

# Accurate gas phase acidities of carboxylic acids estimated by scaling the vibrational contribution of *ab initio* gibbs free energies

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**Abstract** The gas phase Gibbs free energies  $\Delta G^T$  of dissociation reaction of 14 carboxylic acids were calculated on the SCF, as well as G3 and CBS-Q levels. Corresponding accuracies were critically compared with experimental data. Since all of the results suffer from systematic errors, the procedure of scaling of thermal contribution to Gibbs free energy was applied for minimizing differences between theoretical and experimental values of  $\Delta G^T$ . Two parameters were adjusted, namely the scaling of thermal contribution to Gibbs free energy of neutral and anionic forms. The presented results suggest the great effectiveness of such a procedure since for all applied basis sets within the SCF framework the achieved accuracy was below the experimental error. Besides, the proposed low-cost approximation method leads to precision comparable to or even exceeding the quality offered by more sophisticated composite quantum chemistry methods. The extension of the set of training molecules up to 82 has an insignificant impact on the overall quality of  $\Delta G^T$  estimation, which suggests that a wisely chosen set of reference data may be used for the character-

istics of the whole class of compounds. There is a straightforward way for the analysis of acidities/basicities of other classes of chemicals such as DNA bases, alcohols, fenols, amines, amino acids, etc.

**Keywords** Gibbs free energy · Carboxylic acids · Gas phase dissociation · Thermodynamics · Hartree-Fock

## Introduction

There are many pH-related physicochemical properties of Brönsted acids and bases such as chemical reactivity, ionization percentage, solubility, lipophilic affinity, drug activity, ion charge, membranes permittivity, etc. [1, 2]. In medicinal chemistry, drug acidity is treated as a significant factor for its ability to pass cellular membranes, receptor interactions, readiness of protonation and toxicity [3]. Many heterocyclic compounds, such as nucleic acid bases and many drugs, may exhibit complex proton-related equilibriums resulting in tautomerism [4, 5] and H-bonding [6, 7]. The acidity [8, 9] or micro-acidity [10, 11] are characterized by pK<sub>a</sub> values often calculated via thermodynamic cycle, in which the first step corresponds to gas phase dissociation, as it is presented in Scheme 1 [12–14]. In this case, the overall error in pK<sub>a</sub> estimation depends on the accuracy of gas phase calculations as well as the quality of estimation of Gibbs free energy of solvation. However, in the gas phase, for all known cases, the dissociation energies are more than 25 times greater than the corresponding dissociation energies in aqueous solution, but the term corresponding to the proton transfer from gas-phase to solution has similar absolute magnitude [6]. Thus, both errors are of the same order and, if they have the same sign, even small inaccuracies will accumulate, which may lead to a significant fault of pK<sub>a</sub>

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values [15–17]. The detailed knowledge of individual inaccuracies of gas phase and water solution calculations is of crucial importance. Since experimental data are available [18] for a broad range of compounds, there is a straightforward method of error analysis. To date, there is no accurate and general method of ensuring the correct characteristics of protonation/deprotonation properties [12–19]. Acidities and basicities in gas phase as well as in water and organic solutions in a variety of compounds were analyzed on different theoretical levels [12–25]. The direct method of Gibbs free energy calculations is provided by statistical thermodynamic calculations via second derivative matrix. This leads to fundamental vibration estimations and thermal corrections with temperature-dependence implicit in the molecular partition function [26]. However, discrepancies are still observed and theoretical harmonic vibrational frequencies are usually larger than the ones observed experimentally. The main sources of this disagreement are neglecting anharmonic effects, an incomplete incorporation of electron correlation and the utilization of finite, non-saturated basis sets [27]. The overestimation of *ab initio* harmonic vibrational frequencies is, however, found to be relatively uniform, and as a result generic frequency scaling factors are often applied [27]. Gao et al. [22] found that MP2/6-311++G(d,p) and B3LYP/6-311++G(2df,p) methods are able to predict the gas-phase acidities of 105 various organic acids with a precision of 2.2 and 2.3 kcal mol<sup>-1</sup>, respectively. The enthalpy of deprotonation of small protolytical molecules were estimated by Smith and Radom [20] using *ab initio* molecular orbital calculations at the G2 level. Their results indicate that this method is sufficiently reliable for an accurate description of anionic and neutral species, leading to uncertainty of theoretical predictions smaller than experimental error. Most authors [21–25] described acidities of organic acids by the utilization of the commonly accepted [27] calibration factor for the zero-point energies, thermal corrections to energy or entropies. The Gibbs free energy of the dissociation process in gas phase may be defined as follows:



$$\Delta G^T = \Delta H^T - T \cdot \Delta S^T - 6.28 \quad (2)$$

where superscript T denotes the given temperature of reaction (1). Since all further calculations correspond to room

temperature the subscript will be omitted for simplicity. The constant value in equation (2) represents the Gibbs free energy of proton formation in the gas phase at 1 atm and 25 °C expressed in kcal mol<sup>-1</sup>. This value is calculated via the Sackur-Tetrode equation [28]. Reaction enthalpy is defined as a sum of relative reactant energies, the difference in reactant zero point vibration energies and thermal corrections to the energy, according to the following formulas:

$$\Delta H = \Delta E^o + \Delta E^{therm} \quad (3)$$

$$\Delta E^o = E_{A^-}^o - E_{HA}^o \quad (4)$$

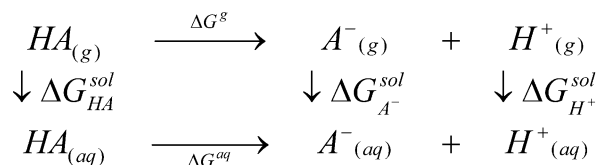
$$\Delta E^{therm} = \Delta E^{novib} + E_{A^-}^{vib}(\alpha_{A^-}) - E_{HA}^{vib}(\alpha_{HA}) \quad (5)$$

$$\Delta S^{therm} = \Delta S^{novib} + S_{A^-}^{vib}(\alpha_{A^-}) - S_{HA}^{vib}(\alpha_{HA}) \quad (6)$$

$$\Delta S^{therm} = S_{A^-}^{therm}(\alpha_{A^-}) - S_{HA}^{therm}(\alpha_{HA}) \quad (7)$$

In practice, all thermal corrections are scaled by arbitral parameter since the *ab initio* vibrational frequencies are often several percent in error compared to experimental data. Compensation for this error was proposed 10 years ago by Scott and Radom [27] by the utilization of different parameters for different basis sets, different methods used and even different experimental data. For example, they suggested scaling the HF/6-31G\* frequencies by 0.8953 to predict fundamental frequencies, by 0.9135 to compute ZPV, by 0.8905 to predict enthalpy differences H<sup>298.15</sup>–H<sup>0</sup>, and by 0.8978 to predict S<sup>298.15</sup>. Besides, the originally proposed scaling factors [27] were calculated for a limited number of fundamental frequencies of neutral species. However, anions are characterized not only by an alternative set of motions resulting from different geometries but are also influenced by an electrostatic field coming from a negative charge. Thus, two distinct parameters are used here:  $\alpha_{HA}$  and  $\alpha_{A^-}$  corresponding to the scaling of the neutral and deprotonated form of carboxylic acid, respectively. A detailed relation to reduced vibrational temper-

**Scheme 1** A simple thermodynamic cycle for pKa estimation in the gas phase and in solvent



$$pK_a = \Delta G^{aq} / (RT \ln(10))$$

Where

$$\Delta G^{aq} = \Delta G^g + \Delta \Delta G^{sol}$$

$$\Delta G^g = G_{A^-}^g + \Delta G_{H^+}^g - G_{HA}^g$$

$$\Delta \Delta G^{sol} = \Delta G_{A^-}^{sol} + \Delta G_{H^+}^{sol} - \Delta G_{HA}^{sol}$$

atures  $\tau_{vib,i} = T_{vib,i}/T$  and scaling factor  $\alpha_k$  is usually [29] presented in the following form:

$$E_k^{vib} = k_B T \cdot \alpha_k \cdot \sum_i \tau_k^{vib,i} \left( \frac{1}{2} + \frac{1}{e^{\alpha_k \cdot \tau_k^{vib,i}} - 1} \right) \quad (8)$$

$$S_k^{vib} = k_B \sum_i \left( \frac{\alpha_k \cdot \tau_k^{vib,i}}{e^{\alpha_k \cdot \tau_k^{vib,i}} - 1} - \ln \left( 1 - e^{-\alpha_k \cdot \tau_k^{vib,i}} \right) \right) \quad (9)$$

where  $k$  denotes acid (HA) or its deprotonated form ( $A^-$ ). The so-called zero point vibrational energy ZPV is defined by the first term in equation (7). Scaling the frequencies several times for a particular purpose is impractical and has no physical meaning. Particularly in the case of Gibbs free energies, the ZPV, thermal energy and entropic contributions are to be mutually scaled. However, there is no such set of parameters. Since all thermal corrections, except for the entropic one, are very sensitive to scaling parameter values, even a slight modification of such a factor leads to significant changes of scaled quantity. At first, one must see whether any scaling is necessary at all. A set of 14 different carboxylic acids, presented in Table 1, was chosen as the subject of analysis. The carboxylic acids analyzed in this study are characterized by a broad spectrum of acidities. The corresponding  $pK_a$  values belong to the range from  $-0.25$  up to  $5.05$ . In Fig. 1, the results of  $\Delta G^T$  calculations are presented without any corrections imposed on reaction Gibbs free energy. This means that  $\alpha_{HA} = \alpha_{A^-} = 1$ . The broad spectrum of basis sets was applied starting from very poor 6–31G\* basis up to 6–311++G(3df,3pd), which is quite rich in polarization and diffusion functions on heavy and hydrogen atoms. In addition, G3 model chemistry was

applied. As one can conclude from Fig. 1, all of the results suffer from systematic errors. Even the most sophisticated G3 method is not perfect in the case of gas phase carboxylic acid dissociation. Of course, for this level of calculations, the discrepancy between predicted and observed data is the smallest among all applied methods, but there is still room for improvement. The existence of systematic errors was observed and commented on by Schuurmann et al. [16] and by other investigators [12–19]. Schuurmann et al. [16] demonstrated the existence of a linear relationship between calculated dissociation energy in aqueous solution and experimental  $pK_a$  values. In addition, they discussed the usefulness of analyzed linear regression coefficients in context of similarities of different compound classes into one (empirically derived) equation. Adam [30] proposed theoretically derived linear relationships between  $pK_a$  and structural properties related to Bader's theory of atoms in molecules (AIM) [31]. These relations were successfully tested on sets of aliphatic carboxylic acids, substituted benzoic acids, phenols, anilinium ions and pyridinium ions. Adam also found that only an energy computed via the quantum chemistry route is able to describe both the entropy driven dissociations of the carboxylic and benzoic acids as well as the enthalpy-driven dissociation of the anilinium and pyridinium ions. Machado and Hinchliffe [32] studied relationships between the HOMO energies and  $pK_a$  values of monocyclic and bicyclic azines and found that the basicities may be directly interpreted in terms of predictions of frontier orbitals. Also, the molecular basicities may be reflected by minima of the electronic potential surface calculated at nuclear positions. Citra [33] demonstrated applicability of linear relationships of quantitative structure properties obtained for a training set of molecules to acidities of a variety of phenols, carboxylic acids and alcohols. The gas-phase acidities of some substituted benzoic acids were fairly well correlated with the sigma and pi substituents effect [34]. Olasz et al. [35] analyzed the impact of the stacking of aromatic rings on the acidic properties of phenol and found linear relationships between  $pK_a$  and such properties as electrostatic interaction energy between the stacked rings, electronegativity of the stacking benzenes and the local hardness, which accumulates of a negative charge, above the substituted benzene ring in para position with the substituents. All of these observations encourage the seeking of a linear relationship between observed Gibbs free energy of dissociation reaction and some features of individual carboxylic acids.

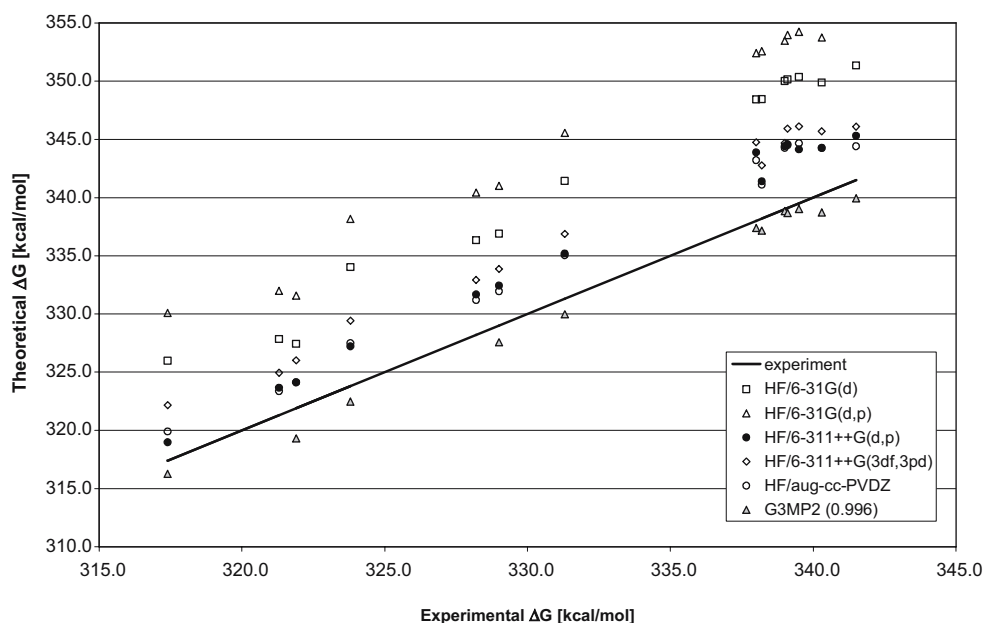
Statistical thermodynamics linking results of *ab initio* calculations with phenomenological observations impose several simplifications. They result mainly from the assumption of non-interacting particles and therefore apply strictly only to the ideal gases. This limitation introduces some error, depending on the non-ideality of the studied system. In addition, it is assumed that the first and higher

**Table 1** The names of carboxylic acids studied in this paper

		$\Delta G^{\ddagger}$
1	Acetic acid	341.5
2	Propionic acid	340.3
3	n-butanoic acid	339.5
4	n-pentanoic acid	339.1
5	2-methyl propionic acid	339.0
6	Formic acid	338.2
7	Tert-butanoic acid	338.0
8	Fluoro acetic acid	331.3
9	Chloro acetic acid	329.0
10	Bromo acetic acid	328.2
11	Drifluoro acetic acid	323.8
12	Dichloro acetic acid	321.9
13	Dibromo acetic acid	321.3
14	Trifluoro acetic acid	317.4

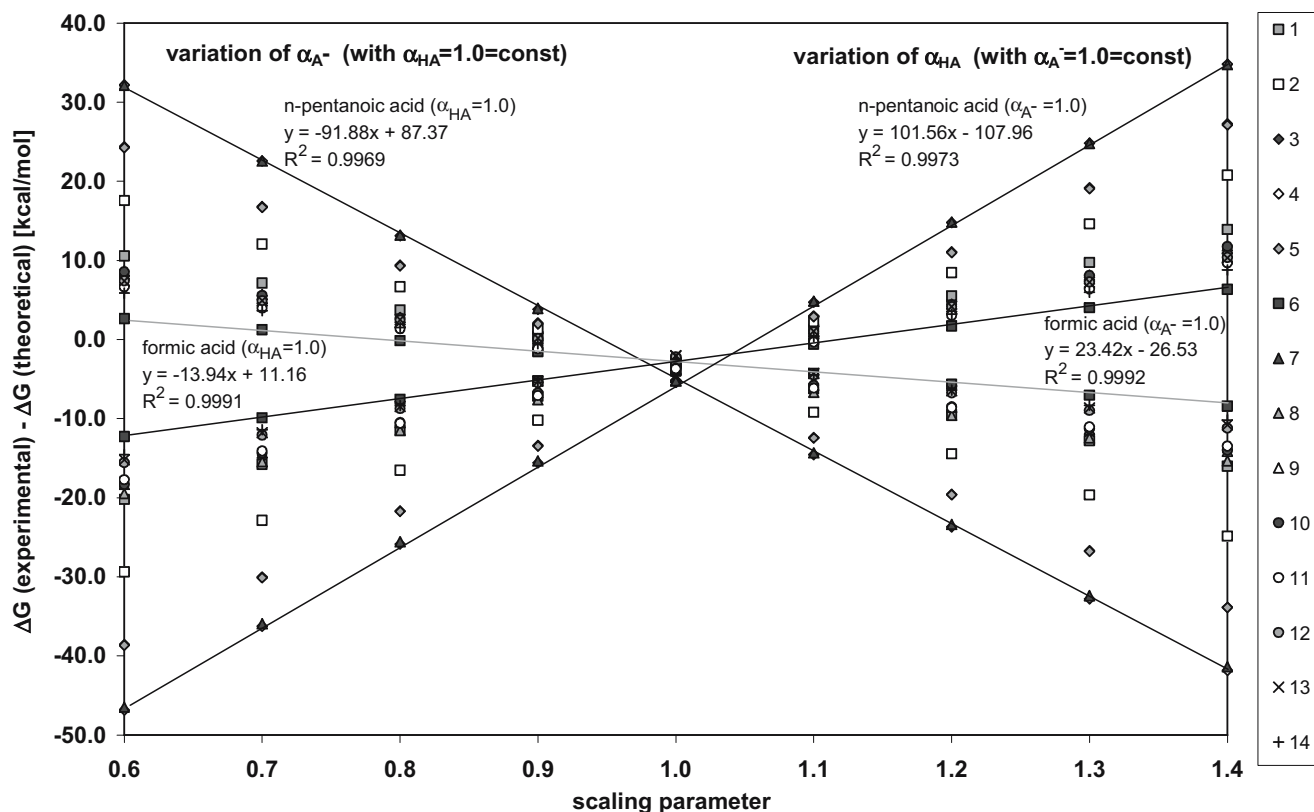
The last column presents experimental [8] values of gas phase Gibbs free energies (in kcal mol<sup>-1</sup>) of the dissociation process presented in Scheme 1.

**Fig. 1** The accuracy of gas phase Gibbs free energy estimated for the set of 14 carboxylic acids presented in Table 1. The Hartree-Fock level with different basis sets and G3 model chemistry level were applied. Temperature equals 298.15 K

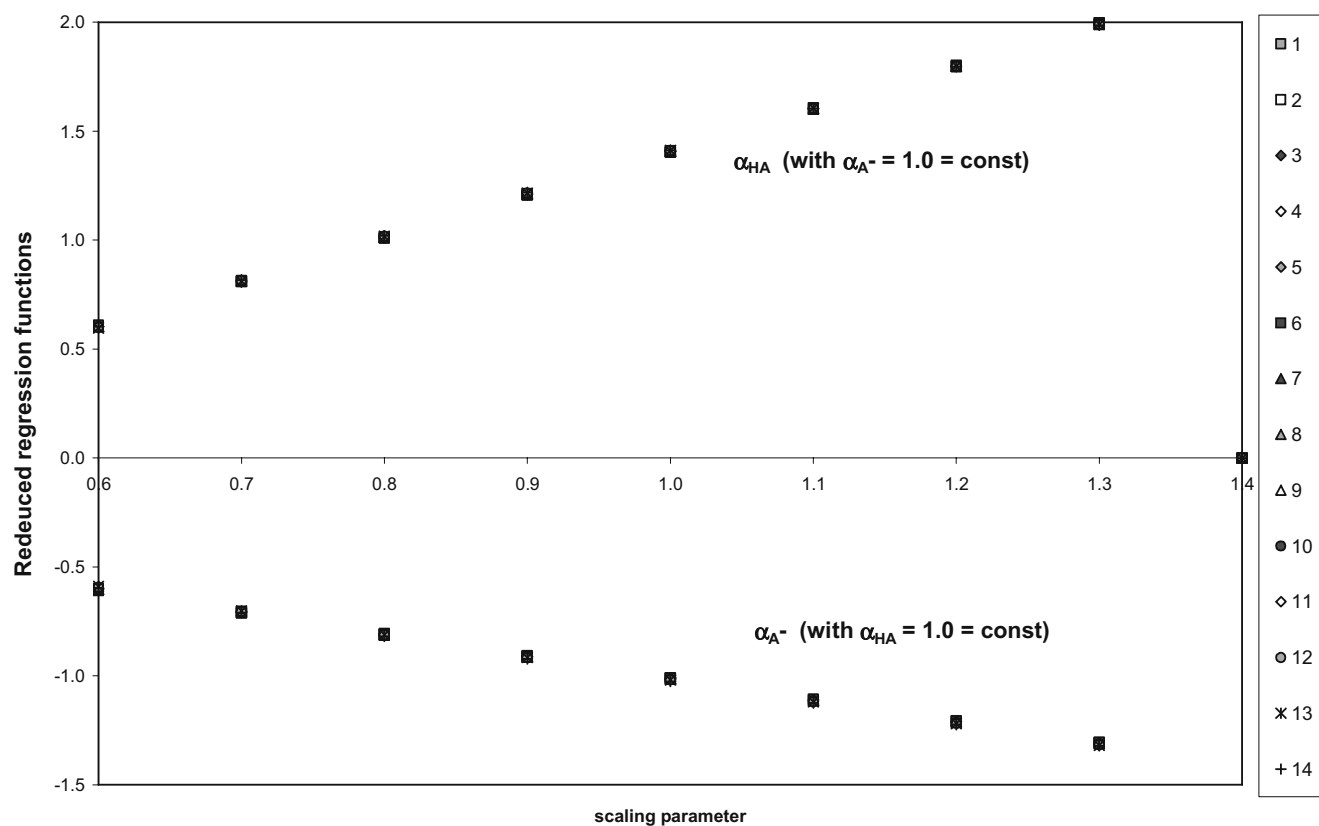


excited states are entirely inaccessible, which can also contribute to some errors for systems with low lying electronic excited states. Furthermore, the *ab initio* harmonic vibrational frequencies are usually overestimated compared to the fundamentals observed experimentally. The main source of this disagreement is the neglecting of anharmonicity effects in the theoretical treatments, incomplete basis

set representations or inappropriate incorporation of electron correlation. It is well known that anionic forms are the main source of error due to the loosely bound nature of the extra electron [17]. Thus, there are distinct sources of errors imposed on thermodynamic functions such as Gibbs free energy estimated by quantum chemistry calculations. However, the magnitude of errors of *ab initio* harmonic



**Fig. 2** Plots describing the difference between the experimental and theoretical values of  $\Delta G$  as a function of scaling parameters  $\alpha_{HA}$  and  $\alpha_{A^-}$ . The data were plotted using HF/aug-cc-pVDZ results. Temperature equals 298.15 K



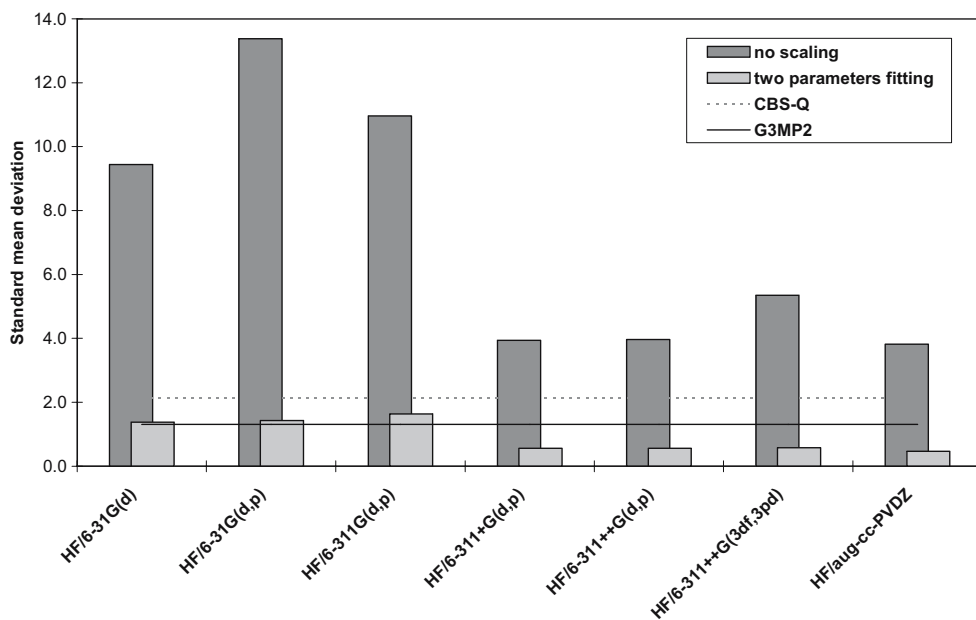
**Fig. 3** The plots of reduced regression function defined by equation (9) as a function of scaling parameters for the set of 14 carboxylic acids studied in this paper. The data were plotted using HF/aug-cc-pVDZ results

vibrational frequencies, as well as other contributions to Gibbs free energies for many reactions, have been found to be relatively uniform, which was demonstrated in Fig. 1. Thus, this study is devoted to the analysis of errors in  $\Delta G^T$  of dissociation reaction in the gas phase. The simple and effective procedure relying on the scaling of thermal contributions to Gibbs free energy is proposed and verified.

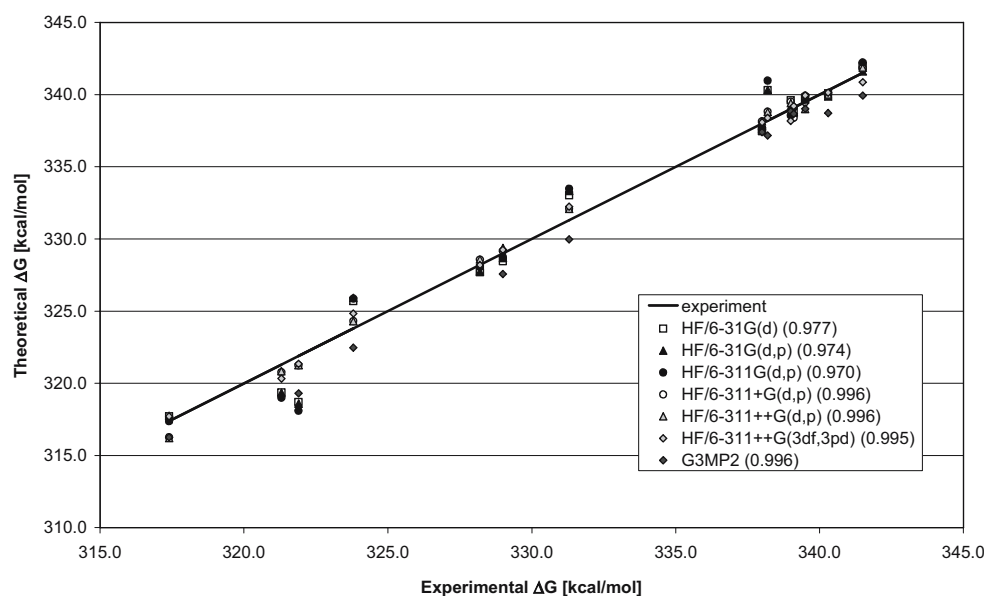
**Methods**

The systematic study of scaling effectiveness was performed in framework of SCF methodology along with seven basis sets. Results corresponding to G3 model chemistry [36] and complete basis set CBS-Q [37] calculations were also provided. A tight criterion for all optimizations was imposed

**Fig. 4** The standard mean deviation of  $\Delta G$  calculated for the set of 14 carboxylic acids based on different methods and basis sets. The plots correspond to both the raw results as well as those resulting from fitting procedure (10). Temperature equals 298.15 K



**Fig. 5** The correlation between predicted and observed gas phase Gibbs free energy estimated for the set of 14 carboxylic acids based on fitting procedure proposed by equation. The unscaled results of G3 method were also provided. Temperature equals 298.15 K. The  $R^2$  data are in parenthesis



and vibrational analysis was performed. All structures were carefully checked against the imaginary modes of vibrations, which ensures that all structures are in their global minima. The Gaussian03 program [38] was employed for all calculations. The hindered rotations were also taken into consideration although their impact on the overall Gibbs free energy was insignificant. In this study, one set of parameters was used,  $\alpha_{\text{HA}}$  and  $\alpha_{\text{A}^-}$  for the given basis set and the particular theory level for all 14 carboxylic acids under consideration.

## Results and discussion

It is interesting to analyze first the impact of variation of scaling parameters on the final value of Gibbs free energy of reaction (1). Plots corresponding to the difference between the experimental and theoretical value of  $\Delta G^T$  as a function of scaling parameter values are presented in Fig. 2. It is noteworthy that for all carboxylic acids studied in this paper such errors are linear functions with respect to scaling parameters  $\alpha_{\text{HA}}$  and  $\alpha_{\text{A}^-}$  varying in broad range (from 40% up to 140% of vibrational frequencies). The correlation coefficients are close to unity for all the analyzed acids. The detailed information resulting from regression analysis is provided in Fig. 2 for two chosen carboxylic acids. The formic acid and n-pentanoic acid are characterized by extreme values of line slopes. Although Fig. 2 presents data for the particular HF/aug-cc-pVDZ method, the same conclusions are valid for all other levels of calculations. This leads to the conclusion that the fitting procedure might be applied for each carboxylic acid for minimizing the difference between theoretical and experimental values of  $\Delta G^T$ . However, it is not obvious whether the same values of  $\alpha_{\text{HA}}$  and  $\alpha_{\text{A}^-}$  would provide significant improvement for the

whole set of analyzed compounds. The answer to this question is presented in Fig. 3. The discrepancy between experimental and theoretical Gibbs free energies was related to regression coefficients and a reduced regression function was defined as follows:

$$\delta G_i = \frac{(\Delta G_i^{T,\text{exp}} - \Delta G_i^{T,\text{theor}}) - b_i}{a_i} \quad (10)$$

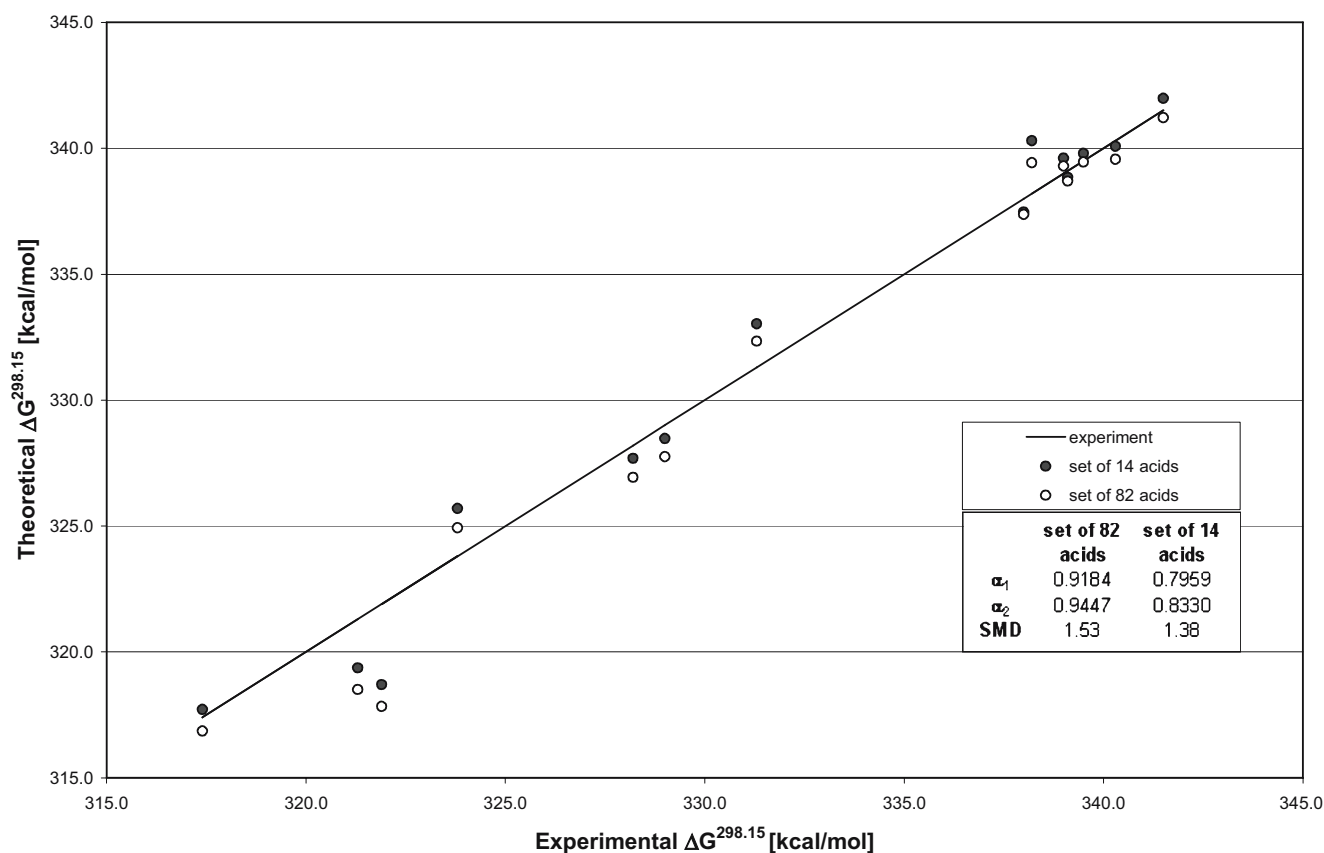
where  $a_i$  and  $b_i$  stand for values of parameters coming from regression analysis for  $i$ -th compound. Values for  $a_i$  and  $b_i$  are supplied in the supporting materials. The most important conclusion coming from Fig. 3 is that there are values of  $\alpha_{\text{HA}}$  and  $\alpha_{\text{A}^-}$  which may be applied to the whole set of acids. The procedure applied in this study was based on this observation. However, instead of scaling vibrational modes, the vibrational contribution to Gibbs free energy is scaled by arbitral parameters  $\alpha_{\text{HA}}$  and  $\alpha_{\text{A}^-}$ , the same for the whole set of studied compounds. Thus, the following formula defines the proposed method:

$$\Delta G^T = \Delta G_o + \alpha_{\text{HA}} \cdot G_{\text{corr}}^{\text{vib}}(\text{HA}) - \alpha_{\text{A}^-} \cdot G_{\text{corr}}^{\text{vib}}(\text{A}^-) - 6.28$$

**Table 2** The parameters optimized for the set of studied carboxylic acids by means of scaling vibrational contribution to Gibbs free energy estimated on Hartree-Fock level

	$\alpha_{\text{HA}}$	$\alpha_{\text{A}^-}$
6-31G(d)	0.7959	0.8330
6-31G(d,p)	1.2530	1.2803
6-311G(d,p)	0.9789	1.0076
6-311+G(d,p)	0.1696	0.2123
6-311++G(d,p)	0.1734	0.2159
6-311++G(3df,3pd)	0.3997	0.4291
aug-cc-PVDZ	0.1698	0.2110





**Fig. 6** The correspondence of theoretical and experimental Gibbs free energies estimated for the set of 14 carboxylic acids based on the scaling parameters estimated for two different training sets of compounds. The results correspond to HF/6–31G(d) level. Temperature equals 298.15 K

We believe that such a procedure is easily extendable and may be applied not only to carboxylic acids but also to other similar molecules. The fitting parameters will then be characteristic of a given class of compounds on a given level of computations. The quality of such a procedure may be analyzed based on the results presented in Fig. 4. It is clearly evident that the standard means deviation (SMD) calculated for the whole set of carboxylic acids has been significantly improved after the application of the scaling procedure. The experimental error of  $\Delta G^T$  is about  $2 \text{ kcal mol}^{-1}$ . For the ordinary SCF calculations with all applied basis sets the resulting Gibbs free energies are so inaccurate that their error significantly exceeds the experimental precision. The predictions of more advanced levels such as G3 and CBS-Q are within the experimental accuracy. Unfortunately, the application of these methods for bigger molecules is limited by computer resources and the time of computations. However, the method proposed in this paper is as accurate as much more sophisticated treatments even for a relatively modest level such as HF/6–31G\*. For richer basis sets the scaling procedure leads to even better results than model chemistries. The comparison of Figs. 1 and 5 clearly gives an impression of the improvement of  $\Delta G^T$  estimation. The values of parameters obtained according to the proposed scheme are supplied in Table 2. Of course, these parameters may not be

treated as general ones and are presented in this paper only for demonstration and verification purposes. More studies are currently in progress. Nevertheless, the idea of application is simple and is as follows: a training set of molecules for which experimental data are available should be chosen. Compounds should be as similar to each other as possible. For example, carboxylic acids, amines, alcohols, fenols, heterocyclic compounds such as DNA bases or their constituents, and so on, may be used. Then, after calculations of vibrational contributions to Gibbs free energy, the scaling parameters should be determined by simple fitting procedure. Some tests not presented in this paper were performed and produced very encouraging results. For example, one of the first shortcomings, which should be emphasized, is the way of declaring the set of training compounds. The question may be asked whether they are used solely as a justification of the proposed procedure or if they are sufficiently representative? In order to analyze this problem the set of carboxylic acids was extended up to 82 compounds. On the HF/6–31G(d) level the scaling parameters were calculated for such an extended set. Then the  $\Delta G^T$  was estimated for compounds studied in this paper based on scaling parameters estimated for 14 carboxylic acids and additionally for 82 carboxylic acids. The results are presented in Fig. 6. The standard mean deviation for such an extended set of compounds is slightly

higher but is still less than that of the experimental error. However, what is more interesting, the application of the fitting parameters estimated for the extended set of compounds to carboxylic acids presented in Table 1 does not significantly influence the quality of  $\Delta G^{\text{T}}$  prediction. This justifies the idea that a wisely chosen training set of molecules may be used for the estimation of scaling parameters and applied for calculations of Gibbs free energy of dissociation in gas phase for other compounds not present in the training set.

## Conclusions

The presented results suggest that the simple procedure of vibrational contributions scaling leads to a significant reduction of  $\Delta G^{\text{T}}$  error for carboxylic acids dissociation reaction in the gas phase. Both the standard deviation and medians are reduced compared to raw data. The extension of the set of training molecules leads to slightly different values of scaling parameters but the quality of  $\Delta G^{\text{T}}$  estimation remains the same. There is a straightforward way for analysis of other classes of compounds (DNA bases, alcohols, fenols, amines, amino acids, etc.) and suitable computations are in progress. There is a potential route for  $\text{pK}_{\text{a}}$  prediction by application of a similar procedure to dissociation reaction in solvent solutions instead of the gas phase. The suggested procedure may be treated as a low-cost semi-empirical interpolation/extrapolation method for the prediction of acidities for series of similar molecules.

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