard deviation of 1.18. The equivalent values for the empirical model are 0.976, 0.9996, 0.90 and 1.04 respectively. It therefore appears that the AM1 method is suitable for calculating the zero-point energy of molecular systems.

The comparison of the AM1 method with our empirical model shows that the latter provides a simple and economical method of obtaining results with an accuracy comparable to those obtained by AM1.

available on the one hand and with the values obtained using the semi-empirical method (AM1) on the other. Results show that the empirical model provides a simple and quick method of calculating ZPE values of non-aromatic silicon compounds.

Table 1

Atom increments (in kcal/mol)	
Atom	Atom increment
H	7.12 ^a
C	3.88 ^a
N	4.05 ^b
O	3.40 ^b
F	3.27 ^b
Cl	2.22 ^b
S	1.87 ^c
Br	1.60 ^c
I	1.58 ^d
Si	-3.51 ^e

a Ref [10], b Ref [11], c Ref [12], d Ref [13], e this stu

Table (2)

Comparison of calculated (empirical, AM1) zero-point energy with experimental values.

Formula	Molecular	ZPE (Kcal/mol)			DIF. (Kcal/mol) ^a		Ref.
		Exp.	Emp.	AM1 ^b	Emp.	AM1	
SiH ₄	Silane	19.9	18.78	18.64	1.12	1.26	[16]
SiH ₃ N ₃	silyl azide	23.41	23.81	23.88	-0.4	-0.47	[17]
Si ₂ H ₆	disilane	30.08	29.51	28.73	0.57	1.35	[18]
Si ₂ H ₄ Cl ₂	trans -dichlorodisilane	20.27	19.67	21.56	0.6	-1.29	[19]
SH ₄ Si	staggered silanethiol	21.16	20.65	19	0.51	2.16	[20]
CH ₆ Si ₂ N ₂	disilylcarbodiimide	40.01	41.49	40.28	-1.48	-0.27	[21]
CH ₆ Si	methyl silane	37.21	36.9	37.4	0.31	-0.19	[18]
CH ₅ SiCl	chloromethylsilane	32.48	31.98	32.23	0.5	0.25	[22]
CH ₄ SiCl ₂	dichloromethylsilane	27.09	27.06	26.6	0.03	0.49	[22]
C ₂ H ₅ SiCl	cis vinyl silyl chloride	37.31	35.86	37.51	1.45	-0.20	[23]
C ₂ H ₅ SiCl	gauche vinyl silyl chloride	37.31	35.86	37.47	1.45	-0.16	[23]
C ₂ H ₆ SiCl ₂	2-chloroethylsilyl chloride C-trans-Si-gauche (Tg)	46.46	45.18	46.36	1.28	0.10	[24]
C ₂ H ₆ SiCl ₃	2-chloroethylsilyl chloride C-gauche-Si-gauche (Gg)	46.49	45.18	46.48	1.31	0.01	[24]
C ₂ H ₆ SiCl ₄	2-chloroethylsilyl chloride C-gauche-Si-trans (Gt)	46.71	45.18	46.5	1.53	0.21	[24]
C ₂ H ₆ SiCl ₅	2-chloroethylsilyl chloride C-trans-Si-trans (Tt)	46.62	45.18	46.34	1.44	0.28	[24]
C ₂ H ₇ SiCl	1-chloroethylsilane	49.7	50.1	49.9	-0.4	-0.20	[25]
C ₂ H ₇ SiCl	gauche 2-chloroethyl silane	49.75	50.1	50.12	-0.35	-0.37	[26]
C ₂ H ₇ SiCl	Gauche Ethyl Chlorosilane	51.38	50.1	51.78	1.28	-0.40	[27]
C ₂ H ₇ SiCl	trans 2-chloroethyl silane	49.82	50.1	50.3	-0.28	-0.48	[26]
C ₂ H ₇ SiCl	Trans Ethyl Chlorosilane	51.42	50.1	51.78	1.32	-0.36	[27]
C ₂ H ₈ Si	Ethylsilane	54.79	55.02	55.54	-0.23	-0.75	[28]
C ₃ H ₁₀ OSi	trimethylsilanol	75.37	76.54	76.99	-1.17	-1.62	[29]
C ₃ H ₁₀ Si	anti -n -propylsilane	72.07	73.14	73.69	-1.07	-1.62	[30]
C ₃ H ₁₀ Si	gauche - n -propylsilane	72.29	73.14	73.9	-0.85	-1.61	[30]

Table (2) (continued)

Formula	Molecular	ZPE (Kcal/mol)			DIF. (Kcal/mol) ^a		Ref.		
		Exp.	Emp.	AMI ^b	Emp.	AMI			
C ₃ H ₁₀ Si	gauche ethylmethylsilane			72.27	73.14	73.95	-0.87	-1.68	[31]
C ₃ H ₁₀ Si	trans ethylmethylsilane			72.14	73.14	73.9	-1	-1.76	[31]
C ₃ H ₁₀ Si	trimethylsilane			71.95	73.14	73.9	-1.19	-1.95	[29]
C ₃ H ₁₂ Si ₂	1,1,1-trimethyldisilane molecule			82.56	83.87	83.94	-1.31	-1.38	[32]
C ₃ H ₅ SiF ₃	Gauche Allyltrifluorosilane			48.71	47.35	51.03	1.36	-2.32	[33]
C ₃ H ₆ Si	1-silylpropyne			43.96	44.66	44.97	-0.7	-1.01	[34]
C ₃ H ₇ SiCl	cis-cyclopropylchlorosilane			55.47	53.98	56.62	1.49	-1.15	[35]
C ₃ H ₇ SiCl	methylvinyl silyl chloride (CIE)			54.89	53.98	55.19	0.91	-0.30	[36]
C ₃ H ₇ SiCl	methylvinyl silyl chloride (HE)			54.48	53.98	55.18	0.5	-0.70	[36]
C ₃ H ₇ SiCl	methylvinyl silyl chloride (ME)			54.91	53.98	55.7	0.93	-0.79	[36]
C ₃ H ₈ Si	Allylsilane			57.75	58.9	59.08	-1.15	-1.33	[37]
C ₃ H ₈ SiCl ₂	gauche dichloromethyldimethyl silane			61.73	63.3	62.93	-1.57	-1.20	[38]
C ₃ H ₈ SiCl ₃	anti dichloromethyldimethyl silane			62.42	63.3	62.99	-0.88	-0.57	[38]
C ₃ H ₉ SiBr	bromotrimethylsilane			67.78	67.62	69.61	0.16	-1.83	[29]
C ₃ H ₉ SiCl	chlorotrimethylsilane			68.16	68.22	69.61	-0.06	-1.45	[29]
C ₃ H ₉ SiF	fluorotrimethylsilane			68.64	69.29	70.78	-0.65	-2.14	[29]
C ₄ H ₁₀ Si	cis methylsilylcyclopropane			76.81	77.02	78.79	-0.21	-1.98	[39]
C ₄ H ₁₀ Si	gauche methylsilylcyclopropane			76.44	77.02	78.75	-0.58	-2.31	[39]
C ₄ H ₁₂ OSi	methoxytrimethylsilane			93.41	94.66	95.35	-1.25	-1.94	[29]
C ₄ H ₁₂ Si	diethylsilane			90.68	91.26	91.98	-0.58	-1.30	[16]
C ₅ H ₁₂ Si	cyclopentylsilane			94.6	95.14	98.14	-0.54	-3.54	[40]
C ₆ H ₁₄ Si	cyclohexyl silane (chair-axial)			112.93	113.26	116.06	-0.33	-3.13	[41]
C ₆ H ₁₄ Si	cyclohexyl silane (chair-equatorial)			112.15	113.26	115.16	-1.11	-3.01	[41]
C ₆ H ₁₆ Si	triethylsilane			125.98	127.50	128.21	-1.52	-2.23	[16]
C ₈ H ₂₀ Si	tetraethylsilane			161.23	163.74	164.31	-2.51	-3.08	[16]

a ZPE (experimental) – ZPE (calculated) •

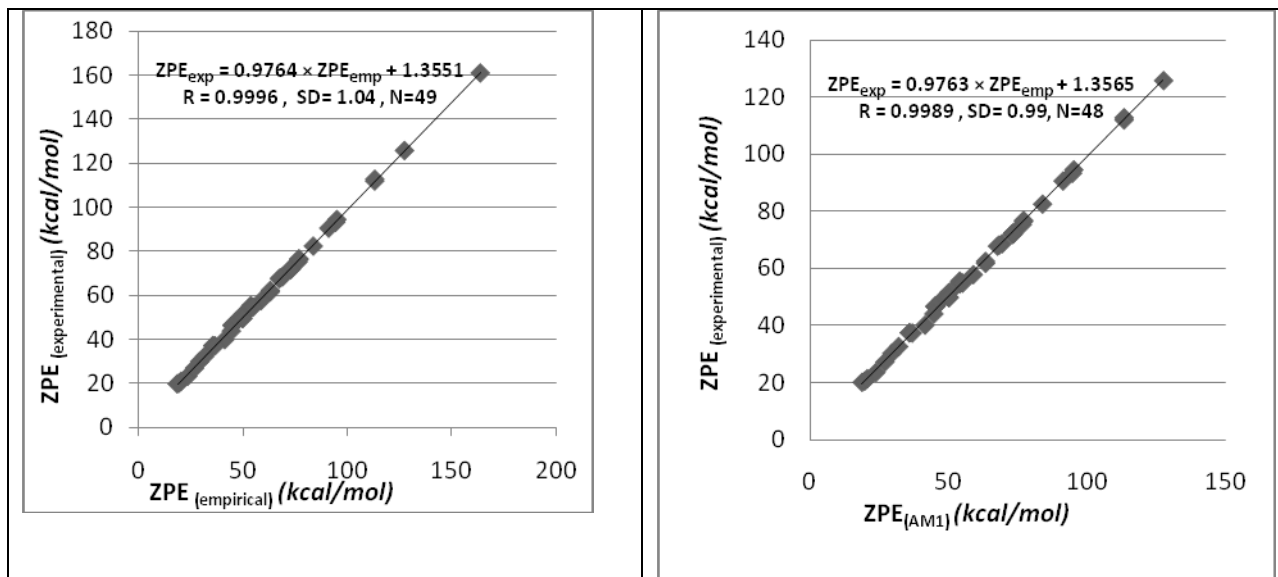


Fig. 1a

Fig. 1b

Fig.1. Comparison between experimental ZPE's and empirical values calculated using Eq.(4). (a) all compounds ; (b) without tert-Ethylsilane value.

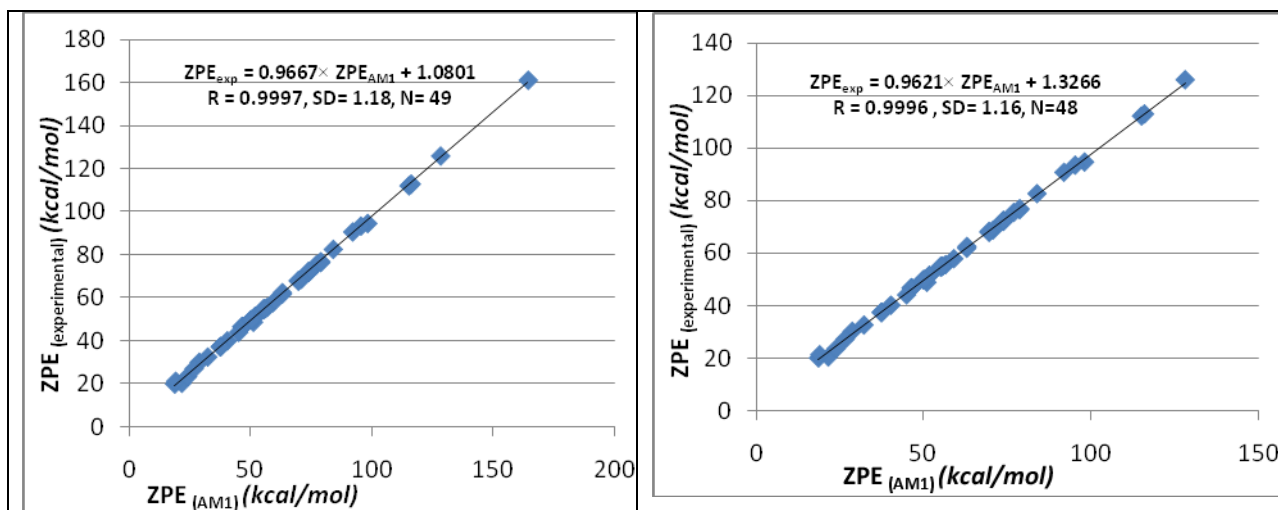


Fig. 2a

Fig. 2b

Fig.2. Comparison between experimental ZPE's and AM1 values. (a) all compounds ; (b) without tert-Ethylsilane value.

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