Evaluation of Accuracy of Ideal-Gas Heat Capacity and Entropy Calculations by Density Functional Theory (DFT) for Rigid Molecules

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S *Supporting Information*

ABSTRACT: Quantum mechanical calculations, coupled with statistical thermodynamics, provide a means to obtain thermodynamic properties of ideal gas. In this work, we performed density functional theory (DFT) and statistical thermodynamic calculations of ideal-gas heat capacities and entropies for a set of 93 rigid molecules, which do not contain large amplitude motions, such as internal rotations or ring puckering, and for which reliable reference data were found in the literature. The effect of the size of basis sets and scale factors was systematically examined and statistically evaluated. The absolute average percentage deviations of the heat capacities and entropies calculated using unscaled harmonic frequencies from reference values were less than 2.5 % for all of the basis sets studied. Both heat capacities and entropies were, however, systematically underestimated, and the relative deviations of heat capacities showed a significant temperature dependence with a maximum deviation near ambient temperatures. Scaling the calculated frequencies by a single value of scale factor from the literature led to slightly more accurate results, but the relative deviations remained biased (values were systematically overestimated) and significantly temperature-dependent. We propose a new wavenumber and bond-dependent set of scale factors that significantly improves the agreement between the theory and the reference data and provides an unbiased distribution of the relative deviations and a temperature dependence of the ideal-gas heat capacities which is closer to the reference data.

INTRODUCTION

Knowledge of the heat capacity in the ideal-gas state is indispensable for the calculation of fundamental thermodynamic functions of ideal gas which are useful approximations to the properties of real gases at low pressures. Furthermore, if knowledge of the state behavior of the fluid and its ideal-gas heat capacities is available, the thermodynamic properties of real fluids can be obtained by basic thermodynamic relationships. Ideal-gas heat capacities also find application in studying solute—solvent interactions through the solvation heat capacities and in temperature adjustments of enthalpies of vaporization or sublimation. Specifically in our laboratory, the ideal-gas heat capacities are employed as necessary inputs in the multiproperty simultaneous correlation of vapor pressure and related thermal data.[1,2] This method was used for the development of recommended vapor pressure equations over wide temperature ranges for several groups of liquid and crystalline compounds.[1,3−6] Often, the applicability of this approach was limited by the unavailability and/or inaccurate estimates of ideal-gas heat capacities. As the simultaneous correlation requires the heat capacity values with an uncertainty less than 1 %, we decided to explore the current possibilities of quantum chemistry methods coupled with statistical mechanics to achieve this goal. As a natural starting point, we selected a set of rigid molecules without internal rotations around a single bond and other large amplitude motions for which reliable experimental data for both fundamental vibrations and ideal-gas heat capacities were found in the literature. However, the number of molecules that would fulfill these criteria was very

limited. Particularly, direct or indirect measurements of ideal-gas heat capacities are very scarce, and most of the data are obtained by the methods of statistical thermodynamics using either experimental or calculated fundamental vibrations. Therefore, we extended the database of rigid molecules by selected data from the TRC database[7] obtained by statistical thermodynamics using reliable experimental spectral data. To validate the results obtained for heat capacities, we performed calculations of ideal-gas entropies for rigid compounds for which reliable third-law entropies, derived from experimental data on heat capacities of condensed phases, vapor pressure measurements, and a description or estimate of state behavior of fluid, were available. In this work, we performed density functional theory (DFT) and statistical thermodynamic calculations for a set of 93 molecules. The effect of the basis sets and scale factors was thoroughly examined and statistically evaluated in this work.

THEORETICAL SECTION

The basic approach to calculate the thermodynamic properties of molecules in the ideal-gas state by statistical thermodynamics is based on the rigid rotor—harmonic oscillator (RRHO) model. One assumes here the harmonicity of all vibrational modes and free rotation of the molecule which remains rigid during the rotation—bond lengths and angles are not deformed, and all

atoms of the molecule rotate with the same angular velocity and in the same sense. The mathematical expressions for the computations of heat capacity and entropy using the RRHO model are described in many textbooks,[7−10] and therefore they are not repeated here. The necessary inputs for these formulas, the principal moments of inertia and molecular vibrations, can be obtained by spectroscopy or quantum mechanical calculations. The latter approach was used in this work. Several approximations are introduced when using the RRHO model coupled with quantum mechanical calculations. First, every solution of the Schrödinger equation is approximate, and the choice of the level of approximation affects the calculated vibrational frequencies. Furthermore, in the RRHO model, the anharmonicity of vibrations, rotational−vibrational coupling, and centrifugal distortion are neglected. The deviation from harmonicity varies depending on the type of the mode. Bond angles deformation modes, such as rocking, waging, twisting, and scissoring, are only slightly anharmonic, while the stretching modes, where the bond length changes, show a higher extent of anharmonicity. The Morse potential would be a better choice for these modes, but it is not used extensively as it requires more parameters specific for each bond. The assumption of the rigidity is not valid for most of molecules. Only a minority of organic chemical structures can be considered as relatively rigid—generally unsaturated hydrocarbons and their derivatives such as ethene, benzene, and so forth. For these structures, the model RRHO should be appropriate and give accurate results. In many polyatomic molecules some of the intramolecular degrees of freedom can exist as torsional motions. There are three ways how to treat torsional motions, depending upon the height of the barrier to rotation. The vibrational treatment is appropriate as long as the barrier is much higher than the thermal energy. When the barrier is comparable to or smaller than the thermal energy the torsional motion should be treated as a hindered or free internal rotation, respectively. This decision considerably affects the final values of the thermodynamic properties and presents another source of uncertainty besides the uncertainty in vibrational frequencies. To eliminate uncertainties connected with the treatment of internal rotations, we focused only on rigid structures in this work. For these molecules, the main source of uncertainty in the thermodynamic properties remains equal to the uncertainties in vibrational frequencies. It is a common practice to scale calculated frequencies by empirical scale factors[11−13] which are assumed to absorb most of the anharmonic effects, as well as errors in the force constants due to approximations in the electronic structure calculations. Usually a single scale factor for a given theory and basis set is determined by a comparison of experimental and calculated frequencies for scaling all frequencies. This implies that on average every calculated frequency should show the same deviation from the corresponding experimental value. The deviations, however, usually show certain frequency and bond dependences. Moreover, for calculations of thermodynamic properties, the accuracy of low-frequency vibrations is much more important, as demonstrated for example by Chirico et al.[14] for dimethylpyridines. We have already shown in our previous work[6] that, using a single scale factor, which was developed by comparing all experimental with calculated frequencies for a molecule, does not lead to a significant improvement of the accuracy of the ideal-gas thermodynamic properties. The deviations from the experimental data were about the same when using unscaled or scaled frequencies, but they had the opposite signs.
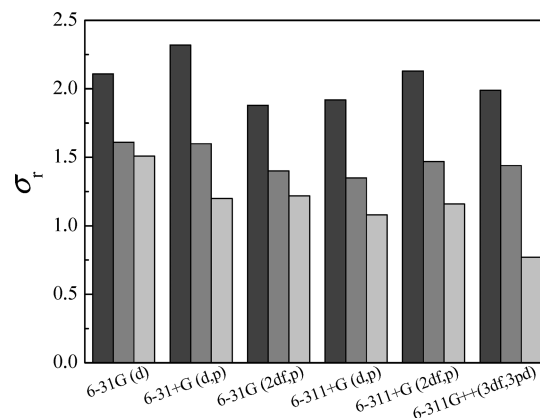
Figure 1. Average absolute percentage deviation, σ_r (eq 1), of the ideal-gas heat capacities calculated using unscaled harmonic frequencies from the reference values[7,16] (see Table S1 of the SI). Black ■, T = 300 K; dark gray ■, T = 500 K; light gray ■, T = 1000 K.

Some authors (e.g., ref 11) use different scaling factors for different thermodynamic properties, namely, for the heat capacity or entropy. In this case, the frequencies are optimized to improve the agreement with a given experimental thermodynamic property. This approach, however, can lead to thermodynamically inconsistent data and therefore was not considered in this work.
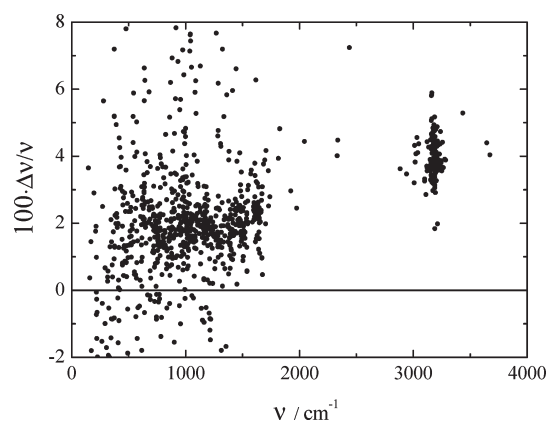
■ RESULTS

All quantum chemistry calculations were performed using the program package Gaussian, version 03.[15] Molecular geometry optimizations and vibrational frequencies calculations were carried out using the density functional theory (DFT) with the B3LYP functional, which is recommended for thermochemistry calculations.[8,11] The performance of six basis sets, 6-31G(d), 6-31+G(d,p), 6-31G(2df,p), 6-311+G(d,p), 6-311+G(2df,p), and 6-311++G(3df,3pd), was evaluated and compared. The RRHO model was used with (i) unscaled frequencies, (ii) frequencies scaled by the scale factors recommended by Merrick et al.,[11] and (iii) newly developed wavenumber and bond-dependent scale factors. Calculated ideal-gas heat capacities were compared with the reference values which were taken from the National Institute of Standards and Technology (NIST)[16] and Thermodynamic Research Center (TRC) databases.[7] The reference third-law entropies were culled from various literature sources reporting calorimetric and vapor pressure measurements[17−26] and data compilations.[7,27] The experimental fundamental vibrations were taken from the compilations by Shimanouchi[28−30] except for indene,[31] biphenylene,[32] fluorene,[33] purine,[34] pyrimidine,[35] pyridazine,[36] pyrazine,[36] 1-chloronaphthalene,[7] 2-chloronaphthalene,[7] 1,4-dichloronaphthalene,[7] 1-fluoronaphthalene,[7] and 2-fluoronaphthalene.[7] The deviations from the reference data are represented by the average absolute percentage deviation σ_r defined as

$$\sigma_r = 100/n \sum_{i=1}^{n} \left(|Y^{calc} - Y^{ref}|/Y^{ref} \right)_i \tag{1}$$

where Y is either the ideal-gas heat capacity or entropy, n is the number of data points in the data set, and superscripts "calc" and "ref" stand for the calculated and for reference property, respectively.

228

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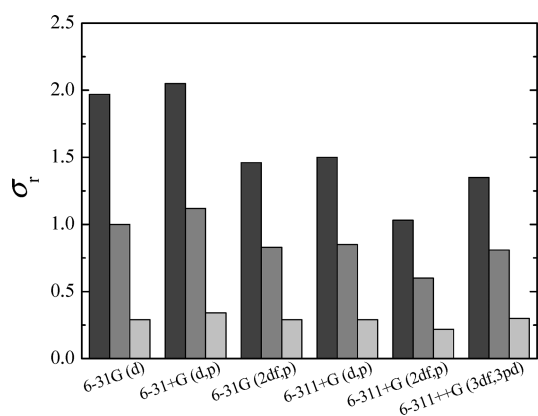
Figure 2. Average absolute percentage deviation, σ_r (eq 1), of the ideal-gas heat capacities calculated using the scaling factors recommended by Merrick et al.[11] from the reference values[7,16] (see Table S2 of the SI). Black ■, T = 300 K; dark gray ■, T = 500 K; light gray ■, T = 1000 K.

Table 1. Scale Factors for DFT with the B3LYP Functional

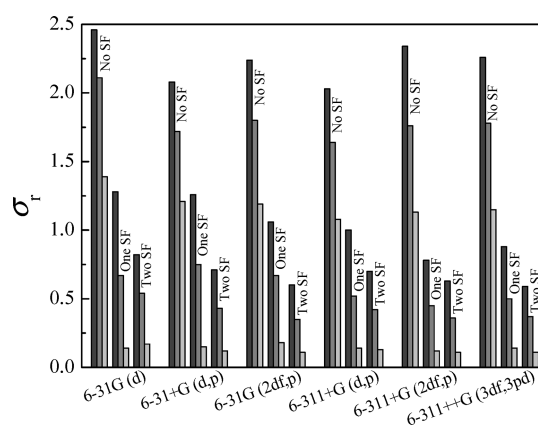| basis set	wavenumber <2000 cm^{-1}	wavenumber >2000 cm^{-1}
	sp^2 Structures	
6-31G(d)	0.9749	0.9551
6-31+G(d,p)	0.9795	0.9566
6-31G(2df,p)	0.9777	0.9592
6-311+G(d,p)	0.9808	0.9618
6-311+G(2df,p)	0.9767	0.9629
6-311++G(3df,3pd)	0.9787	0.9606
	sp Structures	
6-31G(d)	0.9135	0.9527
6-31+G(d,p)	0.9103	0.9572
6-31G(2df,p)	0.9318	0.9526
6-311+G(d,p)	0.9334	0.9586
6-311+G(2df,p)	0.9398	0.9602
6-311++G(3df,3pd)	0.9411	0.9595

Figure 3. Relative deviations $\{v(\text{calc}) - v(\text{exp})\}/v(\text{exp})$ of the wavenumbers calculated using the DFT at the B3LYP/6-311+G(d,p) level of theory $v(\text{calc})$ from those obtained experimentally $v(\text{exp})$. Rigid molecules contain carbon atoms mostly in the sp^2 hybridization (list of compounds is given in Table S3 of the SI).

Figure 4. Average absolute percentage deviation, σ_r (eq 1), of the calculated ideal-gas heat capacities from the reference values[7,16] for sp^2 structures (Tables S4 and S5 of the SI). "No SF" stands for unscaled harmonic frequencies, "One SF" for harmonic frequencies scaled by the scaling factor suggested by Merrick et al.,[11] and "Two SF" for harmonic frequencies scaled by the two scaling factors developed in this work. Black ■, T = 300 K; dark gray ■, T = 500 K; light gray ■, T = 1000 K.

Effect of Basis Sets and Literature Scaling Factors. Figure 1 shows the average absolute percentage deviation, σ_r (eq 1), of the isobaric heat capacities obtained using unscaled calculated frequencies from the reference values for all the basis sets studied. The relative deviations for all compounds in the data set as well as σ_r and bias distribution are given in Table S1 in the Supporting Information (SI). σ_r does not exceed 2.4 % at 300 K and 1.6 % at 1000 K. The calculated heat capacities are strongly biased (87 % calculated values are lower than the reference values). This reflects the fact that the calculated vibrational frequencies are systematically overestimated which leads to underestimated vibrational contributions of the heat capacity.

Analogous deviations are summarized in Figure 2 and Table S2 in the SI, where the vibrational frequencies were scaled by the scale factors suggested by Merrick et al.[11] Scaling the calculated frequencies by the corresponding single value leads to more accurate results of heat capacities for all of the examined basis sets. The improvement is more significant at higher temperatures. The ratio of the negative deviations of calculated heat capacities changes significantly, and positive deviations are obtained in about 77 % of the cases.

Scaling Factors for Rigid Compounds Containing Atoms in the sp^2 Hybridization. A set of 35 organic rigid molecules (Table S3 in SI) containing carbon atoms mainly in the sp^2 hybridization, for which the assignment of fundamental frequencies based on spectroscopic measurements was available in the literature, was selected. In total 972 fundamental wavenumbers were calculated using all basis sets considered in this work and compared with the experimental values. The relative deviations obtained for the 6-311+G(d,p) basis set are plotted as a function of wavenumber in Figure 3 (the picture is very similar for the rest of the basis sets). As can be seen, most of the calculated wavenumbers display a positive deviation from the experimental values. The wavenumbers corresponding to the C—H bond stretching modes, at approximately 3000 cm^{-1}, deviate by approximately 4 % on average. The lower wavenumbers under 2000 cm^{-1} display a much higher scatter, which reflects the fact that more types of vibrational modes are included here. However, an average deviation of approximately 2 % can be determined.
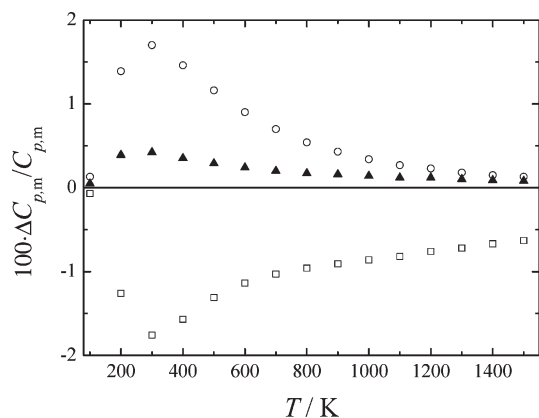
Figure 5. Relative deviations $\{C_{p,m}(\text{calc}) - C_{p,m}(\text{ref})\}/C_{p,m}(\text{ref})$ of the calculated ideal-heat capacities from the reference values for furan.[16] Harmonic frequencies were obtained using the DFT at the B3LYP/6-311+G(d,p) level of theory. □, unscaled harmonic frequencies; ○, harmonic frequencies scaled by the scaling factor suggested by Merrick et al.;[11] ▲, harmonic frequencies scaled by the two scaling factors developed in this work.
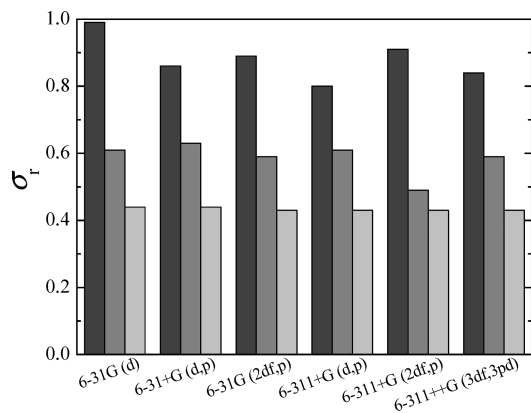
Figure 6. Average absolute percentage deviation, σ_r (eq 1), of the calculated ideal-gas entropies from experimental values[17-27] for sp^2 structures (Table S6 of the SI). Black ■, unscaled harmonic frequencies; dark gray ■, harmonic frequencies scaled by the scaling factor suggested by Merrick et al.;[11] light gray ■, harmonic frequencies scaled by the two scaling factors developed in this work.

Based on this analysis, the scaling factors for each basis set and wavenumber region were evaluated and tabulated in Table 1. As already mentioned, the high-frequency vibrations play a minor role in statistical thermodynamic calculations, and therefore it is important to avoid averaging the scale factors over the whole vibrational spectrum. One can either determine one scale factor from only low frequencies or two values for low and high frequencies, respectively. Given the ease of applying two scale factors, we decided to tabulate two values of scale factors for regions below and above 2000 cm^{-1}, respectively, although scaling high frequencies brings in many cases only a slight improvement of the calculated thermodynamic properties. The isobaric heat capacities were recalculated for the set of 20 molecules with carbon atoms in the sp^2 hybridization using these two scaling factors (Table S4 in the SI). The deviations are compared with those obtained using none or one scale factor in Figure 4 and Table S5 in the SI. As can be seen, two newly
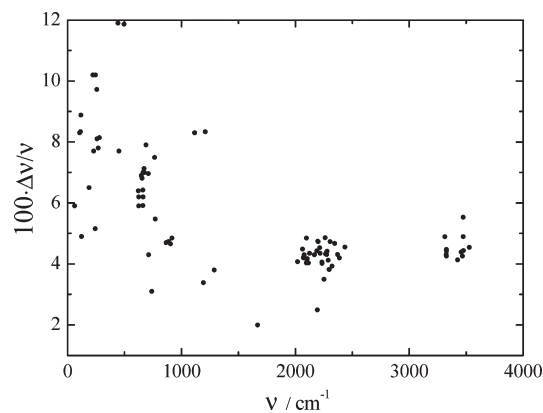
Figure 7. Relative deviations $\{\nu(\text{calc}) - \nu(\text{exp})\}/\nu(\text{exp})$ of the wavenumbers calculated using the DFT at the B3LYP/6-311+G(d,p) level of theory $\nu(\text{calc})$ from those obtained experimentally $\nu(\text{exp})$. Rigid molecules containing mostly carbon and nitrogen atoms in the sp hybridization (see Table S7 of the SI).

suggested scale factors significantly lower σ_r (eq 1) which is less than 0.7 % at 300 K and about 0.1 % at 1000 K. Such deviations are within the uncertainty of the experimental determination.

As shown for a typical case represented by furan in Figure 5, when unscaled frequencies are used, negative deviations and a significant minimum around 300 K are obtained. When scaling all of the frequencies with a single scale factor, the deviations flip over the temperature axis and become positive. Using two scale factors leads to the temperature dependence of ideal-gas heat capacities that is closer to the reference data.[16] This is a significant improvement for applications such as the simultaneous correlation of vapor pressure and related thermal data which require a correct temperature dependence of the ideal-gas heat capacity often down to 200 K.

Two newly determined scaling factors were validated on a set of 15 rigid molecules for which experimental third-law entropies were found in the literature.[17-26] The obtained results are summarized in Figure 6 and Table S6 in the SI. The RRHO model with unscaled frequencies yielded σ_r (eq 1) of 0.9 %. The deviations are negative in 79 % of the cases. By using one scale factor as recommended by Merrick et al.,[11] σ_r changed to 0.6 % with only 18 % of the deviations being negative. When we applied our two scaling factors, we obtained an unbiased distribution of the relative deviations (48 % negative deviations), and σ_r amounted to 0.4 %.

Scaling Factors for Rigid Compounds Containing Atoms in the sp Hybridization. A group of 12 compounds containing carbon and nitrogen atoms in the sp hybridization was selected for this study (Table S7 in the SI). The number of suitable compounds with available experimental frequencies was very limited. The relative deviations of calculated fundamental frequencies (at the B3-LYP/6-311+G(d,p) level of theory; the situation for other basis sets is very similar) from experimental values are plotted as a function of wavenumbers in Figure 7. The deviations at around 3500 cm^{-1} and 2200 cm^{-1} amount to approximately (4 to 5) %. These regions can be assigned to the C–H bond and triple bond stretching modes, respectively. The deviations of the lower wavenumbers vary significantly with the average value of (7 to 8) %. Based on this analysis, two scaling factors were determined (Table 1).
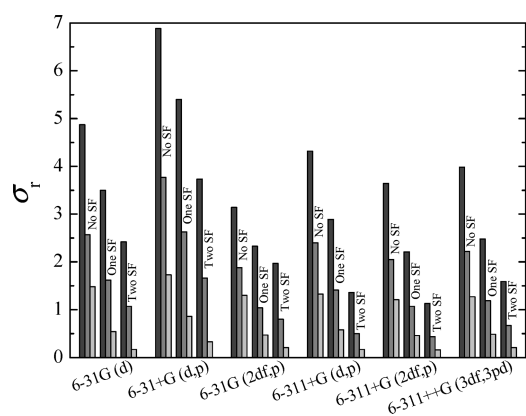
Figure 8. Average absolute percentage deviation, σ_r (eq 1), of the calculated ideal-gas heat capacities from the reference values[7,16] for sp structures (Tables S8 and S9 of the SI). "No SF" stands for unscaled harmonic frequencies, "One SF" for harmonic frequencies scaled by the scaling factor suggested by Merrick et al.,[11] and "Two SF" for harmonic frequencies scaled by the two scaling factors developed in this work. Black ■, $T = 300$ K; dark gray ■, $T = 500$ K; light gray ■, $T = 1000$ K.
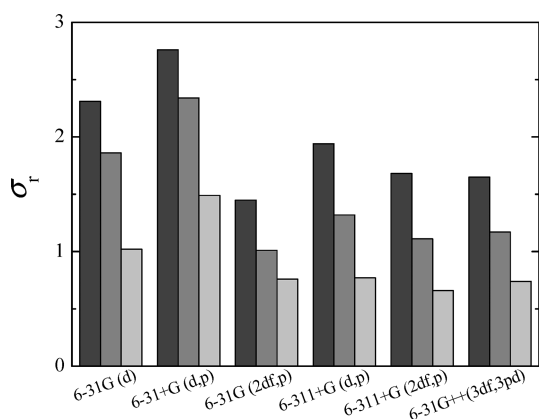
Figure 9. Average absolute percentage deviation, σ_r (eq 1), of the calculated ideal-gas entropies from the reference values[7] for sp structures (Table S10 of the SI). Black ■, unscaled harmonic frequencies; dark gray ■, harmonic frequencies scaled by the scaling factor suggested by Merrick et al.;[11] light gray ■, harmonic frequencies scaled by the two scaling factors developed in this work.

The isobaric heat capacities were recalculated for this set of molecules using these two scaling factors (Table S8 in the SI). Figure 8 and Table S9 in the SI summarize the results obtained (i) with unscaled frequencies, (ii) with one scaling factor suggested by Merrick et al.,[11] and (iii) with two scaling factors suggested in this work. Relative deviations obtained with unscaled frequencies are predominantly negative (99 % negative deviations) and show a significant temperature dependence. The usage of a single scaling factor suggested by Merrick et al.[11] lower σ_r (eq 1) by approximately 1 %. However, the distribution of the relative deviations remains strongly biased with only 6 % negative deviations. Two scaling values developed in this work provide better results for this set of molecules. The deviations are on the average about 1 %, and the ratio of positive and negative deviations is more balanced.

Two newly determined scaling factors were validated by comparison of calculated entropies with reference values[7] (Figure 9 and

Table S10 in the SI). σ_r is 0.9 % when using the two scale factors from this work, 1.5 % when one scale factor suggested by Merrick et al.[11] is applied, and 2.0 % when unscaled frequencies are used. The two scale factors also provide the most balanced distribution of relative deviations.

■ CONCLUSIONS

The results of the present study show that ideal-gas heat capacities and entropies of rigid molecules can be calculated with the accuracy less than 2.5 % using the unscaled frequencies obtained by the DFT with the B3LYP functional. The calculated heat capacities are, however, systematically underestimated, and the deviations from reference values are temperature-dependent. Scaling the calculated frequencies by a single value leads to slightly more accurate results, but the heat capacities are systematically overestimated, and the temperature dependence of the deviations is not corrected. Closer agreement between the calculated and the reference ideal-gas heat capacities is achieved by using wavenumber-dependent scaling factors. As illustrated in this work, the type of chemical bonds should also be taken into account when developing scaling factors. Two frequency dependent sets of scaling factors are suggested for two groups of rigid structures containing atoms in the sp^2 and sp hybridization, respectively (see Table 1). This procedure avoids the averaging of scale factors over the whole vibrational spectrum and ensures the correct scaling of more important low frequencies. Therefore, these scale factors significantly improve the agreement between the calculated and the reference data for both heat capacity and entropy and provide a temperature dependence of the ideal-gas heat capacities which is closer to the experiment. In the case of compounds containing atoms in both sp^2 and sp hybridizations we suggest visualizing the vibrational modes to determine which modes correspond to atoms in a given hybridization and perform the scaling accordingly. The analysis performed for rigid structures was limited mainly by a low number of reliable reference data for such types of chemical species. The results for molecules containing internal rotations will be published separately.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables S1–S10 as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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