

The calculations of absolute entropy. Gaussian vs. “classical” calculation by method of statistical thermodynamics

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The absolute entropy values at 298.15 K of several oxygen and nitrogen-containing organic compounds were calculated within the rigid rotator – harmonic oscillator approximation using various methods of quantum chemistry incorporated in the Gaussian 09 software package. The obtained values have been compared with the ones from published sources. The impact of the computing method (HF, B3LYP, MP2) and the basis set (6-31G(d,p), 6-311++G(3df,3pd), aug-cc-pvtz) on the accuracy of obtained absolute entropy values has been discussed. B3LYP/6-31(d,p) is the most optimal combination of the computing method/utilized basis set for a fast estimation of the entropy values of small organic compounds.

Key words: *thermodynamic properties, ab initio calculations, ideal gas state, absolute entropies, Gaussian.*

1. Introduction

Currently, methods of statistical physics and thermodynamics are extensively used in physical chemistry to calculate a variety of different properties of substances, for instance, the enthalpy of formation or entropy. The combination of physical models and quantum-chemical approaches provides valuable information in many fields of chemistry. The ability of these methods to calculate various thermodynamic functions relatively fast and accurately in a wide temperature interval is not only one benefit. In addition, they enable validation of the experimental values of the properties and theoretically justify the selection of measurement methods.

The precise relationships of statistical physics and the thermodynamics of bonded multi-particle states that do not use empirical approximations refer to the gaseous phase. Most experimental measurements of thermodynamic properties are carried out with substances in a condensed state, either crystalline or liquid, since measurements of the thermodynamic properties of compounds in the gaseous phase involve experimental difficulties. However, the experimentally measured values of enthalpy and entropy characteristics of compounds in a condensed state can be converted into thermo-

dynamic properties in the gaseous phase using the thermodynamic properties of phase transitions and simple thermochemical equations (Eqs. 1-2):

$$\Delta_f H_m^o(g) = \Delta_f H_m^o(cr) - \Delta_{cr}^g H_m^o \quad (1)$$

$$\Delta_f S_m^o(g) = \Delta_f S_m^o(cr) - \Delta_{cr}^g S_m^o \quad (2)$$

A comparison of experimentally obtained and computed via methods of statistical physics values enables a conclusion about the degree of reliability and inter-consistency of the primary experimental results.

It should be noted that the calculation of the thermodynamic functions of polyatomic compounds is a nontrivial task. It requires the knowledge of a complete conformational composition of the substance to account for the entropy of mixing, an adjustment due to strong intramolecular interactions, for instance, due to the presence of an intramolecular hydrogen bond along with the contribution of high amplitude motion – torsional vibrations and internal rotation, atomic inversions in the cyclic systems, etc.

Gaussian [1] is the most popular software package widely used in the field of quantum chemistry. Chemists frequently use this program to calculate the enthalpy of formation of substances in the gaseous phase via composite methods: the most com-

mon among them are G-n [2], CBS-n [3] and sometimes W-n [4]. Additionally, this software package [1] allows an estimation of the thermodynamic functions values of organic compounds in the ideal gas state within rigid rotator - harmonic oscillator approximation using a set of harmonic fundamental frequencies. However, the standard approach does not reflect the presence of different conformers of the compound and the high amplitude motion so, in our opinion, it is a type of express method to estimate the thermodynamic functions values of the substances, for instance, the absolute entropy values.

This work represents an attempt to estimate how the combining this method and the basis during geometry optimization and the computing of a set of harmonic fundamental vibrational frequencies impact the accuracy of the evaluated property. The published absolute entropy values of several oxygen and nitrogen containing compounds at 298.15 K have been taken from [5-7]. A comparison has been performed using computed results of the entropy values of a variety of substances via methods HF [8], B3LYP [9], MP2 [10] with the bases 6-31G(d,p) [11], 6-311++G(3df,3pd) [12] and aug-cc-pvtz [13]. The performed comparison enabled us to recommend the most applicable combination of the method/basis set for *express* estimation of the absolute entropy value of small organic compounds in the ideal gas state.

2. Methods

Quantum chemical calculations were performed with the Gaussian 09 series software [1]. An initial search for the stable conformers was performed with the force field MMFF94 method [14]. At that, the molecule geometric parameters – bond length, angles and dihedral angles – have been modified randomly with preserving the cyclic structure (if it was present) with further molecule geometry optimization. A further molecule geometry optimization continued for an identified as the most stable conformer using various combinations of methods and bases followed by an additional calculation of harmonic vibrational frequencies. The absolute entropy value of the substances was taken directly from the output file of the Gaussian 09 software package.

3. Results

The theoretical absolute entropy value is independent of the total electron energy or the zero-point energy but is related only to the molecular structure and, to a higher extend, to the vibrational spectrum (transition energies), especially in higher infrared interval ($< 1000 \text{ cm}^{-1}$). Modern quantum-chemical methods produce molecule geometric pa-

rameters close to the experimental ones. Therefore, we can indirectly assert regarding the accuracy of the computed vibrational spectrum within the low-frequency region relying on the obtained results.

The computed results are presented in Tables 1-4. A set of absolute entropies of the substances computed in the bases 6-311++G(3df,3pd) via methods HF, B3LYP and MP2 are shown in Table 1. The average deviations of the determined values from the literature data are equal to ± 11.36 , ± 10.76 and $\pm 9.89 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively. The consecutive decrease in the average deviation naturally explains the increase of the accuracy of the accounting for the electron correlation among the methods HF - B3LYP - MP2. The highest deviations were recorded for butanol-1, butanone-2, propan-2-amine – the substances with the most number of conformers.

The absolute entropy values for the substances computed via B3LYP method in different bases are presented in Table 2. The produced average deviations are located approximately on the same level $\pm 10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. However, the lesser deviation has several values computed in the smaller basis set 6-31G(d,p). It may be random compensation of the calculation error of the low frequency vibrational spectra with a structural contribution to the entropy. Employing a small basis set leads to overlooking the intramolecular interactions and underestimation of vibrational frequencies of large fragments relative to each other. In other words, insufficiently constraining interaction reduces force constants and compensates for the lack of structural contribution [15]. The main deviation of the large-sized bases refers to nitroethane, butanol-1 и butanone-2. This fact most likely relates to the inability of selecting of one conformer as a reference one to account for the gosh effect [16-18] that is accumulating with increasing size and degree of branching of the molecule. On the other hand, the expansion of the basis set usually leads to an increase in internuclear distances and an increase in the accounting for the accuracy of interelectron correlation produces their reduction and, consequently, a rise of vibrational frequencies. It means the error of the vibrational contribution decreases at the constant error in the structural component of the properties.

The absolute entropies obtained using the perturbation theory of the second order MP2 are presented in Table 3. Here the increase of a number of bases functions is expressed in the decrease of properties computing error. This confirms the conclusion drawn above that an increase in the basis set leads to a decline in internuclear distances and an increase in force constants. This phenomenon can significantly skew the frequencies of valent vibrations of hydrogen atom but this impact on the entropy is insignificant. At the same time, it slightly

Table 1

The values of absolute entropies at 298.15 K, calculated different methods with basis set 6-311++G(3df,3pd), J·K⁻¹·mol⁻¹

Compounds	Literature	HF	/delta/	B3LYP	/delta/	MP2	/delta/
methanol	239.81 [5]	237.53	2.28	238.65	1.16	238.45	1.36
methanal	218.76 [5]	217.93	0.83	218.47	0.29	218.55	0.21
nitromethane	282.86 [7]	295.14	12.28	266.06	16.80	291.52	8.66
methanamine	242.88 [6]	239.40	3.48	240.69	2.19	240.27	2.61
methanoic acid	248.99 [5]	247.05	1.94	248.27	0.72	248.28	0.71
ethanol	250.90 [5]	267.86	16.96	270.58	19.68	269.72	18.82
ethanal	263.95 [5]	260.38	3.57	262.12	1.83	262.06	1.89
ethanamine	283.77 [6]	269.40	14.37	272.02	11.75	270.97	12.80
ethandiol	303.80 [5]	290.90	12.90	294.70	9.10	292.95	10.85
ethanoic acid	283.47 [5]	282.86	0.61	287.49	4.02	287.02	3.55
nitroethane	320.51 [7]	313.41	7.10	291.67	28.84	317.03	3.48
nitroethylene	300.50 [7]	290.39	10.11	294.60	5.90	295.61	4.89
methylmethanoate	285.28 [5]	280.78	4.50	284.49	0.79	282.47	2.81
dimethylether	267.34 [5]	268.92	1.58	270.54	3.20	269.52	2.18
propanol-2	309.20 [5]	294.24	14.96	298.55	10.65	296.99	12.21
propanone	297.62 [5]	302.63	5.01	308.16	10.54	305.90	8.28
propan-1-amine	325.44 [6]	300.16	25.28	304.28	21.16	302.84	22.60
propan-2-amine	312.24 [6]	295.43	16.81	299.66	12.58	298.13	14.11
methylethanoate	324.38 [5]	316.68	7.70	325.90	1.52	324.14	0.24
diethylether	342.67 [5]	329.42	13.25	334.35	8.32	332.86	9.81
butanal	343.67 [5]	319.82	23.85	324.62	19.05	322.81	20.86
butanol-1	361.59 [5]	329.74	31.85	335.56	26.03	333.80	27.79
butanone-2	339.90 [5]	366.59	26.69	379.12	39.22	370.00	30.10
furane	267.25 [5]	269.48	2.23	272.25	5.00	272.71	5.46
2,5-dihydrofurane	284.25 [5]	272.54	11.71	275.32	8.93	275.34	8.91
tetrahydrofurane	302.41 [5]	278.96	23.45	312.82	10.41	280.46	21.95
average			± 11.36		± 10.76		± 9.89

Table 2

The values of absolute entropies at 298.15 K, calculated B3LYP with different basis set, J·K⁻¹·mol⁻¹

Compounds	Literature	6-31G (d,p)	/delta/	6-311++G (3df,3pd)	/delta/	aug-cc- pvtz	/delta/
methanol	239.81 [5]	237.55	2.26	238.65	1.16	238.60	1.21
methanal	218.76 [5]	218.56	0.20	218.47	0.29	218.48	0.28
nitromethane	282.86 [7]	295.88	13.02	266.06	16.80	266.05	16.81
methanamine	242.88 [6]	239.81	3.07	240.69	2.19	240.76	2.12
methanoic acid	248.99 [5]	248.20	0.79	248.27	0.72	248.30	0.69
ethanol	250.90 [5]	269.64	18.74	270.58	19.68	270.50	19.60
ethanal	263.95 [5]	262.40	1.55	262.12	1.83	262.14	1.81
ethanamine	283.77 [6]	270.93	12.84	272.02	11.75	272.15	11.62
ethandiol	303.80 [5]	291.78	12.02	294.70	9.10	294.71	9.09
ethanoic acid	283.47 [5]	288.52	5.05	287.49	4.02	287.42	3.95
nitroethane	320.51 [7]	316.39	4.12	291.67	28.84	291.69	28.82
nitroethylene	300.50 [7]	294.40	6.10	294.60	5.90	294.42	6.08

Compounds	Literature	6-31G (d,p)	/delta/	6-311++G (3df,3pd)	/delta/	aug-cc- pvtz	/delta/
methylmethanoate	285.28 [5]	285.24	0.04	284.49	0.79	284.57	0.71
dimethylether	267.34 [5]	269.69	2.35	270.54	3.20	270.55	3.21
propanol-2	309.20 [5]	297.08	12.12	298.55	10.65	298.58	10.62
propanone	297.62 [5]	307.24	9.62	308.16	10.54	309.06	11.44
propan-1-amine	325.44 [6]	302.90	22.54	304.28	21.16	304.36	21.08
propan-2-amine	312.24 [6]	298.54	13.70	299.66	12.58	299.69	12.55
methylethanoate	324.38 [5]	325.24	0.86	325.90	1.52	325.41	1.03
diethylether	342.67 [5]	333.51	9.16	334.35	8.32	334.36	8.31
butanal	343.67 [5]	324.98	18.69	324.62	19.05	324.54	19.13
butanol-1	361.59 [5]	333.60	27.99	335.56	26.03	335.36	26.23
butanone-2	339.90 [5]	367.21	27.31	379.12	39.22	373.15	33.25
furane	267.25 [5]	272.34	5.09	272.25	5.00	272.10	4.85
2,5-dihydrofurane	284.25 [5]	275.38	8.87	275.32	8.93	275.28	8.97
tetrahydrofurane	302.41 [5]	307.85	5.44	312.82	10.41	304.37	1.96
average			± 9.37		± 10.76		± 10.21

Table 3

The values of absolute entropies at 298.15 K, calculated MP2 with different basis set, J·K⁻¹·mol⁻¹

Compounds	Literature	6-31G (d,p)	/delta/	6-311++G (3df,3pd)	/delta/	aug-cc- pvtz	/delta/
methanol	239.81 [5]	237.24	2.57	238.45	1.36	238.51	1.30
methanal	218.76 [5]	218.61	0.15	218.55	0.21	218.59	0.17
nitromethane	282.86 [7]	288.25	5.39	291.52	8.66	294.06	11.20
methanamine	242.88 [6]	239.24	3.64	240.27	2.61	240.48	2.40
methanoic acid	248.99 [5]	248.22	0.77	248.28	0.71	248.32	0.67
ethanol	250.90 [5]	268.38	17.48	269.72	18.82	269.72	18.82
ethanal	263.95 [5]	262.49	1.46	262.06	1.89	262.09	1.86
ethanamine	283.77 [6]	269.29	14.48	270.97	12.80	271.49	12.28
ethandiol	303.80 [5]	290.11	13.69	292.95	10.85	292.95	10.85
ethanoic acid	283.47 [5]	285.81	2.34	287.02	3.55	286.73	3.26
nitroethane	320.51 [7]	290.59	29.92	317.03	3.48	319.04	1.47
nitroethylene	300.50 [7]	296.14	4.36	295.61	4.89	294.99	5.51
methylmethanoate	285.28 [5]	282.74	2.54	282.47	2.81	282.31	2.97
dimethylether	267.34 [5]	269.01	1.67	269.52	2.18	269.47	2.13
propanol-2	309.20 [5]	295.05	14.15	296.99	12.21	297.47	11.73
propanone	297.62 [5]	303.56	5.94	305.90	8.28	307.08	9.46
propan-1-amine	325.44 [6]	300.84	24.60	302.84	22.60	303.42	22.02
propan-2-amine	312.24 [6]	296.35	15.89	298.13	14.11	298.60	13.64
methylethanoate	324.38 [5]	322.33	2.05	324.14	0.24	323.16	1.22
diethylether	342.67 [5]	332.05	10.62	332.86	9.81	332.85	9.82
butanal	343.67 [5]	322.48	21.19	322.81	20.86	323.07	20.60
butanol-1	361.59 [5]	332.08	29.51	333.80	27.79	333.95	27.64
butanone-2	339.90 [5]	366.77	26.87	370.00	30.10	368.12	28.22
furane	267.25 [5]	273.02	5.77	272.71	5.46	272.45	5.20
2,5-dihydrofurane	284.25 [5]	275.20	9.05	275.34	8.91	275.26	8.99
tetrahydrofurane	302.41 [5]	280.11	22.30	280.46	21.95	303.06	0.65
deviation			± 11.09		± 9.89		± 9.00

Table 4

The values of absolute entropies at 298.15 K, calculated different methods with basis set aug-cc-pvtz, $J \cdot K^{-1} \cdot mol^{-1}$

Compounds	Literature	HF	/delta/	B3LYP	/delta/	MP2	/delta/
methanol	239.81 [5]	237.48	2.33	238.60	1.21	238.51	1.30
methanal	218.76 [5]	217.95	0.81	218.48	0.28	218.59	0.17
nitromethane	282.86 [7]	288.09	5.23	266.05	16.81	294.06	11.20
methanamine	242.88 [6]	239.46	3.42	240.76	2.12	240.48	2.40
methanoic acid	248.99 [5]	247.09	1.90	248.30	0.69	248.32	0.67
ethanol	250.90 [5]	267.82	16.92	270.50	19.60	269.72	18.82
ethanal	263.95 [5]	260.44	3.51	262.14	1.81	262.09	1.86
ethanamine	283.77 [6]	269.53	14.24	272.15	11.62	271.49	12.28
ethandiol	303.80 [5]	290.91	12.89	294.71	9.09	292.95	10.85
ethanoic acid	283.47 [5]	283.17	0.30	287.42	3.95	286.73	3.26
nitroethane	320.51 [7]	312.49	8.02	291.69	28.82	319.04	1.47
nitroethylene	300.50 [7]	290.33	10.17	294.42	6.08	294.99	5.51
methylmethanoate	285.28 [5]	280.95	4.33	284.57	0.71	282.31	2.97
dimethylether	267.34 [5]	268.94	1.60	270.55	3.21	269.47	2.13
propanol-2	309.20 [5]	294.37	14.83	298.58	10.62	297.47	11.73
propanone	297.62 [5]	303.57	5.95	309.06	11.44	307.08	9.46
propan-1-amine	325.44 [6]	300.25	25.19	304.36	21.08	303.42	22.02
propan-2-amine	312.24 [6]	295.52	16.72	299.69	12.55	298.60	13.64
methylethanoate	324.38 [5]	317.02	7.36	325.41	1.03	323.16	1.22
diethylether	342.67 [5]	329.44	13.23	334.36	8.31	332.85	9.82
butanal	343.67 [5]	319.84	23.83	324.54	19.13	323.07	20.60
butanol-1	361.59 [5]	329.60	31.99	335.36	26.23	333.95	27.64
butanone-2	339.90 [5]	364.54	24.64	373.15	33.25	368.12	28.22
furane	267.25 [5]	269.37	2.12	272.10	4.85	272.45	5.20
2,5-dihydrofurane	284.25 [5]	272.51	11.74	275.28	8.97	275.26	8.99
tetrahydrofurane	302.41 [5]	278.99	23.42	304.37	1.96	303.06	0.65
deviation			± 11.03		± 10.21		± 9.00

improves the reproduction of the vibrational frequencies with high amplitude and their contribution to the entropy at the constant error of the contribution of the structural component.

Finally, Table 4 contains the absolute entropy values determined using a combination of methods with the largest basis set aug-cc-pvtz. As it was shown above, the expansion of the basis set improves the reproduction of the vibrational spectrum and the contribution of vibrational motions to the thermodynamic properties of a substance. The average deviation of the theoretical values from the experimental ones is large enough, but it is explained by using the "rigid rotator - harmonic oscillator" model and neglecting a conformational variety. The last contribution is within the scope of standard relations of sta-

tistical physics in performing the conformational analysis.

4. Conclusion

Analysis of Tables 1-4 enables a conclusion that the determining the entropy based on data obtained by perturbation theory is most preferable. However, this type of calculations requires the use of the largest available basis set and is extremely resource-intensive. Along with this, the calculation with the help of functional B3LYP is not only less resource-intensive but with insignificant deterioration of the final values depends less on the size of the basis set. In the outcome, we recommend the B3LYP method in combination in a 6-31(d,p) basis set for a fast estimation of the absolute entropy of small organic compounds, although it sound paradoxically.

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