

Comparison of Ab Initio and Group Additive Ideal Gas Heat Capacities

Robert A. Marriott and Mary Anne White

Dept. of Chemistry and Institute for Research in Materials, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

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Three case studies comparing molecular ideal gas heat capacity estimations using empirical group additive methods and statistical mechanical methods using ab initio vibrational frequencies are reported. In the first study, results from several ab initio levels of theory are compared with the experimental heat capacities of piperidine and the heat capacities calculated from the observed vibrational frequencies. In the second study, heat capacities for a benchmark group of 27 organic molecules were calculated using vibrational frequencies from AM1, HF/3-21G(d), and B3LYP/6-31G(d) theory level, and the results were compared to three recently updated additivity schemes. In the third study, semiempirical corrections to the heat capacities of n-alkanes were investigated. The strength of additivity schemes is that they are easy to use and understand, and often give reasonable results, but predict the same thermodynamic properties for isomers containing the same functional groups, and are of limited accuracy when the near-neighbor interactions are strong or if the input data set is not appropriate. Ab initio vibrational frequencies can rapidly provide accurate heat capacities using the harmonic oscillator model, especially if one conformer dominates. The results can be comparable to additivity, and better for rigid molecules containing heteroatoms. Furthermore, ab initio results do not require a calibration data set. © 2004 American Institute of Chemical Engineers AIChE J, 51: 292–297, 2005

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Introduction

Correlation equations have long been useful to estimate thermodynamic properties for industrial process models because of their simplicity and ease of use.¹ In particular, group additivity schemes provide a useful approach to estimate properties for organic molecules, such as in a temperature or pressure range where experimental data are not available. The ideal gas heat capacity is one of the most basic properties required for process modeling.

Even for condensed phases, correlation equations of state often require an estimate of ideal gas heat capacities to delineate intramolecular and intermolecular contributions. For solu-

tions, ideal gas heat capacities give information about solute–solvent interactions (through the solvation heat capacity, that is, the heat capacity change for a molecule going from an ideal gas to an infinitely dilute solution) and the Henry's Law constant at different temperatures and pressures.² The overall reliability of the equation of state can be limited by the accuracy of the ideal gas estimations. For example, Yezdimer et al.³ reported an additivity scheme that can be used to estimate apparent molar heat capacities for a wide range of aqueous organic species at infinite dilution, using ideal gas heat capacities estimated by the additivity method of Joback.^{4,5}

Given the fundamental importance of ideal gas heat capacities and the fact that ab initio methods are now easy to use, readily available, and of high accuracy (see, for example, Karni et al.,⁶ Dorofeeva et al.,⁷ Lin and Sandler,⁸ Sum and Sandler⁹), unlike when Benson and Buss¹⁰ first proposed their additivity scheme, we thought it worthwhile to compare ab initio and

Correspondence concerning this article should be addressed to M. A. White at Mary.Anne.White@dal.ca.

additivity methods. In addition to Joback's additivity method,^{4,5} there are many similar schemes to predict ideal gas properties.^{11,12} As with other empirical correlation models, they all suffer from external validity problems. Furthermore, group additivity predicts the same thermodynamic properties for isomers containing the same functional groups and has limited accuracy when near-neighbor interactions are strong.³ Indeed, some newer additivity schemes have been parameterized using high-level ab initio calculations.¹³

In testing the feasibility of a more theoretically based estimation method, we performed exploratory calculations of ideal gas heat capacities using simple ab initio methods, for three case studies: (1) heat capacity of piperidine using ab initio predicted zero-point vibrations compared with the experimental fundamental vibrations; (2) comparison of the heat capacities of a series of organic compounds from low-level ab initio vibrational frequencies with those of a recent evaluation of additivity schemes;¹¹ (3) empirical corrections to the theoretical heat capacities for some small to medium *n*-alkanes using low-level ab initio vibrational frequencies.¹⁴ Our aim was to determine whether ab initio frequencies can be used to predict ideal gas heat capacities, especially where additivity would have inherent limitations.

Computational Details

All ab initio calculations were performed using the Gaussian98[®] package¹⁵ for Windows on an Intel[®] Pentium[®] IV 2.4-GHz processor. Calculations were made as harmonic oscillators with the zero-point vibrations as the fundamental frequencies. All frequencies were scaled using the factors of Scott and Radom.¹⁶

Translational and rotational heat capacity contributions have been taken from equipartition, that is, $C_{V,rot} = (3/2)R$ and $C_{V,trans} = (3/2)R$. These contributions, with $C_p - C_v = R$, yield the external isobaric ideal gas heat capacity, $C_{p,ext} = 4R$. Vibrational heat capacity contributions were calculated for *n* 1-D harmonic oscillators

$$C_{V,vib} = R \sum_{i=1}^n \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} \quad (1)$$

with

$$x_i = \frac{h\nu_i}{kT} \quad (2)$$

where T is the temperature and ν_i is the *i*th vibrational frequency. Corrections for vibrational anharmonicity and rotational stretching were neglected. In some rare cases, a minimum was not located in the tight ab initio optimizations; the heat capacity contribution for imaginary frequencies was assigned the maximum value, R .

Errors in the calculated heat capacity, $\delta C_p = \delta C_{V,vib}$, were estimated by

$$\delta C_{V,vib} = \frac{Rhc}{kT} \sqrt{\delta v^2 \left[\sum_{i=1}^n \frac{x_i^2 e^{2x_i} (x_i e^{x_i} + x_i - 2e^{x_i} + 2)^2}{(e^{x_i} - 1)^6} \right]} \quad (3)$$

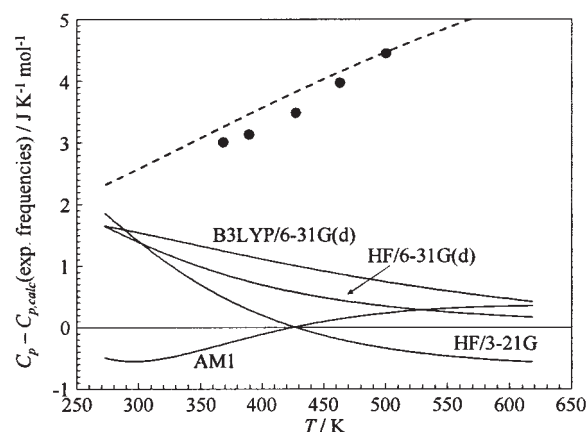


Figure 1. Results for piperidine heat capacity as a function of temperature.

●, the difference between the experimental ideal gas heat capacity¹⁷ and the heat capacity calculated from experimental vibrational frequencies¹⁸; —, curves marked with different levels of ab initio theory correspond to the difference between the heat capacity calculated from vibrational frequencies at that level of theory, and the heat capacity calculated using experimental vibrational frequencies¹⁸; ---, 2.5% of the total heat capacity.

where $\delta\nu$ is the (constant) standard error expected for any frequency.

Results and Discussion

Case I: piperidine

Piperidine provides a useful test because there are reliable experimental values for both its heat capacity¹⁷ and its fully assigned vibrational modes.¹⁸ Furthermore, the difference in heat capacity of its conformers is very small [$C_{p,calc}(\text{equatorial}) - C_{p,calc}(\text{axial}) < 0.15 \text{ J K}^{-1} \text{ mol}^{-1}$ [$< 0.2\%$ of the total heat capacity] for $T = 273\text{--}618 \text{ K}$].

From Fundamental Vibrational Frequencies. The heat capacity of piperidine has been calculated as described above using the experimental vibrational frequencies of Vedral et al.¹⁸ These results compare very well with the experimental heat capacities extrapolated to ideal gas conditions,¹⁷ within 2.5%, as shown in Figure 1, with the experimental heat capacities above the calculated heat capacity. Although at $T = 650 \text{ K}$ the vibrational contribution is less than 40% of its maximum value ($45R$), it is more than 70% of the experimental heat capacity for this relatively small molecule at a moderate temperature. Because the largest contribution to the heat capacity is vibrational, it is worth considering the effect of frequency errors on the total heat capacity (Eq. 3).

The estimated error for the calculated vibrational heat capacity of (equatorial) piperidine is shown in Figure 2 for $\delta\tilde{\nu} = \pm 50 \text{ cm}^{-1}$. Although $\delta\tilde{\nu} = \pm 50 \text{ cm}^{-1}$ is likely an overestimate of the experimental error in frequencies for a piperidine molecule, it provides a benchmark. The contributions of the individual modes show that most of the error occurs below room temperature and for the low-frequency modes. With large low-temperature errors, one could expect a significant error in standard state formation entropies and enthalpies. However, this example calculation for piperidine shows that vibrational frequencies above about 200 cm^{-1} and within $\pm 50 \text{ cm}^{-1}$ of the

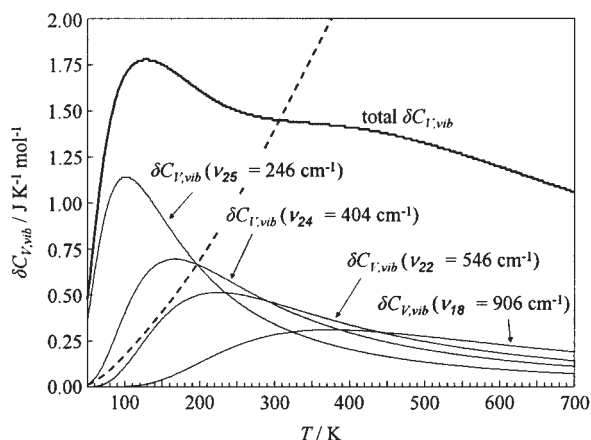


Figure 2. Effect of frequency uncertainty of 50 cm^{-1} on the error in vibrational heat capacity, $\delta C_{v,\text{vib}}$ for various modes of piperidine.

Vibrational frequencies are those of Vedal et al.¹⁸ and --- is 2% of the total vibrational heat capacity.

real values are sufficient to calculate heat capacities, especially at or above room temperature, within a few percent.

From Ab Initio Vibrational Frequencies. Scott and Radom¹⁶ reported a set of semiempirical scaling factors for vibrational frequencies at many different levels of ab initio theory. The frequency scaling factors, their root-mean-square (rms) deviations, and the rms deviations for the 45 fundamental frequencies of piperidine¹⁸ are given in Table 1. Generally, the rms vibrational frequency uncertainties are within the benchmark $\delta \tilde{\nu} \pm 50\text{ cm}^{-1}$. The differences between the heat capacity of piperidine calculated with the experimental and the low-level ab initio theories are shown in Figure 1, where the agreement is very good. Based on accuracy for heat capacities, formation enthalpies and entropies, and computational cost, Scott and Radom¹⁶ recommended use of the B3LYP hybrid density function theory in combination with the 6-31G(d) basis set. This also gives good results here.

As an alternative, one can use the Benson and Buss additivity scheme^{10,19} to estimate the ideal gas heat capacity of piperidine; however, temperature-dependent corrections for ring compounds are required. CHETAHTM Version 7.2²⁰ gives piperidine ring correction factors of -24.7 to $17.58\text{ J K}^{-1}\text{ mol}^{-1}$ for $T = 298\text{--}1000\text{ K}$ ($-3.77\text{ J K}^{-1}\text{ mol}^{-1}$ at $T = 600\text{ K}$). These correction factors are much larger than the uncertainty in the ab initio predictions of the heat capacity, showing that when the temperature-dependent ring corrections are omitted, as in early additivity methods, the error in the heat capacities from additivity methods is greater than that from ab initio predictions.

Case II: comparison of ab initio methods to additivity methods

Poling et al.¹¹ evaluated the additivity schemes of Benson and Buss,^{10,19} Joback,^{4,5} and Constantinou and Gani²¹ for 27 organic compounds, as a benchmark group. All three methods were found to be adequate at estimating heat capacities (within a few percent) at $T = 298.15$ and 700 K . The Benson and Buss^{10,19} scheme was recommended for the highest accuracy,

but the schemes of Joback^{4,5} and Constantinou and Gani²¹ are less complicated.

The errors in heat capacity, relative to the experimental heat capacities, as given by Poling et al.¹¹ for these 27 compounds, are shown in Figure 3, along with relative errors for the heat capacities of these molecules, as calculated using our zero-point vibrational results at the AM1, HF/3-21G, and B3LYP/6-31G(d) theory levels. (No conformational contributions are included; vibrational frequencies are applicable to only one minimized structure.) The average heat capacity error at all three ab initio theory levels is within 2%, similar to that of the additivity schemes. In all methods, the uncertainty is greater at $T = 298\text{ K}$ than that at $T = 700\text{ K}$.

The ab initio results are better than those from additivity methods for propanenitrile, octafluorocyclobutane, 3-methylthiophene, and 2-methyl-2-butanethiol (see Appendix). The average absolute deviation from the experimental heat capacity is 1.7% from ab initio methods and 7.0% from additivity approaches for those four compounds. Indeed, within the 27 benchmark compounds, where additivity methods show an average deviation of more than about 2%, ab initio methods show a substantial improvement.

Some of the extreme data in Figure 3 can be explained by neglect of conformational effects. For example, heptane has internal rotation that would be expected to cause significant deviation from the harmonic oscillator assumption in the ab initio methods; the relative error in the heat capacity at $T = 298\text{ K}$ is about 1% using the additivity methods and about -7% using the ab initio methods.

Overall, this limited data set shows that ab initio frequencies, determined with very little computational cost, can predict ideal gas heat capacities for organic compounds with accuracy similar to that of predictions from recently updated additivity schemes. Furthermore, the temperature dependency of the ab initio heat capacities arises directly from statistical thermodynamics and therefore does not require correlation-type equations or additional fitting parameters, as for additivity schemes.

Table 1. Frequency Scaling Factor and Root-Mean-Square Deviations of Scott and Radom¹⁶

Method	Scale Factor	rms_{OV}^* (cm^{-1})	rms_{pip}^{**} (cm^{-1})
AM1	0.9532	126	54
PM3	0.9761	159	68
HF/3-21G	0.9085	87	34
HF/6-31G(d)	0.8953	50	20
HF/6-31+G(d)	0.8970	49	20
HF/6-31G(d,p)	0.8992	53	21
HF/6-311G(d,p)	0.9051	54	22
HF/6-311G(df,p)	0.9054	56	22
MP2-fu/6-31G(d)	0.9427	61	27
MP2-fc/6-31G(d)	0.9434	63	28
QCISD-fc/6-31G(d)	0.9537	37	25
BLYP/6-31G(d)	0.9945	45	31
BLYP/6-311G(df,p)	0.9986	42	34
BP86/6-31G(d)	0.9914	41	29
B3LYP/6-31G(d)	0.9614	34	25
B3P86/6-31G(d)	0.9558	38	26
B3PW91/6-31G(d)	0.9573	34	26

* rms_{OV} is the overall root-mean-square deviation for the 1066 fundamental vibrations of Scott and Radom.¹⁶

** rms_{pip} is the root-mean-square deviation from the 45 experimental fundamental frequencies of piperidine, from Vedal et al.¹⁸

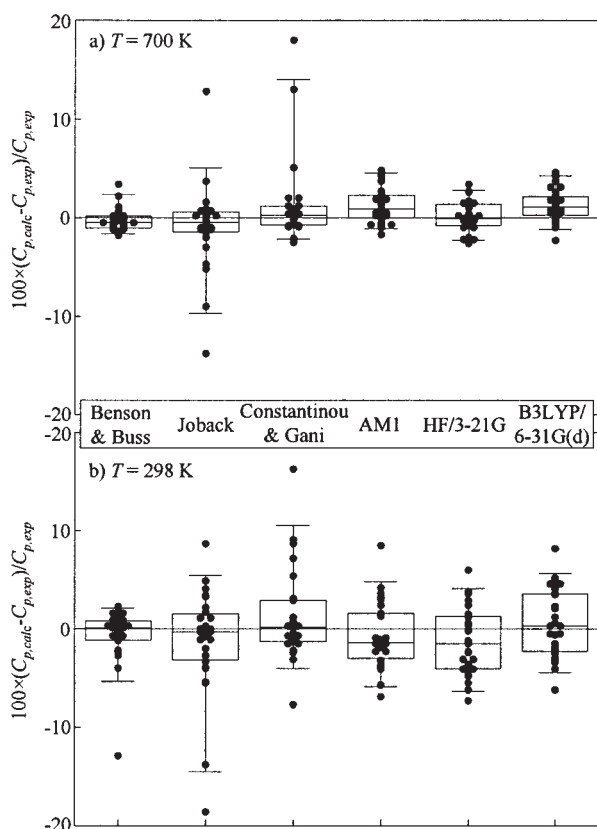


Figure 3. Relative errors of heat capacities for 27 organic compounds calculated by three additivity schemes¹¹ and from the present ab initio results.

● are individual points (data given in the Appendix); box shows 25th to 75th percentiles; box centerline is the mean; bars are the 5th and 95th percentiles.

The additivity methods and the ab initio methods are both good at higher temperatures. Because this assessment does not include conformational effects, this matter seemed to be worth a separate investigation.

Case III: *n*-alkanes

Internal rotation is an example where the harmonic oscillator approximation fails. Since Pitzer²² first modeled *n*-alkanes using a hindered rotator model, the field has grown considerably, although very few models are both simple and computationally inexpensive.^{14,23}

Recently, Vansteenkiste et al.¹⁴ calculated heat capacities and entropies of some gas phase *n*-alkanes by replacing torsional modes with uncoupled hindered internal rotators. Zero-point energies and transition energies were calculated at the B3LYP/6-311G(d,p) level of theory. The success of the model was demonstrated by good agreement with the experimental entropies from $T = 298.15$ to 1500 K. The heat capacity predictions are somewhat better than those calculated using only the uncorrected harmonic oscillator approximation, especially at the lowest temperatures.

Guthrie²⁴ tested Gaussian94 results at the B3LYP/6-31G(d,p) level for the prediction of entropies for 128 organic

compounds, accounting for conformers through the entropy of mixing of low-lying conformers. Absolute entropies at $T = 298$ K were predicted within an overall standard deviation $\delta S \pm 5.4$ J K⁻¹ mol⁻¹ ($\approx 2\%$).²⁴ All internal modes were treated as harmonic oscillators and, although this works well with some types of conformational freedom, it will not work for molecules with free (or nearly free) rotors.

These two investigations indicate that first-principles calculations have not completely replaced empirical estimations. Therefore, we have explored the possibility of using empirical corrections to the ab initio harmonic oscillator heat capacity predictions, realizing that the validity of these types of corrections would be limited to compounds similar to those used to produce the correction.

Our first semiempirical heat capacity correction uses residual entropy. After all, both statistical mechanics and classical thermodynamics suggest such a relationship. Several linear correlations between the residual entropy and the residual heat capacity for the *n*-alkanes were tested by best-subset regression. We found the best way to estimate the heat capacities was by use of the following expression

$$C_p = 4R + C_{v,vib} + (a_1 + a_2T)(S_{exp} - S_{calc,HO}) \quad (4)$$

where S_{exp} is the experimental absolute entropy, $S_{calc,HO}$ is the entropy calculated using the harmonic oscillator approximation [B3LYP/6-31G(d)], and a_1 and a_2 are empirical fitting coefficients. We fit 30 data sets (experimental vs. calculated heat capacities) to Eq. 4 for ethane through decane at temperatures of $T = 298.15$ –1000 K.²⁵ Coefficients of $a_1 = 0.58 \pm 0.02$ and $a_2 = -0.00096 \pm 0.00003$ K⁻¹ were found to reproduce heat capacities with a standard error of $\delta C_p = 0.14R$ (all but two points within 1%; $R^2 = 0.976$), as shown in Figure 4. The uncertainty is a significant improvement, as exemplified by the heptane results (within 0.2% of experiment, compared with 6% error without this correction). Equation 4 has only three empirical parameters, including the scaling factor of Scott and Radom.¹⁶

However, the applicability of the residual entropy correla-

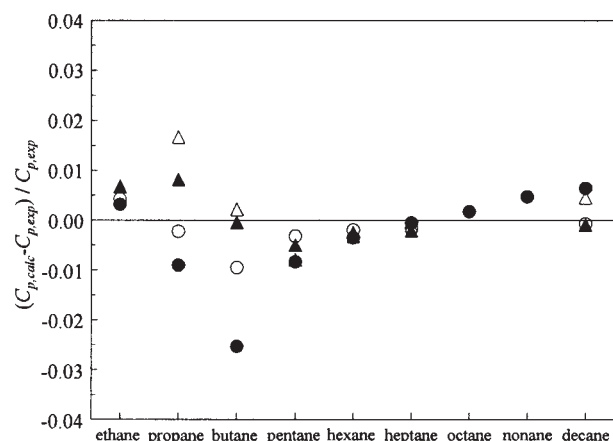


Figure 4. Relative heat capacity errors from Eq. 4 for some *n*-alkanes.

●, $T = 298.15$ K; ○, $T = 500$ K; ▲, $T = 700$ K; and △, $T = 1000$ K.

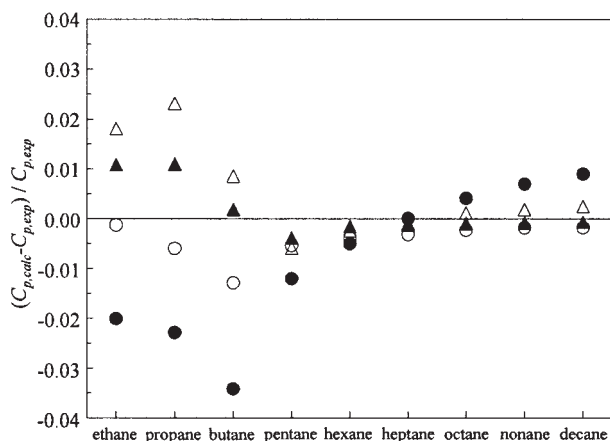


Figure 5. Relative heat capacity errors from Eq. 5 for some n -alkanes.

●, $T = 298.15$ K; ○, $T = 500$ K; ▲, $T = 700$ K; and △, $T = 1000$ K.

tion is rather limited because experimental entropies usually are calculated from experimental heat capacities, and the results would not be expected to apply beyond the family of compounds used for the correlation. Nevertheless, the success of Eq. 4 shows there is a robust empirical correlation between conformational entropy correction and conformational heat capacity correction.

Thus, we sought a correlation based on well-known contributions to multiple conformation entropy, that is, the number of possible conformations and the internal rotation symmetry numbers, σ_{int} . Note that the Benson and Buss scheme^{10,19} uses this approach to correct for isomerization and symmetry.

The number of conformations and the symmetry of a potential energy surface can be estimated by simply examining the structure. The conformational contribution to the entropy is $R \ln(\phi/\sigma_{int})$, where $\phi = \prod \phi_i$ and ϕ_i is the number of minima for rotation of bond i . For example, for butane, $\sigma_{int} = 3^2 \times 2$ (3 for each $-\text{CH}_3$, 2 for $-\text{CH}_2-\text{CH}_2-$) and $\phi = 3^3$ (3 for each $\text{C}-\text{C}$ bond). Use of these factors gives

$$C_p = 4R + C_{vib} + (a_3 + a_4T)R \ln\left(\frac{\phi}{\sigma_{int}}\right) \quad (5)$$

which is a simple semiempirical method to estimate heat capacities using only three fitting parameters, simple ab initio calculations, and knowledge of the molecular connectivity. We fit 36 data sets (experimental vs. calculated heat capacities) for ethane through decane at temperatures of $T = 298.15$ – 1000 K²⁵ to Eq. 5. Coefficients of $a_3 = 1.42 \pm 0.05$ and $a_4 = -0.00235 \pm 0.00007$ K⁻¹ were found to reproduce heat capacities with a standard error of $\delta C_p = 0.17R$ (all but a few points within 1.5%; $R^2 = 0.972$). The relative errors are shown in Figure 5. This is an improvement over ab initio methods alone, again especially for heptane, with little complication and computational effort. However, this type of correlation still suffers from an external validity problem because the fit parameters given above for Eq. 5 are applicable only to the n -alkanes.

Conclusions

Our exploratory case studies have shown that a large portion of the ideal gas heat capacity can be estimated (with temperature dependency) using the harmonic oscillator model and the ab initio frequencies, especially if one conformer dominates.

The piperidine example showed that the simple harmonic oscillator model and experimental vibrational frequencies can be used successfully to provide a close estimate of the ideal gas heat capacity. Rather large errors in fundamental vibrational frequencies were found to have little impact on the heat capacity of piperidine.

Low-level ab initio frequencies provided the heat capacity of piperidine and 34 additional compounds in good agreement with experimental values. The ab initio calculated heat capacities were found to be comparable to recently updated additivity schemes,¹¹ especially reducing the number of outlying heat capacities in the benchmark data set.

Multiple conformations and internal rotation effects on the heat capacity of some n -alkanes were investigated further, and it was shown that simple structural attributes can be used to correct for conformational disorder.

It is worth noting that the harmonic oscillator model works surprisingly well. From the 68 data sets used in these case studies, the average uncertainty in the vibrational heat capacity is small $(C_{vib,exp} - C_{vib,HO})/R = -0.2 \pm 0.6$.

Collectively, these results show that ab initio frequencies can be used to calculate ideal gas heat capacities for organic molecules, comparable to additivity methods and better than additivity methods for rigid molecules containing heteroatoms.

Acknowledgments

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Appendix

Relative error of estimated ideal gas heat capacities

Formula	Chemical Name	C_p (exp)*		Benson		Joback		C/G		AM1		HF/3-21G		B3LYP/6-31G(d)	
		298**	700**	298**	700**	298**	700**	298**	700**	298**	700**	298**	700**	298**	700**
C ₂ HCl ₃	Trichloroethene	80.25	109.30	0.9	-0.3	-4.0	-4.7	-1.5	0.0	-1.6	-0.7	1.3	-0.1	1.2	0.4
C ₂ H ₄ F ₂	1,1-Difluoroethane	68.49	117.53	-2.2	-0.5	-1.1	-1.2	0.3	2.0	-2.3	0.2	-2.3	-1.0	-1.5	0.2
C ₃ H ₅ N	Propanenitrile	73.92	126.62	-1.2	-0.5	8.7	12.8	-0.4	-0.6	-4.1	0.8	-4.8	-1.0	-1.9	0.5
C ₃ H ₈	Propane	73.76	143.11	0.3	-0.1	1.1	-0.5	-0.9	-0.7	-2.3	2.2	-3.9	-0.4	-2.5	0.8
C ₃ H ₉ N	Trimethylamine	91.77	177.08	0.3	-0.1	0.0	-0.7	0.1	0.1	-1.5	0.5	-3.1	-2.0	-3.0	-1.0
C ₄ F ₈	Octafluorocyclobutane	156.08	236.99	-12.9	-0.8	-13.8	0.7	3.1	13.0	3.2	-1.0	3.8	0.2	-0.5	-2.3
C ₄ H ₈	trans-2-Butene	80.3	160.5	0.9	-1.6	3.4	0.0	8.7	2.0	8.5	3.7	6.0	1.6	8.2	3.1
C ₄ H ₈ O	Butanone	103.40	177.66	-2.3	0.2	-5.4	0.8	-2.2	0.9	-3.7	4.8	-4.1	3.4	-2.2	4.6
C ₄ H ₈ O ₂	1,4-Dioxane	92.35	200.12	-0.4	-0.6	1.7	0.9	9.1	0.6	-1.3	-0.7	2.9	-0.8	2.3	-0.1
C ₄ H ₈ O ₂	Ethylacetate	113.58	200.00	-4.0	-0.5	-0.1	-0.3	-7.7	-0.5	-0.9	2.7	-1.5	1.5	-0.5	2.6
C ₄ H ₉ NO ₂	2-Nitrobutane	123.6	232.8	0.3	-0.8	-3.9	-9.0	0.7	-0.8	1.6	1.5	3.6	1.7	3.5	1.8
C ₅ H ₆ S	3-Methylthiophene	95.71	181.04	1.4	1.1	-18.6	-13.8	—	—	1.5	0.7	1.5	0.3	4.6	1.8
C ₅ H ₈	2-Methyl-1,3-butadiene	102.64	187.53	2.3	0.3	-3.3	-2.0	-1.5	-2.5	-3.2	-0.7	-6.2	-2.2	-3.1	-0.5
C ₅ H ₈	2-Pentyne	98.70	178.86	-0.7	0.1	2.2	0.2	1.2	0.2	2.4	3.8	-0.1	1.5	4.1	3.2
C ₅ H ₁₂ S	1-Thiahexane	140.84	254.60	0.1	0.2	-0.3	0.3	0.2	-0.2	-3.9	2.3	-3.6	0.4	-3.4	1.2
C ₅ H ₁₂ S	2-Methyl-1-2-butanethiol	143.50	259.49	0.4	-0.6	-5.5	-5.2	16.3	18.0	-1.4	1.4	-2.4	-0.3	-0.6	0.8
C ₆ H ₅ Br	Bromobenzene	100.71	190.04	-0.7	-1.1	-2.7	-1.0	-2.4	-0.9	-0.9	-1.7	-5.5	-2.6	0.3	-0.6
C ₆ H ₇ N	3-Methylpyridine	99.88	206.07	2.1	-0.5	3.3	0.2	0.3	0.4	3.6	0.9	0.4	-0.1	4.9	1.4
C ₆ H ₁₂	3,3-Dimethyl-1-butene	126.40	245.71	0.5	3.4	4.9	3.7	7.2	5.1	4.2	4.5	2.4	2.7	5.2	4.2
C ₆ H ₁₄ O	Di-(methylethyl)ether	158.27	288.65	-0.8	2.2	-0.8	-1.5	-1.1	-2.1	-3.3	4.2	-3.1	2.6	-2.3	3.7
C ₆ H ₁₄ S ₂	4,5-Dithiaoctane	187.09	322.66	-0.6	0.7	-2.0	0.7	-0.7	1.2	-5.7	1.9	-4.7	0.2	-4.1	1.1
C ₇ H ₈ O	4-Methylphenol	124.86	240.91	0.1	-1.2	-0.3	-1.2	2.9	0.3	1.3	0.2	-0.2	0.2	3.6	1.6
C ₇ H ₁₄	cis-1,3-Dimethylcyclopentane	134.60	292.64	-2.7	-1.2	0.0	1.6	-3.1	1.2	-1.1	0.5	0.6	-0.5	2.1	0.6
C ₇ H ₁₆	Heptane	165.80	318.38	-1.1	0.1	0.3	-1.0	-1.3	-0.9	-6.9	1.3	-7.3	-0.6	-6.2	0.5
C ₇ H ₁₆	2,2,3-Trimethylbutane	163.39	326.73	1.6	-1.1	1.1	-3.0	1.1	-0.8	-1.5	-0.5	-1.2	-2.2	0.6	-0.9
C ₉ H ₁₂	1-Methyl-4-ethylbenzene	148.60	303.30	1.6	-1.8	4.1	0.2	5.4	0.5	3.0	1.9	1.2	1.0	4.6	2.3
C ₁₁ H ₁₀	2-Methylnaphthalene	159.79	319.32	-2.4	-1.4	-1.1	-0.6	-0.7	0.4	-1.9	-0.1	-4.1	-0.3	0.3	1.3

Experimental and additive calculations from Poling et al.,¹¹ deviations in percent, *in J K⁻¹ mol⁻¹, **in K.

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