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Statistical thermodynamics of 1-butanol, 2-methyl-1-propanol, and butanal

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The purpose of the present investigation is to calculate partition functions and thermodynamic quantities, viz., entropy, enthalpy, heat capacity, and Gibbs free energies, for 1-butanol, 2-methyl-1-propanol, and butanal in the vapor phase. We employed the multi-structural (MS) anharmonicity method and electronic structure calculations including both explicitly correlated coupled cluster theory and density functional theory. The calculations are performed using all structures for each molecule and employing both the local harmonic approximation (MS-LH) and the inclusion of torsional anharmonicity (MS-T). The results obtained from the MS-T calculations are in excellent agreement with experimental data taken from the Thermodynamics Research Center data series and the *CRC Handbook of Chemistry and Physics*, where available. They are also compared with Benson's empirical group additivity values, where available; in most cases, the present results are more accurate than the group additivity values. In other cases, where experimental data (but not group additivity values) are available, we also obtain good agreement with experiment. This validates the accuracy of the electronic structure calculations when combined with the MS-T method for estimating the thermodynamic properties of systems with multiple torsions, and it increases our confidence in the predictions made with this method for molecules and temperatures where experimental or empirical data are not available. © 2012 American Institute of Physics. [doi:10.1063/1.3674995]

I. INTRODUCTION

Butanol, 2-methyl-1-propanol, and butanal play important roles in alternative-fuel combustion.^{1–5} Therefore, accurate estimation of the thermodynamic properties of these systems is essential. One can, in favorable cases and for certain conditions, obtain these properties either experimentally or by a statistical mechanical approach. Since it is very difficult and often impossible to measure thermodynamic properties of substances for a wide range of temperature by experimental means, it is necessary to calculate them by employing reliable theoretical-methods, validated by experimental data. In the present article we consider four properties, entropy (S_T^o), heat capacity ($C_p^o(T)$), enthalpy (H_T^o), and free energy (G_T^o), that are needed to calculate thermal reaction rate constants and chemical equilibrium constants. We validate the method where experimental or empirical data are available, and we make predictions for the remaining cases.

Limited experimental data are available.^{6–9} Parks⁶ presented heat capacity and free energy data for crystalline and liquid *n*-butyl alcohol at low temperatures. Strömsöe *et al.*⁸ reported vapor-phase heat capacity for various aliphatic alcohols including 1-butanol and 2-methyl-1-propanol; these heat capacities were measured in a flow calorimeter at atmospheric pressure in a temperature range of about 300–600 K. For butanal, Tjebbes⁷ estimated the heats of combustion and heats of formation experimentally. Benson's empirical group additivity (GA) method⁹ has widely been used by researchers to

estimate thermodynamic quantities for systems with no available experimental results. The GA method is empirical and is based on fitting a limited number of experimental data for a limited number of systems. Its reliability and accuracy is questionable when applied to systems not contained in its training set, but the accuracy is high for cases for which it represents a convenient fit to available experimental data.

The recently developed internal-coordinate multi-structural (MS) approximation¹⁰ can be used to compute partition functions and other thermodynamic quantities of systems with multiple structures and torsional (T) anharmonicity, and it has recently been applied successfully to hydrocarbons.^{11,12} Other work on coupled torsions includes the work of Miller and Clary¹³ and that of Waroquier and coworkers.¹⁴ Miller and Clary developed a torsional path integral Monte Carlo algorithm to calculate the conformational thermodynamics of molecules; their treatment provides a coupled, anharmonic description of the torsional contributions to the partition functions, a harmonic treatment of the other internal modes, and an *ab initio* description of the potential energy surface. Waroquier and coworkers developed an internal-coordinate scheme for coupling neighboring torsions.

The MS-T method developed in our group combines both MS anharmonicity and T anharmonicity. In the low-temperature limit, where the MS anharmonicity is most important, the MS-T method reduces to the local-harmonic (LH) approximation, while in the high-temperature limit, it gives the free-rotor result and thus includes the T anharmonicity effect. In this work, we have included anharmonicity in three ways:

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1. Scaling of harmonic frequencies by empirical factors¹⁵ that depend on the electronic model chemistry. This is done in order to reduce the error in zero-point energies, which are calculated by the LH approximation.
2. Using all structures for a particular system. The presence of multiple local minima on a potential energy surface is an anharmonic effect.
3. Inclusion of torsions and their coupling to one another and to overall rotation.

In the present study, we focus our attention on the determination of various thermodynamic properties of 1-butanol, 2-methyl-1-propanol, and butanal in the gas-phase. We employed three Minnesota density functionals, M06-2X (Ref. 16), M08-SO (Ref. 17), and M08-HX (Ref. 17) along with the explicitly correlated coupled-cluster (CC) wave function method in order to determine standard state entropies, heat capacities, enthalpies, and Gibbs free energies. Even at temperatures below the boiling point, all the calculations are performed for a pure ideal gas at a pressure of 1 bar. Molecular dissociation is not included.

II. COMPUTATIONAL DETAILS

The geometry optimizations and frequency calculations for 1-butanol were performed with M06-2X (Ref. 16), M08-HX (Ref. 17), and M08-SO (Ref. 17) with the 6-311+G(2df,2p) basis set.¹⁸ The 6-311+G(2df,2p) basis is the same as MG3S (Ref. 19) for H, C, and O, and we will use the shorter name “MG3S”. For 2-methyl-1-propanol, geometries and frequencies were calculated with M08-HX/MG3S, and for butanal they were calculated by M08-HX with the minimally augmented correlation-consistent triple-zeta basis set, i.e., maug-cc-pVTZ.²⁰ We also performed single-point calculations with the F12a explicit correlation extension of coupled cluster theory with single and double excitations and a quasiperturbative treatment of connected triple excitations (CCSD(T)-F12a) (Ref. 21) and the jul-cc-pVTZ (Ref. 20) basis sets for the one-electron part of the basis set.

All the density functional calculations were carried out with the GAUSSIAN 09 (Ref. 22) suite of programs, and the CCSD(T)-F12a results were obtained using MOLPRO.²³ The density functional frequency calculations involve 99 radial shells and 974 angular points per shell and are scaled by standard scaling factors¹⁵ of 0.970 for M06-2X/MG3S, 0.973 for M08-HX/MG3S, 0.983 for M08-SO/MG3S, and 0.976 for M08-HX/maug-cc-pVTZ.

The MS-T method for the partition functions and thermodynamic quantities takes into account all the conformational structures of a system and improves over the harmonic results by using torsional factors.¹⁰ In the local harmonic (LH) approximation, the conformational-rotational-vibrational partition functions can be written as

$$Q_{\text{con-rovib}}^{\text{MS-LH}} = \sum_{j=1}^J Q_{\text{rot},j} \exp(-\beta U_j) Q_j^{\text{HO}}, \quad (1)$$

where j labels a structure, J is the number of structures, the term “con” means conformational, “rovib” denotes rotational-vibrational, $Q_{\text{rot},j}$ is the rotational partition func-

tion of structure j , which includes the rotational symmetry number, σ_j , in the denominator, and Q_j^{HO} is the normal-mode local-harmonic-oscillator vibrational partition function calculated at structure j . Including the torsional factors in Eq. (1), the partition function becomes

$$Q_{\text{con-rovib}}^{\text{MS-T}} = \sum_{j=1}^J Q_{\text{rot},j} \exp(-\beta U_j) Q_j^{\text{HO}} Z_j \prod_{\tau=1}^l f_{j,\tau}, \quad (2)$$

where Z_j is a factor that is designed to ensure that the MS-T approach reaches the high-temperature limit, $f_{j,\tau}$ is an internal-coordinate torsional anharmonicity function, and τ is the torsional motion. The MS-T and MS-LH methods are implemented in the MSTor program.²⁴

The total partition function is the product of the contributions of electronic, translational, and conformational-rotational-vibrational factors. From the partition function, we can calculate entropy, heat capacity, enthalpy, and free energy using the MSTor program.²⁴

III. RESULTS AND DISCUSSION

A. Structure and energetics of 1-butanol, 2-methyl-1-propanol, and butanal

The lowest-energy structures of 1-butanol, 2-methyl-1-propanol, and butanal are shown in Fig. 1. In 1-butanol, there are four torsions, namely, O2-C3, C3-C4, C4-C5, and C5-C6. Of these, internal rotations around C5-C6 do not generate distinguishable conformers, and hence only the other three torsions, i.e., O2-C3, C3-C4, and C4-C5, produce structures that are distinguishable.

The naming convention for the structures is given in Table I. This table was prepared following the IUPAC convention²⁵ with slight modifications. We introduced “g±” and “a±” ranges to be “(±75, ±90)” and “(±90, ±105)”, respectively. The density functional calculations with each of the three functionals yield 29 structures for 1-butanol with 14

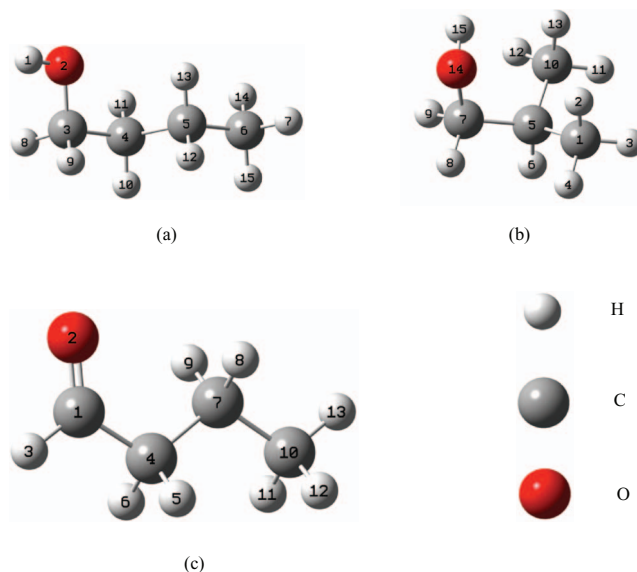


FIG. 1. Structures of (a) 1-butanol, (b) 2-methyl-1-propanol, and (c) butanal.

TABLE I. Name conventions and labeling of structures.^a

Name convention	Abbreviation	Dihedral angle range (in deg) ^b
<i>Cis</i>	C	0
<i>cis</i> [±]	C[±]	(0, ±30)
<i>gauche</i> [±]	G[±]	(±30, ±75) ^c
	g[±]	(±75, ±90)
<i>anti</i> [±]	a[±]	(±90, ±105)
	A[±]	(±105, ±150)
<i>Trans</i> [±]	T[±]	(±150, ±180)
<i>Trans</i>	T	180

^aThe dihedral angles used for torsions are H1–O2–C3–C4, O2–C3–C4–C5, and C3–C4–C5–C6 for 1-butanol; H15–O14–C7–C5 and O14–C7–C5–H6 for 2-methyl-1-propanol; O2–C1–C4–C7 and C1–C4–C7–C10 for butanal.

^b(*x*, *y*) means $x < \tau < y$.

^cThis includes both $-75 < \tau < -30$ and $30 < \tau < 75$.

pairs of mirror images and one structure (**TTT**) that does not have any distinguishable mirror image owing to the plane of symmetry. Note that structures having torsional angles that are all 180° or 0° (excluding the –CH₃ torsions) have indistinguishable mirror images due to the presence of a plane of symmetry; hence we should take into account only one structure. In case of 2-methyl-1-propanol, we have nine structures of which four have distinguishable mirror images; the other has the anti-periplanar (**TT**) arrangement. These nine structures are generated by rotating the molecule around O14–C7 and C5–C7; the other two rotations, viz., C1–C5 and C5–C10 contain –CH₃, and thus, do not contribute any new structures. For butanal the torsions around C1–C4 and C4–C7, produce seven distinguishable structures, and torsion around C7–C10 does not produce more structures. Among these seven structures, we have three pairs of mirror images and one structure (**CT**) with torsional angles of 0° and 180°. The rotational symmetry numbers for all the structures are one because they have no rotational symmetry axis.

Table II lists all the structures with their names and both zero-point-exclusive and zero-point-inclusive relative conformational energies. Although we performed geometry optimizations and frequency calculations using M08-HX, M08-SO, and M06-2X for 1-butanol, Table II only shows the data for M08-HX since the coupled cluster calculations were carried out with M08-HX geometries, and hence this provides a better comparison to the coupled cluster results. The results for the other two functionals are given in the supplementary material.²⁶ Inspection of Table II reveals some noteworthy features of the results. For 1-butanol, the zero-point-exclusive relative conformational energies calculated using the M08-HX functional are lower than those obtained with CCSD(T)-F12a for 18 of the total of 27 non-zero relative energy values. In contrast, for 2-methyl-1-propanol, the zero-point-exclusive relative conformational energies in 4 out of 7 cases are lower when calculated with the coupled cluster method than when M08-HX was used. For 1-butanol and 2-methyl-1-propanol, the most stable geometry is the same in both density functional and coupled cluster methods. In case of butanal, however, the lowest energy structures are different and all the rel-

TABLE II. Names of structures and their relative conformational energies (in kcal/mol).

Compound	Structures	Relative conformational energy		
		Zero-point-exclusive	Zero-point-inclusive	CCSD(T)-F12a ^{b,c}
1-butanol	T⁻G⁺T⁻, T⁺G⁻T⁺	0.00	0.00	0.00
	T⁺G⁺G⁺, T⁻G⁻G⁻	0.05	0.37	0.48
	G⁺G⁺T⁻, G⁻G⁻T⁺	0.19	0.21	0.14
	G⁺G⁻T⁻, G⁻G⁺T⁺	0.20	0.29	0.12
	G⁺G⁺G⁺, G⁻G⁻G⁻	0.23	0.49	0.63
	G⁺G⁻G⁻, G⁻G⁺G⁺	0.33	0.62	0.76
	TTT	0.37	0.32	0.20
	G⁺T⁺T⁺, G⁻T⁻T⁻	0.40	0.37	0.19
	G⁺T⁻G⁻, G⁻T⁺G⁺	0.82	0.89	0.83
	T⁺T⁺G⁺, T⁻T⁻G⁻	0.82	0.89	0.89
	G⁺T⁺G⁺, G⁻T⁻G⁻	0.99	1.02	0.95
	T⁺g⁻G⁻, T⁻g⁺G⁺	1.32	1.34	1.66
	G⁺G⁺G⁻, G⁻G⁻G⁺	1.32	1.40	1.55
	G⁺g⁻G⁺, G⁻g⁺G⁻	1.44	1.71	1.87
	G⁻G⁺a⁻, G⁺G⁻a⁺	1.96	2.19	2.33
2-methyl-1-propanol	T⁻G⁻, T⁺G⁺	0.00	0.00	0.00
	G⁻G⁺, G⁺G⁻	0.11	0.20	0.03
	G⁻G⁻, G⁺G⁺	0.13	0.20	0.07
	TT	0.22	0.34	0.37
	G⁺T⁻, G⁻T⁺	0.28	0.48	0.35
Butanal	C⁻G⁻, C⁺G⁺	0.00	0.03	0.03
	CT	0.10	0.00	0.00
	A⁺G⁻, A⁻G⁺	1.05	0.95	0.67
	A⁻T⁻, A⁺T⁺	1.20	1.10	0.71

^aThe basis set used for M08-HX is MG3S for 1-butanol and 2-methyl-1-propanol and maug-cc-pVTZ for butanal.

^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S for 1-butanol and 2-methyl-1-propanol.

^cCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/maug-cc-pVTZ for butanal.

ative conformational energies are lower according to coupled cluster than the density functional ones.

Some of the torsions in these molecules are strongly coupled (SC). In an ideal situation, where all torsions are independent, alcohols would have 3^{*n*} structures, where *n* is the number of torsions that each generate 3 distinguishable structures. Since *n* is 3 for 1-butanol and 2 for 2-methyl-1-propanol, ideal torsions would generate 27 and 9 structures, respectively. We do have nine structures in the latter case; however, due to coupling between O2–C3 and C4–C5, we identified 29 distinguishable structures for 1-butanol. This is attributed to steric hindrance¹⁰ between terminal –OH and –CH₃ groups. In particular, the expected **G⁻G⁺G⁻** and **G⁺G⁻G⁺** structures become saddle points connecting **G⁻G⁺a⁻/G⁻g⁺G⁻** and **G⁺G⁻a⁺/G⁺g⁻G⁺**, respectively. Hence, instead of 27 structures, we have 29. Earlier studies^{27,28} based on the conformational analysis of 1-butanol have taken into account only 27 structures. Of the four torsions present in 1-butanol, three of them, i.e., O2–C3, C3–C4, and C4–C5 are SC and one (C5–C6) involving the –CH₃ group is nearly separable (NS). In case of

TABLE III. Calculated conformational–rotational–vibrational partition function of 1-butanol.^a

<i>T</i> (K)	MS-LH				MS-T			
	M06-2X ^b	M08-SO ^b	M08-HX ^b	CCSD(T)-F12a ^c	M06-2X ^b	M08-SO ^b	M08-HX ^b	CCSD(T)-F12a ^c
200	4.97×10^{-86}	1.35×10^{-85}	1.20×10^{-85}	1.22×10^{-85}	6.40×10^{-86}	1.75×10^{-85}	1.55×10^{-85}	1.60×10^{-85}
250	3.87×10^{-67}	8.90×10^{-67}	7.98×10^{-67}	7.95×10^{-67}	5.24×10^{-67}	1.21×10^{-66}	1.09×10^{-66}	1.09×10^{-66}
298	7.70×10^{-55}	1.60×10^{-54}	1.44×10^{-54}	1.41×10^{-54}	1.09×10^{-54}	2.26×10^{-54}	2.04×10^{-54}	2.02×10^{-54}
300	2.07×10^{-54}	4.28×10^{-54}	3.87×10^{-54}	3.79×10^{-54}	2.93×10^{-54}	6.07×10^{-54}	5.49×10^{-54}	5.43×10^{-54}
400	3.32×10^{-38}	6.01×10^{-38}	5.50×10^{-38}	5.32×10^{-38}	5.01×10^{-38}	9.08×10^{-38}	8.31×10^{-38}	8.11×10^{-38}
600	3.15×10^{-21}	5.03×10^{-21}	4.68×10^{-21}	4.50×10^{-21}	5.07×10^{-21}	8.04×10^{-21}	7.46×10^{-21}	7.22×10^{-21}
800	5.28×10^{-12}	7.96×10^{-12}	7.46×10^{-12}	7.20×10^{-12}	8.49×10^{-12}	1.26×10^{-11}	1.17×10^{-11}	1.14×10^{-11}
1000	6.25×10^{-6}	9.14×10^{-6}	8.61×10^{-6}	8.34×10^{-6}	9.63×10^{-6}	1.37×10^{-5}	1.29×10^{-5}	1.25×10^{-5}
1500	1.80×10^4	2.54×10^4	2.41×10^4	2.35×10^4	2.29×10^4	3.09×10^4	2.91×10^4	2.84×10^4
2000	1.57×10^{10}	2.18×10^{10}	2.08×10^{10}	2.04×10^{10}	1.59×10^{10}	2.10×10^{10}	1.98×10^{10}	1.94×10^{10}
2400	5.79×10^{13}	7.98×10^{13}	7.63×10^{13}	7.50×10^{13}	4.88×10^{13}	6.38×10^{13}	6.03×10^{13}	5.91×10^{13}

^aThe zero of energy is at the lowest-energy classical equilibrium structure.^bThe basis set used for M08-HX, M08-SO, and M06-2X is MG3S.^cCCSD(T)-F12a/jul-cc-pVTZ/M08-HX/MG3S.

2-methyl-1-propanol, two torsions (O14–C7 and C5–C7) are SC, and the other two, viz., C1–C5 and C5–C10 with –CH₃ group are NS in nature.

It is harder to count the number of ideal structures for butanal, but we find seven structures, which is clearly non-ideal since seven, like 29, is a prime number. Butanal has two SC torsions (C1–C4 and C4–C7) which generate distinguishable structures, and the one containing the –CH₃ group, C7–C10 is NS.

B. Conformational–rotational–vibrational partition functions of 1-butanol, 2-methyl-1-propanol, and butanal

Tables III–V present the conformational–rotational–vibrational partition functions for 1-butanol, 2-methyl-1-propanol, and butanal, respectively. For 1-butanol, the structure with the lowest zero-point-exclusive energy also has the lowest zero-point-inclusive energy. The zero of energy for calculating the partition functions is taken to be the zero-point-exclusive energy of this structure. In case of 2-methyl-1-propanol and butanal, the zero-point-exclusive and zero-point-inclusive energies yield different minimum-energy structures. For 2-methyl-1-propanol, we have taken the zero-point-exclusive energy of the $\mathbf{T}^- \mathbf{G}^-$, $\mathbf{T}^+ \mathbf{G}^+$ structures as the zero of energy to calculate the partition functions; for butanal, the zero-point-exclusive energies of $\mathbf{C}^- \mathbf{G}^-$ and $\mathbf{C}^+ \mathbf{G}^+$ are taken to be the zero of energy for calculating the partition functions.

To calculate the partition functions, one requires local periodicity¹⁰ (M_j, τ) parameters. For NS torsions involving the CH₃ group, M_j, τ is three. However, for the torsions that are SC, we use the Voronoi tessellation method (VTM).^{10,24} We use three-dimensional VTM for 1-butanol, two-dimensional VTM for butanal, and assign integer values for 2-methyl-1-propanol.

Table III illustrates that the partition functions (Q) obtained with M08-HX/MG3S are larger than those obtained with CCSD(T)-F12a at all temperatures above 298 K in both the MS-LH and MS-T approximations. Similar behavior is

TABLE IV. Calculated conformational–rotational–vibrational partition function of 2-methyl-1-propanol.^a

<i>T</i> (K)	MS-LH		MS-T	
	M08-HX ^b	CCSD(T)-F12a ^c	M08-HX ^b	CCSD(T)-F12a ^c
200	1.37×10^{-85}	1.44×10^{-85}	1.76×10^{-85}	1.85×10^{-85}
250	6.76×10^{-67}	6.99×10^{-67}	9.05×10^{-67}	9.36×10^{-67}
298	1.00×10^{-54}	1.03×10^{-54}	1.39×10^{-54}	1.42×10^{-54}
300	2.66×10^{-54}	2.73×10^{-54}	3.70×10^{-54}	3.79×10^{-54}
400	2.93×10^{-38}	2.97×10^{-38}	4.29×10^{-38}	4.36×10^{-38}
600	1.92×10^{-21}	1.94×10^{-21}	2.99×10^{-21}	3.02×10^{-21}
800	2.70×10^{-12}	2.72×10^{-12}	4.22×10^{-12}	4.25×10^{-12}
1000	2.90×10^{-6}	2.91×10^{-6}	4.36×10^{-6}	4.38×10^{-6}
1500	7.35×10^3	7.37×10^3	9.29×10^3	9.32×10^3
2000	6.05×10^9	6.06×10^9	6.18×10^9	6.19×10^9
2400	2.16×10^{13}	2.17×10^{13}	1.86×10^{13}	1.86×10^{13}

^aThe zero of energy is at the lowest-energy classical equilibrium structure ($\mathbf{G}^- \mathbf{T}^-$ in Table II).^bThe basis set used for M08-HX is MG3S.^cCCSD(T)-F12a/jul-cc-pVTZ/M08-HX/MG3S.TABLE V. Calculated conformational–rotational–vibrational partition function of butanal.^a

<i>T</i> (K)	MS-LH		MS-T	
	M08-HX ^b	CCSD(T)-F12a ^c	M08-HX ^b	CCSD(T)-F12a ^c
200	1.47×10^{-70}	2.02×10^{-70}	1.66×10^{-70}	2.33×10^{-70}
250	5.93×10^{-55}	8.25×10^{-55}	7.04×10^{-55}	9.97×10^{-55}
298	8.86×10^{-45}	1.22×10^{-44}	1.10×10^{-44}	1.54×10^{-44}
300	2.01×10^{-44}	2.78×10^{-44}	2.50×10^{-44}	3.51×10^{-44}
400	5.42×10^{-31}	7.25×10^{-31}	7.28×10^{-31}	9.84×10^{-31}
600	7.06×10^{-17}	8.85×10^{-17}	1.03×10^{-16}	1.30×10^{-16}
800	3.53×10^{-9}	4.23×10^{-9}	5.26×10^{-9}	6.31×10^{-9}
1000	4.30×10^{-4}	5.00×10^{-4}	6.31×10^{-4}	7.31×10^{-4}
1500	3.91×10^4	4.34×10^4	5.08×10^4	5.61×10^4
2000	4.12×10^9	4.46×10^9	4.58×10^9	4.93×10^9
2400	4.33×10^{12}	4.64×10^{12}	4.25×10^{12}	4.52×10^{12}

^aThe zero of energy is at the lowest-energy classical equilibrium structure ($\mathbf{C}^- \mathbf{G}^-$ in Table II).^bThe basis set used for M08-HX is maug-cc-pVTZ.^cCCSD(T)-F12a/jul-cc-pVTZ/M08-HX/maug-cc-pVTZ.

TABLE VI. Standard state entropy (in cal mol⁻¹ K⁻¹) of 1-butanol.

T (K)	MS-LH				MS-T				Benson's GA ^c	Expt. ^d
	M06-2X ^a	M08-SO ^a	M08-HX ^a	CCSD(T)-F12a ^b	M06-2X ^a	M08-SO ^a	M08-HX ^a	CCSD(T)-F12a ^b		
200	76.84	77.17	77.02	76.76	77.78	78.11	77.96	77.73		77.52
250	81.72	82.08	81.95	81.74	82.78	83.13	83.02	82.83		
298	86.08	86.46	86.35	86.17	87.23	87.60	87.49	87.34	88.14	86.42
300	86.26	86.64	86.53	86.35	87.41	87.78	87.68	87.52	88.32	86.58
400	94.84	95.25	95.15	95.03	96.09	96.47	96.37	96.26	96.86	95.02
600	110.78	111.24	111.16	111.09	111.90	112.29	112.19	112.12	112.44	110.73
800	125.14	125.63	125.55	125.51	125.89	126.27	126.18	126.12	126.31	124.72
1000	137.99	138.51	138.44	138.41	138.30	138.69	138.59	138.54	138.68	137.17
1500	164.84	165.39	165.32	165.30	164.02	164.43	164.34	164.31		163.01
2000	186.08	186.65	186.58	186.57	184.31	184.73	184.64	184.62		183.39
2400	200.23	200.81	200.74	200.73	197.81	198.23	198.14	198.12		
MUE(6) ^e	0.36	0.51	0.46	0.48	1.03	1.41	1.31	1.21	1.69	
MUE(9) ^f	0.81	1.01	0.98	1.01	0.93	1.31	1.21	1.11		

^aThe basis set used for M08-HX, M08-SO and M06-2X is MG3S.

^bCCSD(T)-F12a/jul-cc-pVTZ/M08-HX/MG3S.

^cUsing Benson's data from Ref. 9 and adding 0.026 cal mol⁻¹ K⁻¹ to convert from a standard pressure of 1 atm to a standard pressure of 1 bar.

^dTaken from Ref. 30.

^eThe mean unsigned errors (MUE) in standard state entropies (cal mol⁻¹ K⁻¹) corresponding to six temperatures where our computed results, Benson's empirical GA values, and experimental data are all available.

^fThe mean unsigned errors (MUE) in standard state entropies (cal mol⁻¹ K⁻¹) corresponding to nine temperatures where our computed results and experimental data are all available.

observed when using M08-SO/MG3S, where we found that the density functional calculations give a larger Q at all temperatures studied here. However, the third density functional, M06-2X, gives smaller Q values than the coupled cluster in both the approximations for all temperature values. In Tables IV and V, the partition functions obtained with M08-HX/MG3S and M08-HX/maug-cc-pVTZ for 2-methyl-1-propanol and butanal, respectively, have smaller Q values than CCSD(T)-F12a irrespective of the temperatures used. Figure 2 shows the percent deviation in Q between M08-HX results and the coupled cluster method. This deviation is calculated as

$$\frac{Q_{\text{CCSD(T)-F12a}} - Q_{\text{M08-HX}}}{Q_{\text{M08-HX}}} \times 100\%. \quad (3)$$

The figure shows that we have a similar trend for alcohols where the percent deviation decreases with increase in temperature and starts to saturate at about 1500 K. The Q values for 1-butanol obtained from coupled cluster and density functional calculations are quite close to each other, and the deviation is 7% or less, whereas for 2-methyl-1-propanol, the percentage ranges up to 16%. The difference in Q values obtained with density functionals and coupled cluster methods for butanal, on the other hand, is quite large, up to 40% (see Fig. 2). As we increase the temperature, the Q values for butanal calculated using density functional and coupled cluster methods get closer.

C. Thermodynamic quantities: Standard state entropy, heat capacity, enthalpy, and free energies of 1-butanol, 2-methyl-1-propanol, and butanal

In order to obtain the standard state entropy, heat capacity, enthalpy, and free energies, we made use of Eqs. (3)–(7) of

Ref. 29. The results are tabulated in Tables VI–XIV. We also applied Benson's GA parameters⁹ to estimate entropies and heat capacities, and they are tabulated in these tables along with the density functional and coupled cluster results. For the calculations of entropy values from Benson's GA data at temperatures above 298 K, we made use of the following equation:

$$S_T^o = S_T^o + \int_{T_0}^T \frac{C_P^o(T)}{T} dT. \quad (4)$$

The standard heat capacity ($C_P^o(T)$) values obtained from the GA tables at available temperatures are fitted to a cubic polynomial and then used in Eq. (4) in order to get entropy values at the desired temperatures. The experimental data are taken from the TRC data series³⁰ and *CRC Handbook of Chemistry and Physics*.³¹ Since Benson's empirical parameters are

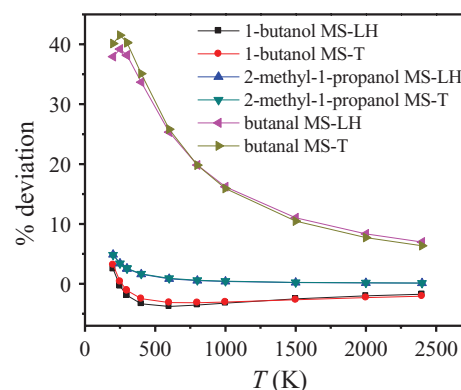


FIG. 2. The percent deviations of the partition function values (as defined in Eq. (3)) between CCSD(T)-F12a and M08-HX results of 1-butanol, 2-methyl-1-propanol, and butanal obtained by MS-LH and MS-T approximations.

TABLE VII. Standard state entropy (in cal mol⁻¹ K⁻¹) of 2-methyl-1-propanol.

<i>T</i> (K)	MS-LH		MS-T		Benson's GA ^c
	M08-HX ^a	CCSD(T)-F12a ^b	M08-HX ^a	CCSD(T)-F12a ^b	
200	74.32	74.27	75.18	75.13	
250	79.18	79.14	80.14	80.11	
298	83.55	83.52	84.59	84.57	87.64
300	83.73	83.70	84.77	84.75	87.82
400	92.35	92.33	93.49	93.47	96.30
600	108.38	108.37	109.43	109.43	111.90
800	122.79	122.79	123.53	123.52	125.81
1000	135.69	135.68	136.01	136.00	138.20
1500	162.57	162.57	161.83	161.83	
2000	183.83	183.83	182.17	182.16	
2400	197.99	197.97	195.68	195.68	

^aThe basis set used for M08-HX is MG3S.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S.^cUsing Benson's data from Ref. 9 and adding 0.026 cal mol⁻¹ K⁻¹ to convert from a standard pressure of 1 atm to a standard pressure of 1 bar.

based on the thermodynamic functions found in the American Petroleum Institute (API) (Ref. 32) tables that correspond to a standard state of 1 atm; in the present work, we correct those values to a standard state of 1 bar. The results from TRC data series and CRC tables are already for a standard state of 1 bar.

Tables VI–VIII give the standard state entropies of 1-butanol, 2-methyl-1-propanol, and butanal, respectively. In all cases, the entropies calculated with MS-LH approximations are smaller than those calculated with the MS-T approximation for temperatures ranging from 200 K to 1000 K; however, beyond 1000 K the MS-LH entropies are larger than the MS-T ones, as shown in Fig. 3. The estimated entropy values obtained from Benson's empirical GA parameters⁹ agree only within 4.1 cal mol⁻¹ K⁻¹ with those obtained from density functional and coupled cluster methods. The experimen-

tal data taken from TRC and CRC data series, on the other hand, agrees well with the computed entropy values. It is very encouraging that for 1-butanol the torsional corrections at high temperatures (1500 K and 2000 K) bring the theory into close agreement with the experimental data.

The heat capacities are given in Tables IX–XI along with Benson's GA values and experimental results. We have computed the $C_p^o(T)$ for density functional and coupled cluster methods using a finite difference approximation to

$$C_p^o(T) = \frac{dH_T^o}{dT}. \quad (5)$$

The $C_p^o(T)$ values calculated using MS-LH approach are less than those calculated using MS-T in the temperature regime up to ~450 K, while beyond that they become larger, as seen

TABLE VIII. Standard state entropy (in cal mol⁻¹ K⁻¹) of butanal.

<i>T</i> (K)	MS-LH		MS-T		Benson's GA ^c	Expt. ^d
	M08-HX ^a	CCSD(T)-F12a ^b	M08-HX ^a	CCSD(T)-F12a ^b		
200	72.51	73.32	73.12	73.98		
250	77.18	77.82	77.98	78.66		
298	81.28	81.77	82.22	82.73	84.17	82.14
300	81.44	81.93	82.39	82.89	84.33	
400	89.31	89.60	90.41	90.69	92.05	
600	103.54	103.67	104.59	104.69	105.92	
800	116.20	116.26	116.98	117.03	118.22	
1000	127.48	127.52	127.94	127.96	129.18	
1500	150.91	150.93	150.59	150.59		
2000	169.37	169.38	168.36	168.35		
2400	181.63	181.64	180.14	180.13		
UE ^e	0.86	0.37	0.084	0.59	2.03	

^aThe basis set used for M08-HX is maug-cc-pVTZ.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/maug-cc-pVTZ.^cUsing Benson's data from Ref. 9 and adding 0.026 cal mol⁻¹ K⁻¹ to convert from a standard pressure of 1 atm to a standard pressure of 1 bar.^dTaken from Ref. 31.^eThe unsigned errors (UE) in standard state entropies (cal mol⁻¹ K⁻¹) corresponding to 298 K temperature where our computed result, Benson's empirical GA, and the experimental value are all available.

TABLE IX. Heat capacity (in cal mol⁻¹ K⁻¹) of 1-butanol.

T (K)	MS-LH				MS-T				Benson's GA ^c	Expt. ^d
	M06-2X ^a	M08-SO ^a	M08-HX ^a	CCSD(T)-F12a ^b	M06-2X ^a	M08-SO ^a	M08-HX ^a	CCSD(T)-F12a ^b		
200	20.57	20.70	20.85	20.99	21.14	21.23	21.40	21.54		19.42
250	23.36	23.49	23.58	23.77	23.91	23.99	24.10	24.28		
298	26.42	26.54	26.61	26.79	26.90	26.97	27.03	27.20		25.82
300	26.55	26.67	26.74	26.93	27.03	27.10	27.15	27.33	26.48	25.95
400	33.42	33.54	33.58	33.75	33.57	33.60	33.61	33.74	32.99	33.02
600	45.47	45.58	45.61	45.72	44.62	44.62	44.62	44.68	44.12	44.54
800	54.30	54.42	54.43	54.51	52.61	52.63	52.62	52.68	52.27	52.71
1000	60.86	60.97	60.98	61.03	58.57	58.61	58.61	58.66	58.38	58.78
1500	71.07	71.14	71.15	71.18	67.97	68.02	68.03	68.06		68.24
2000	76.33	76.38	76.38	76.40	72.86	72.91	72.91	72.94		73.08
2400	78.78	78.82	78.82	78.83	75.15	75.19	75.20	75.22		
MUE(5) ^e	1.03	1.15	1.19	1.32	0.52	0.53	0.56	0.63	0.36	
MUE(9) ^f	1.49	1.60	1.64	1.75	0.59	0.60	0.63	0.69		

^aThe basis set used for M08-HX, M08-SO and M06-2X is MG3S.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S.^cUsing Benson's data from Ref. 9.^dTaken from Ref. 30.^eThe mean unsigned errors (MUE) in heat capacities (cal mol⁻¹ K⁻¹) corresponding to five temperatures where our computed results, Benson's empirical GA values, and experimental data are all available.^fThe mean unsigned errors (MUE) in heat capacities (cal mol⁻¹ K⁻¹) corresponding to nine temperatures where our computed results and experimental data are all available.TABLE X. Heat capacity (in cal mol⁻¹ K⁻¹) of 2-methyl-1-propanol.

T (K)	MS-LH		MS-T		Benson's GA ^c	Expt. ^d
	M08-HX ^a	CCSD(T)-F12a ^b	M08-HX ^a	CCSD(T)-F12a ^b		
200	20.37	20.43	20.84	20.89		
250	23.35	23.41	23.83	23.88		
298	26.51	26.56	26.96	27.00		
300	26.65	26.70	27.09	27.14	26.21	
390.55	32.97	33.01	33.18	33.21	32.40	35.52
397.65	33.46	33.49	33.65	33.68	32.86	35.17
400	33.62	33.66	33.80	33.83	32.93	
406.95	34.10	34.13	34.25	34.28	33.44	35.30
416.95	34.78	34.81	34.89	34.92	34.07	35.41
424.05	35.26	35.29	35.34	35.37	34.51	35.79
441.85	36.44	36.46	36.45	36.47	35.60	36.69
451.25	37.05	37.08	37.03	37.05	36.17	37.40
474.35	38.52	38.55	38.40	38.42	37.53	38.79
477.75	38.74	38.76	38.60	38.62	37.73	38.91
501.55	40.20	40.22	39.95	39.97	39.08	40.08
525.85	41.63	41.65	41.28	41.29	40.40	41.64
546.35	42.80	42.82	42.35	42.37	41.48	42.77
582.95	44.79	44.81	44.18	44.19	43.35	44.46
600	45.68	45.70	44.99	45.00	44.26	
602.55	45.81	45.83	45.11	45.12	44.30	45.81
800	54.48	54.49	52.96	52.97	52.46	
1000	61.00	61.01	58.87	58.87	58.52	
1500	71.15	71.15	68.14	68.14		
2000	76.38	76.38	72.97	72.98		
2400	78.82	78.82	75.24	75.24		
MUE(14) ^e	0.58	0.57	0.65	0.63	1.49	

^aThe basis set used for M08-HX is MG3S.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S.^cUsing Benson's data from Ref. 9.^dTaken from Ref. 8.^eThe mean unsigned errors (MUE) in heat capacities (cal mol⁻¹ K⁻¹) corresponding to 14 temperatures where our computed results, Benson's empirical GA values, and experimental data are all available.

TABLE XI. Heat capacity (in cal mol⁻¹ K⁻¹) of butanal.

<i>T</i> (K)	MS-LH		MS-T		Benson's GA ^c	Expt. ^d
	M08-HX ^a	CCSD(T)-F12a ^b	M08-HX ^a	CCSD(T)-F12a ^b		
200	19.78	19.16	20.64	19.95		
250	22.16	21.32	23.03	22.07		
298	24.62	23.81	25.36	24.45		24.71
300	24.73	23.92	25.46	24.55	24.19	
400	30.25	29.68	30.54	29.92	29.54	
600	40.23	39.96	39.65	39.38	39.19	
800	47.72	47.57	46.53	46.38	46.36	
1000	53.30	53.21	51.68	51.60	51.65	
1500	61.88	61.84	59.66	59.64		
2000	66.21	66.19	63.69	63.69		
2400	68.20	68.18	65.55	65.55		
UE ^e	0.090	0.90	0.65	0.26		

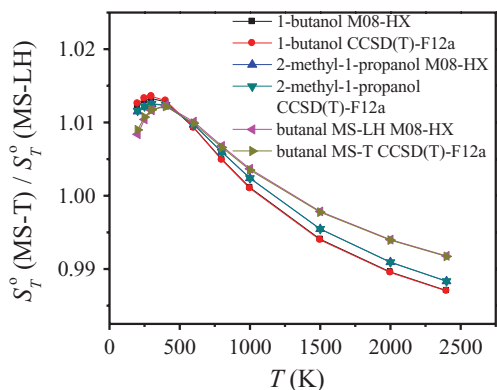
^aThe basis set used for M08-HX is maug-cc-pVTZ.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/maug-cc-pVTZ.^cUsing Benson's data from Ref. 9.^dTaken from Ref. 31.^eThe unsigned errors (UEs) in standard state entropies (cal mol⁻¹ K⁻¹) corresponding to 298 K temperature where our computed result and the experimental value are both available

FIG. 3. The ratio of the standard state entropies of 1-butanol, 2-methyl-1-propanol, and butanal obtained using MS-LH and MS-T approximations at various temperatures.

in Fig. 4. Benson's GA value for the heat capacity agree well with those calculated from the MS-T approach beyond 400 K, while for 300 and 400 K, they are closer to the LH approximation. For 1-butanol, at temperatures greater than or equal to 600 K, the theoretical values are within 0.7 cal mol⁻¹ K⁻¹ of the experiment.³⁰ In case of 2-methyl-1-propanol, the computed $C_p^o(T)$ values have ~ 3 cal mol⁻¹ K⁻¹ difference with experimental results⁸ at low temperatures; however, as the temperature increases, the difference gradually decreases and the computed $C_p^o(T)$ values almost match with experiment.

The mean unsigned errors in standard state entropies and heat capacities were also calculated and are presented in Tables VI–XI. The tables show that our values agree better with the experimental data than Benson's GA values in almost all the cases. The only exception observed is $C_p^o(T)$ values for 1-butanol (see Table IX), where Benson's GA values are

TABLE XII. Standard state enthalpy and free energies (in kcal/mol) of 1-butanol.

<i>T</i> (K)	H_T^o								G_T^o							
	MS-LH				MS-T				MS-LH				MS-T			
	M06-2X ^a	M08-SO ^a	M08-HX ^a	CC ^b	M06-2X ^a	M08-SO ^a	M08-HX ^a	CC ^b	M06-2X ^a	M08-SO ^a	M08-HX ^a	CC ^b	M06-2X ^a	M08-SO ^a	M08-HX ^a	CC ^b
200	86.7	87.1	86.7	86.7	87.1	86.8	86.7	86.7	71.7	71.3	71.3	71.3	71.6	71.2	71.2	71.2
250	87.8	88.2	87.8	87.8	88.2	87.9	8	87.9	67.7	67.3	67.4	67.4	67.6	67.2	67.2	67.2
298	89.0	89.3	89.1	89.0	89.5	89.1	89.2	89.1	63.7	63.3	63.3	63.3	63.5	63.1	63.1	63.1
300	89.1	89.4	89.1	89.1	89.5	89.2	89.2	89.2	63.5	63.1	63.1	63.2	63.3	62.9	62.9	62.9
400	92.1	92.4	92.1	92.1	92.6	92.2	92.3	92.2	54.5	54.0	54.1	54.1	54.1	53.7	53.7	53.8
600	100.14	100.3	100.1	100.1	100.5	100.10	100.2	100.1	33.9	33.3	33.4	33.4	33.3	32.8	32.8	32.9
800	110.1	110.4	110.1	110.2	110.5	109.9	109.9	109.9	10.3	9.6	9.7	9.8	9.5	8.9	9.0	9.0
1000	121.7	121.9	121.7	121.8	121.7	121.0	121.1	121.1	-16.1	-16.8	-16.7	-16.7	-16.9	-17.6	-17.5	-17.5
1500	155.0	155.2	155.0	155.1	154.0	152.9	153.0	153.0	-92.1	-93.1	-92.9	-92.9	-92.8	-93.7	-93.5	-93.4
2000	192.0	192.2	192.1	192.1	189.6	188.3	188.4	188.4	-180.0	-181.3	-181.1	-181.0	-180.0	-181.1	-180.9	-180.8
2400	223.1	223.2	223.1	223.2	219.4	217.9	218.0	218.0	-257.3	-258.9	-258.6	-258.6	-256.5	-257.8	-257.5	-257.4

^aThe basis set used for M08-HX, M08-SO and M06-2X is MG3S.^bCCSD(T)-F12a/jul-cc-pVTZ//M08-HX/MG3S.

TABLE XIII. Standard state enthalpy and free energies (in kcal/mol) of 2-methyl-1-propanol.

T (K)	H_T^o				G_T^o			
	MS-LH		MS-T		MS-LH		MS-T	
	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b
200	86.1	86.1	86.2	86.2	71.3	71.3	71.2	71.2
250	87.2	87.2	87.3	87.3	67.4	67.4	67.3	67.3
298	88.4	88.4	88.6	88.5	63.5	63.5	63.3	63.3
300	88.5	88.5	88.6	88.6	63.4	63.4	63.2	63.2
400	91.5	91.5	91.7	91.6	54.6	54.5	54.3	54.2
600	99.5	99.5	99.6	99.6	34.5	34.5	33.9	33.9
800	109.6	109.5	109.4	109.4	11.3	11.3	10.6	10.6
1000	121.1	121.1	120.6	120.6	-14.6	-14.6	-15.4	-15.4
1500	154.5	154.4	152.7	152.6	-89.4	-89.4	-90.1	-90.1
2000	191.5	191.5	188.1	188.0	-176.2	-176.2	-176.3	-176.3
2400	222.6	222.5	217.7	217.7	-252.6	-252.6	-251.9	-251.9

^aThe basis set used for M08-HX is MG3S.^bCCSD(T)-F12a/jul-cc-pVTZ/M08-HX/MG3S.

TABLE XIV. Standard state enthalpy and free energies (in kcal/mol) of butanal.

T (K)	H_T^o				G_T^o			
	MS-LH		MS-T		MS-LH		MS-T	
	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b	M08-HX ^a	CC ^b
200	72.0	72.1	72.1	72.2	57.5	57.4	57.5	57.4
250	73.1	73.1	73.2	73.2	53.8	53.6	53.7	53.5
298	74.2	74.2	74.4	74.3	50.0	49.8	49.9	49.7
300	74.3	74.2	74.4	74.4	49.8	49.6	49.7	49.5
400	77.0	76.9	77.2	77.1	41.3	41.1	41.1	40.8
600	84.1	83.9	84.3	84.1	22.0	21.7	21.5	21.3
800	92.9	92.7	92.9	92.7	-0.021	-0.31	-0.66	-0.95
1000	103.1	102.8	102.8	102.5	-24.4	-24.7	-25.2	-25.5
1500	132.1	131.8	130.8	130.5	-94.3	-94.6	-95.0	-95.3
2000	164.2	163.9	161.8	161.5	-174.5	-174.8	-174.9	-175.2
2400	191.2	190.9	187.7	187.4	-244.8	-245.1	-244.7	-245.0

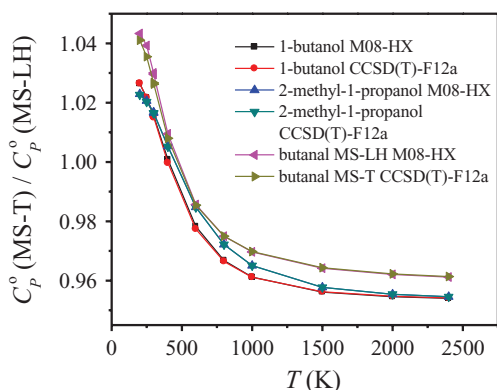
^aThe basis set used for M08-HX is maug-cc-pVTZ.^bCCSD(T)-F12a/jul-cc-pVTZ/M08-HX/maug-cc-pVTZ.

FIG. 4. The ratio of the heat capacities of 1-butanol, 2-methyl-1-propanol, and butanal obtained using MS-LH and MS-T approximations at various temperatures.

slightly better in agreement with the experimental results than those obtained from the MS-T method with M08 or coupled cluster.

Finally, we calculated the standard state enthalpy and Gibbs free energies, and the results are in Tables XII–XIV. Notice that our choice of zero of energy has the consequence that both enthalpy and free energy tend to the zero-point vibrational energy of the molecule under consideration at 0 K. (Thus the results in Tables XII and XIII have different zeros of energy.) Tables XII to XIV reveal that at temperatures of 200–800 K, the enthalpy, H_T^o , is almost same in the MS-LH and MS-T approximations. However, at and above 1000 K, the difference increases. The free energy, G_T^o , on the other hand, shows less difference between the values obtained with the MS-LH and MS-T approximations than is observed for H_T^o . The free energy results show the importance of torsional anharmonicity at high temperatures.

IV. CONCLUSIONS

In the present work, we have calculated the partition functions and four thermodynamic quantities (entropy, enthalpy, heat capacity, and Gibbs free energy) for 1-butanol, 2-methyl-1-propanol, and butanal by applying the recently developed MS-LH and MS-T approximations. Our results for the thermodynamic properties agree well with the experimental values obtained from the TRC data series³⁰ and CRC tables,³¹ where such data are available. The present investigation demonstrates the quantitative importance of torsional anharmonicity in these systems, particularly at high temperatures. The computed thermodynamic quantities agree with the empirical group additivity data of Benson only within $4.1 \text{ cal mol}^{-1} \text{ K}^{-1}$; this demonstrates the unreliability of group additivity.

The present investigation illustrates that high-level electronic structure calculations combined with MS statistical thermodynamic methods can be used reliably for calculating various thermodynamic properties of more complex systems with multiple torsions. Therefore, we can use this statistical mechanical approach to predict thermodynamic quantities even for molecules or temperatures where there are no experimental data or group additivity data.

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