

# Benchmarking Experimental and Computational Thermochemical Data: A Case Study of the Butane Conformers

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**ABSTRACT:** Due to its crucial importance, numerous studies have been conducted to determine the enthalpy difference between the conformers of butane. However, it is shown here that the most reliable experimental values are biased due to the statistical model utilized during the evaluation of the raw experimental data. In this study, using the appropriate statistical model, both the experimental expectation values and the associated uncertainties are revised. For the 133–196 and 223–297 K temperature ranges,  $668 \pm 20$  and  $653 \pm 125$  cal mol<sup>-1</sup>, respectively, are recommended as reference values. Furthermore, to show that present-day quantum chemistry is a favorable alternative to experimental techniques in the determination of enthalpy differences of conformers, a focal-point analysis, based on coupled-cluster electronic structure computations, has been performed that included contributions of up to perturbative quadruple excitations as well as small correction terms beyond the Born–Oppenheimer and nonrelativistic approximations. For the 133–196 and 223–297 K temperature ranges, in exceptional agreement with the corresponding revised experimental data, our computations yielded  $668 \pm 3$  and  $650 \pm 6$  cal mol<sup>-1</sup>, respectively. The most reliable enthalpy difference values for 0 and 298.15 K are also provided by the computational approach,  $680.9 \pm 2.5$  and  $647.4 \pm 7.0$  cal mol<sup>-1</sup>, respectively.

## ■ INTRODUCTION

We have been witnessing an ongoing race in thermochemistry between experiment and theory, with the aim to predict basic quantities with unprecedented accuracy. One quantity of central interest in thermochemistry is the enthalpy of formation of chemical species, including molecules, radicals, and ions. The experimental technique capable of producing the most accurate values is spectroscopy.<sup>1,2</sup> Even spectroscopic results can have sizable uncertainties, as proved most directly by the now classic case of the enthalpy of formation surrounding the OH radical.<sup>3</sup> Nevertheless, this is the exception and not the rule. The best quantum chemical techniques can result in energy values which can have an accuracy similar to that achievable spectroscopically.<sup>4,5</sup> For polyatomic and polyelectronic systems, the ultimate accuracy of spectroscopic measurements, much below 1 cm<sup>-1</sup>, can hardly be matched by even the most sophisticated quantum chemical procedures. This accuracy, however, is rarely achieved experimentally for quantities of thermochemical interest. In the majority of cases the sub-kJ mol<sup>-1</sup> level of accuracy is only reachable by well-designed quantum chemical computations. One must also mention a third kind of player in the thermochemical arena, that which uses network theory and active database approaches, like active thermochemical tables (ATcT)<sup>6</sup> and network of computed reaction enthalpies to atom-based thermochemistry (NEAT).<sup>7</sup> These approaches result in the most accurate and most consistent enthalpies of formation.<sup>8</sup> Nevertheless, these thermochemical networks are only as good as the data they are built upon. Therefore, there is a clear need for ever more accurate experimental and/or theoretical determinations of at least the enthalpies of

formation. With the development of quantum chemical methods, the time-proven assumption that it is usually experiment which provides reference values for quantum chemical approaches has changed. These days, it is often quantum chemistry which provides thermochemical quantities of higher accuracy, as can be judged by the best values based on the simultaneous analysis of all experimental and computational information, e.g., by the active database approaches.

One particularly successful application of high-level quantum chemistry is the determination of conformational energy differences and conformational barriers.<sup>9,10</sup> Here the structural and electronic similarities of the stationary points on the potential energy surface (PES) of the molecule mean that within a focal-point analysis (FPA)<sup>9,10</sup> approach, especially fast convergence is expected, and thus the residual uncertainties of the computations are minimized. Note that the FPA approach has been used to determine conformational energy and enthalpy differences not only of larger molecules, including natural amino acids glycine,<sup>11</sup> L-alanine,<sup>12</sup> L-proline,<sup>13</sup> cysteine,<sup>14</sup> and threonine,<sup>15</sup> but also for smaller molecules of outstanding interest,<sup>16–19</sup> including butane.<sup>20</sup> The aim of this study is the computational determination of the most reliable value for the enthalpy difference between the conformers of butane at various temperatures and to show that, for conformational energy prototypes, quantum chemistry can yield even more accurate results than careful experimental Raman or infrared spectroscopy investigation.

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## METHODS

**Experimental Section.** Butane,  $C_4H_{10}$ , is the simplest normal hydrocarbon in which rotational isomerization can occur: the trans (anti) form, the global minimum on the ground electronic state PES and the less stable gauche form exist in a conformational equilibrium. The accurate determination of the temperature-dependent enthalpy difference ( $\Delta H_{tg}$ ) between these two conformers has been the focus of numerous experimental studies during the last seven decades;<sup>21–47</sup>  $\Delta H_{tg} = H_g - H_t$ , where  $H_t$  and  $H_g$  are the enthalpies of the trans and gauche forms, respectively. Among these experimental results, one can find enthalpy differences referring to the gas phase,<sup>21–23,29–37,40–47</sup> but just as well can be found liquid-phase data obtained for pure butane<sup>24–28</sup> or those referring to various solvents.<sup>31,38,39</sup> The gas-phase  $\Delta H_{tg}$  values are summarized in Table 1 and are detailed below.

**Table 1. Experimental Gas-Phase Enthalpy Differences at Temperature  $T$  for Butane<sup>a</sup>**

$\Delta H_{tg}$ (cal mol <sup>-1</sup> )	$T$ (K)	parameter estimation <sup>b</sup>	ref
800 <sup>c</sup>			21
760 <sup>c</sup>	298		22
700 <sup>c</sup>	0		23
966 ± 54 <sup>d</sup>	285–455	OLLS	29
703 ± 50 <sup>e</sup>		OLLS	30
669 ± 96 <sup>f</sup>	223–297	OLLS	31
660 ± 22 <sup>d</sup>	133–196	OLLS	32
886 <sup>g</sup>		ONLS	33
889 ± 29 <sup>h</sup>		ONLS	34
1095 ± 49 <sup>g</sup>		ONLS	35
690 ± 100 <sup>i</sup>	298	ONLS	36
681 ± 35 <sup>j</sup>	182–336	ONLS	40
730 <sup>k</sup>	298		41
630 <sup>l</sup>	287	ONLS	42, 43
650 <sup>l</sup>	298	ONLS	44
497 ± 220 <sup>l</sup>	300	ONLS	45
750 <sup>l</sup>	298	ONLS	46, 47

<sup>a</sup>See text for the details of the experimental methods. <sup>b</sup>OLLS: ordinary linearized least-squares fit; ONLS: ordinary nonlinear least-squares fit. <sup>c</sup>Thermodynamic study. <sup>d</sup>Raman spectroscopy, temperature dependence. <sup>e</sup>Laser absorption, temperature dependence. <sup>f</sup>Infrared spectroscopy, temperature dependence. <sup>g</sup>Raman/infrared, torsional analysis. <sup>h</sup>Raman, torsional analysis. <sup>i</sup>Raman/infrared, intensity analysis. <sup>j</sup>NMR spectroscopy, temperature dependence. <sup>k</sup>Matrix trapping, infrared irradiation. <sup>l</sup>Electron diffraction.

The first determinations of  $\Delta H_{tg}$  were the results of the analysis of already existing thermodynamic data. Pitzer<sup>21</sup> and later Chen and co-workers<sup>22</sup> selected the most appropriate value for  $\Delta H_{tg}$  in order to obtain the best possible agreement with experimental thermodynamic functions determined on the mixture of conformers. The relative enthalpy of the gauche form reported by Ito<sup>23</sup> is based on the assumption that the intramolecular potential can be expressed as the sum of the interatomic bonding energies and internonbonding atomic potential energies.

Nevertheless, the majority of the studies concerned with the conformational equilibrium utilized vibrational (infrared or Raman) spectroscopy.<sup>24–32,48</sup> In these studies the temperature dependence of the spectrum was recorded,<sup>48</sup> and the logarithm of the ratio of the intensities of pairs of vibrational bands belonging to the two conformers was plotted against the

inverse temperature. The slope of the fitted straight line was then used to determine  $\Delta H_{tg}$ . Consequently, the determination of  $\Delta H_{tg}$  is based on a linearized least-squares (LS) fit.

Other vibrational studies<sup>33,34</sup> relied on conformational analysis to determine the potential function for the internal rotation. In refs 33 and 34, the value of  $\Delta H_{tg}$  was varied to obtain the best fit with experiment using a nonlinear LS method. In the study of Durig and associates,<sup>35</sup> the value of  $\Delta H_{tg}$  obtained from the temperature dependence of the spectrum, was used as an initial parameter for the conformational analysis, and the final value for  $\Delta H_{tg}$  was derived from the torsional potential function.

Another technique, used by Murphy and co-workers,<sup>36,37</sup> is the intensity analysis of the Raman bands, i.e., the Raman trace scattering cross sections were measured, and in a nonlinear LS optimization procedure, the initial estimates for the intensity parameters were adjusted to fit the observed trace scattering cross sections. The relative trans/gauche abundance was assumed to be a variable parameter.

Although the temperature dependence of the NMR spectral parameters<sup>40</sup> and the interconversion of the conformers by infrared radiation<sup>41</sup> were also exploited to determine  $\Delta H_{tg}$ , the most widely used experimental technique, besides vibrational spectroscopy, was gas-electron diffraction.<sup>42–47</sup> In most cases, the determination of the trans/gauche ratio was accomplished by the comparison of the experimental temperature-dependent radial distribution curves with those calculated using models based on different trans concentrations. LS cycles of the fits between experimental and calculated radial distribution curves were run until optimum structural parameters were obtained for all concentrations. Then,  $\Delta H_{tg}$  was determined from a parabolic fit of the root-mean-square deviations between experimental and calculated curves.

It can be observed in Table 1 that the most accurate experimental value,  $\Delta H_{tg} = 660 \pm 22$  cal mol<sup>-1</sup>, was reported<sup>32</sup> for the 133–196 K temperature range. Furthermore, (i) about half of the  $\Delta H_{tg}$  values have no associated uncertainty estimate; (ii) for about one-third of the values the reference temperature was not reported; and (iii) at room temperature the  $\Delta H_{tg}$  values fall in the range of 500–760 cal mol<sup>-1</sup>. On the basis of the above analysis, it is safe to say that accurate determination of  $\Delta H_{tg}$  at most of the temperatures investigated has not been achieved.

**Parameter Estimation.** In the majority of the experimental studies the ordinary nonlinear LS (ONLS) method was used to provide statistical measures for  $\Delta H_{tg}$ , as indicated in Table 1. This procedure is widely exploited and well-suited for these types of problems. Ordinary linear LS (OLLS) fits have also been utilized in a few cases; however, it is known<sup>49</sup> that linearization may bias the statistical parameters. Therefore, both the ONLS and OLLS as well as the weighted linear LS (WLLS) methods are used in this study to check the consistency of the evaluated data and to avoid the biasing problem mentioned. The program described in ref 49 was utilized for both the linear and nonlinear regression analyses.

**Computational Section.** Computational chemistry has emerged as an important tool for studying the thermodynamic functions of small molecules. Since the pioneering work of Petersson and associates<sup>50</sup> and that of Pople and co-workers,<sup>51</sup> several composite approaches have been designed to provide accurate thermochemical data.<sup>10,52–81</sup> Model chemistries, which can achieve chemical (1 kcal mol<sup>-1</sup>) or even higher accuracy, rely on the observation that different contributions to the

energy reach convergence at different levels of theory. The additivity of the considered contributions is usually assumed, and sometimes empirical corrections, carefully calibrated on accurate experimental data, are used as well. We note here that the vast majority of the empirical corrections do not depend on the molecular conformation; thus despite a recent claim,<sup>82</sup> these protocols should be regarded as *ab initio* when differences of thermodynamic quantities are calculated among conformers. Nevertheless, the most accurate model chemistries do not include empirical parameters. They are usually based on the coupled cluster<sup>83</sup> (CC) singles, doubles, and perturbative triples [CCSD(T)] method,<sup>84,85</sup> referred to as “gold standard” in quantum chemistry, and are further augmented, following the philosophy of the FPA technique,<sup>9,10</sup> by relativistic, post-Born–Oppenheimer, and high-order correlation terms.<sup>10,61,65–68,73–75</sup> It has been proven that these cutting-edge protocols can provide an accuracy superior to experimental methods.<sup>17–19,67,69,73–75,86–96</sup> It is reasonable to expect that especially accurate data can be obtained when the difference between the enthalpies of conformers of the same molecule is investigated.

Due to its fundamental importance in conformational analysis, numerous computational studies have been conducted to determine the energy and/or enthalpy difference between the conformers of butane. The most accurate investigations are summarized in Table 2 and are discussed as follows.

**Table 2. Previous Theoretical Gas-Phase Energy and Enthalpy Differences at Temperature  $T$  for Butane**

$\Delta E_{\text{tg}}$ (cal mol <sup>-1</sup> )	$\Delta H_{\text{tg}}$ (cal mol <sup>-1</sup> )	$T$ (K)	method	ref
–	640	0	G2	97
–	950	0	CBS-Q	
590	–	0		99
–	700	0	CCSD(T)/cc-pVTZ	
–	660	220		
–	640	298		
620	–	0	focal-point	20
–	645	0	G2	100
–	621	298		
628	–	0	MP2:CC/cc-pVQZ	101
621	–	0	MP2:CC/cc-pVSZ	
596	–	0	W2-like	102

Murcko and associates<sup>97</sup> studied the carbon–carbon rotational barriers in butane, 1-butene, and 1,3-butadiene by means of the G2 theory<sup>56</sup> and a variant of the complete basis set (CBS) method, CBS-Q<sup>55</sup> of Petersson and co-workers. In the case of butane, the effect of the theoretical level on the equilibrium molecular geometries was also investigated using molecular structures obtained with the MP2 method and various basis sets ranging from 6-31G\* to 6-311++G(2df,2pd). It was found that the relative QCISD(T)/6-311++G\*\* energies<sup>98</sup> practically did not depend on the size of the basis set applied in the geometry optimization. Therefore, the MP2/6-31G\* structures were used for higher-level single-point calculations. For  $\Delta H_{\text{tg}}$  at 0 K, the G2 method yielded 640 cal mol<sup>-1</sup>, while the CBS-Q model chemistry gave 950 cal mol<sup>-1</sup>.

Smith and Jaffe<sup>99</sup> obtained  $590 \pm 100$  cal mol<sup>-1</sup> for the gauche–trans energy difference ( $\Delta E_{\text{tg}}$ ) at 0 K at the CCSD(T)/cc-pVTZ//MP2/6-31G(2df,p) level of theory;  $\Delta E_{\text{tg}} = E_g - E_t$ , where  $E_g$  and  $E_t$  are the total energies of the gauche and trans conformers, respectively. To calculate  $\Delta H_{\text{tg}}$ ,

the zero-point energy as well as thermal corrections, using scaled MP2/6-311G\*\* frequencies, were taken into account, and  $700 \pm 100$ ,  $660 \pm 100$ , and  $640 \pm 100$  cal mol<sup>-1</sup> were reported at 0, 220, and 298 K, respectively.

The first exhaustive computational report appeared in 1997. Allinger and co-workers<sup>20</sup> performed an FPA study<sup>10</sup> on the convergence of the butane conformational energies and rotational barriers. The HF, MP2, MP3, CCSD, and CCSD(T) methods were applied with successively smaller and smaller basis sets and freezing not only core but also 16 virtual orbitals. The basis sets at the HF and MP2 levels contained as many as 840 contracted Gaussian functions (CGFs), while the CCSD(T) computations used 186 CGFs. The reference structures were optimized at the CISD/DZP level. Their FPA approach yielded 620 cal mol<sup>-1</sup> for  $\Delta E_{\text{tg}}$ .

In 1998 Tasi and Mizukami<sup>100</sup> introduced an all-electron tight-binding method parametrized for aliphatic alkanes using MP2/6-311G\*\* equilibrium structures as reference geometries, HF/6-311++G\*\* permanent electric dipole moment vectors obtained at the reference geometries, and, finally, high-quality G2 total molecular energies at 0 K along with zero-point vibrational energy corrections. For  $\Delta H_{\text{tg}}$  at 0 and 298 K, 645 and 621 cal mol<sup>-1</sup> were obtained, respectively.

Klauda et al.<sup>101</sup> approximated CCSD(T)/cc-pVQZ energies via the following equation:

$$\begin{aligned} E[\text{MP2: CC}] &= E[\text{CCSD(T)/cc-pVQZ}] \\ &\cong E[\text{CCSD(T)/cc-pVDZ}] \\ &\quad + (E[\text{MP2/cc-pVQZ}] \\ &\quad - E[\text{MP2/cc-pVDZ}]) \end{aligned} \quad (1)$$

The molecular geometries were obtained at the MP2/cc-pVDZ level, and the MP2:CC method yielded  $\Delta E_{\text{tg}} = 628$  cal mol<sup>-1</sup>. Substituting the cc-pVQZ basis set by cc-pVSZ,  $\Delta E_{\text{tg}}$  lowered by only 7 cal mol<sup>-1</sup>, therefore it was assumed that the approximate CCSD(T)/cc-pVQZ energy difference is accurate to within 1–2% of the CCSD(T) CBS limit.

In an extensive benchmark study, Martin et al.<sup>102</sup> investigated the performance of *ab initio* and DFT methods for conformational equilibria of alkane isomers up to octane. Their best result for  $\Delta E_{\text{tg}}$ , 596 cal mol<sup>-1</sup>, was obtained by a W2-like method using MP2/cc-pVTZ optimized reference structures. They also studied the importance of post-CCSD(T) contributions for the trans–gauche separation by performing CCSDT(Q) calculations with a double- $\zeta$  quality basis set, and it was found that higher-order excitations stabilize the gauche structure by 4 cal mol<sup>-1</sup>.

The computational studies, similar to the experimental investigations, have not delivered accurate and consistent data for  $\Delta H_{\text{tg}}$  so far, and the  $\Delta E_{\text{tg}}$  results are also somewhat inconsistent.

**An Improved *Ab Initio* Model Chemistry.** The composition of the model applied in this paper is mostly inspired by the Weizmann- $n$  ( $W_n$ )<sup>66–69</sup> and HEAT family of protocols.<sup>73–75</sup> Usually, to circumvent the problems arising from the incompleteness of the basis sets applied, most of the contributions are extrapolated to the CBS limit. Several extrapolation formulas have been advised to accelerate the convergence of the correlation energy,<sup>50,52–55,70,103–113</sup> and different models<sup>69–72,75,108,114,115</sup> rely on different functions, however, studies showed that no extrapolation formula can

outperform the others for all basis set combinations and all type of molecules.<sup>70–72,116</sup> In this study, the two-point extrapolation formula introduced by Helgaker and associates<sup>105</sup> is used because it is more or less backed by theory.<sup>117</sup>

The equilibrium structures were taken from geometry optimizations carried out by the CCSD(T) method using various correlation basis sets,<sup>118,119</sup> including cc-pVDZ, cc-pVTZ, and cc-pVQZ.

At a temperature  $T$  and pressure of 1 bar, the enthalpy difference,  $\Delta H_{\text{tg}}(T)$ , is defined as

$$\Delta H_{\text{tg}}(T) = H_{\text{g}}(T) - H_{\text{t}}(T) \quad (2)$$

where  $H_{\text{g}}(T)$  and  $H_{\text{t}}(T)$  are the enthalpies of the gauche and trans conformers, respectively. The enthalpies of the conformers are calculated according to the following equation:

$$\begin{aligned} H(T) = & E_{\text{HF}} + \Delta E_{\text{MP2}} + \Delta E_{\text{CCSD}} + \Delta E_{(T)} \\ & + \Delta E_{\text{HO}} + \Delta E_{\text{DBOC}} + \Delta E_{\text{SR}} + \Delta E_{\text{ZPE}} \\ & + \frac{RT^2}{\Omega} \frac{\partial \Omega}{\partial T} + RT \end{aligned} \quad (3)$$

In eq 3, (i)  $E_{\text{HF}}$  is the Hartree–Fock (HF) self-consistent field (SCF) energy calculated with the cc-pV6Z<sup>120</sup> basis set; (ii)  $\Delta E_{\text{MP2}}$  is the correlation energy evaluated by the second-order Møller–Plesset (MP2)<sup>121</sup> method and extrapolated to the CBS limit using the cc-pVSZ and cc-pV6Z basis set results; (iii)  $\Delta E_{\text{CCSD}}$  and  $\Delta E_{(T)}$  are correlation contributions defined as  $\Delta E_{\text{CCSD}} = E_{\text{CCSD}} - E_{\text{MP2}}$  and  $\Delta E_{(T)} = E_{\text{CCSD(T)}} - E_{\text{CCSD}}$ , respectively;  $E_{\text{MP2}}$ ,  $E_{\text{CCSD}}$ , and  $E_{\text{CCSD(T)}}$  are total energies obtained, respectively, with the MP2, CC singles and doubles<sup>122</sup> (CCSD), and CCSD(T) methods and extrapolated to the CBS limit using the cc-pVTZ and cc-pVQZ basis set results; (iv)  $\Delta E_{\text{HO}}$  is the higher-order correlation contribution beyond the CCSD(T) method calculated as  $\Delta E_{\text{HO}} = E_{\text{CCSDT(Q)}} - E_{\text{CCSD(T)}}$ ;  $E_{\text{CCSDT(Q)}}$  and  $E_{\text{CCSD(T)}}$  are total energies determined, respectively, with the CC singles, doubles, triples, and perturbative quadruples [CCSDT(Q)]<sup>123,124</sup> and CCSD(T) methods using the cc-pVDZ basis set; (v)  $\Delta E_{\text{DBOC}}$  is the diagonal Born–Oppenheimer correction<sup>125</sup> (DBOC) calculated at the HF/aug-cc-pCVTZ<sup>126</sup> level; (vi)  $\Delta E_{\text{SR}}$  is the scalar relativistic contribution determined using the fourth-order Douglas–Kroll–Hess (DKH) Hamiltonian<sup>127–130</sup> in CCSD(T)/aug-cc-pCVQZ-DK calculations; (vii)  $\Delta E_{\text{ZPE}}$  is the zero-point vibrational energy and is determined from CCSD(T) calculations; for harmonic frequencies the cc-pVTZ basis set and the analytic second derivatives were used,<sup>131,132</sup> the  $G_0$  term and the anharmonicity constants were taken from MP2/6-31G\* quartic force fields obtained by numerical differentiation of analytic second derivatives;<sup>74,133</sup> (viii)  $\Omega$ ,  $R$ , and  $T$  denote the molecular partition function, the ideal gas constant, and the absolute temperature, respectively;  $\Omega$  is calculated via the standard formulas of statistical thermodynamics within the ideal gas approximation,<sup>134</sup> for the rotational and vibrational degrees of freedom, the rigid rotor-harmonic oscillator approximation is invoked. Although hindered rotors exist in butane, it is reasonable to expect that their treatment as harmonic oscillators does not substantially affect the value of  $\Delta H_{\text{tg}}$ .<sup>135</sup>

The CCSDT(Q) computations were carried out with the MRCC suite of quantum chemical programs<sup>136</sup> interfaced to the C<sub>FOUR</sub> package.<sup>137</sup> For the MP2 and DKH computations, the MOLPRO package<sup>138</sup> was utilized; all other results were obtained

with C<sub>FOUR</sub>.<sup>137</sup> In all calculations restricted HF orbitals were used.

## RESULTS AND DISCUSSION

**Re-evaluation of Previous Experimental Data.** In the Experimental Section of this paper, the experimental enthalpy differences between the two conformers of butane in the gas phase have been reviewed in detail. However, it can be shown that, in most cases, the original treatment of the raw experimental data needs certain improvement. Let us consider, for example, the two most accepted evaluations of Herrebout et al.<sup>31</sup> and Balabin<sup>32</sup> from the literature. It is worth noting that the temperature ranges of their experiments are disjoint, i.e., they have performed their spectroscopic measurements at distinct temperatures (see Table 1). Furthermore, for the evaluation of the raw experimental data the OLLS method was used with the linearized form (eq 5) of the correct nonlinear function (eq 4).

$$\frac{I_{\text{g}}}{I_{\text{t}}} = \exp\left(\frac{\Delta S_{\text{tg}}}{R}\right) \exp\left(-\frac{\Delta H_{\text{tg}}}{RT}\right) \quad (4)$$

$$\ln \frac{I_{\text{g}}}{I_{\text{t}}} = -\frac{\Delta H_{\text{tg}}}{RT} + \frac{\Delta S_{\text{tg}}}{R} \quad (5)$$

where  $\Delta S_{\text{tg}}$  is the entropy difference of the conformers,  $\Delta S_{\text{tg}} = S_{\text{g}} - S_{\text{t}}$  as well as  $I_{\text{g}}$  and  $I_{\text{t}}$  are the intensities of the appropriate bands corresponding to the two conformers in the vibrational spectra.

It has been shown<sup>49</sup> that the bias effect of the linearization on the estimated parameter values and their standard errors can be corrected with appropriate weighting using the WLLS method, although it is better to use the correct nonlinear function (ONLS fit with eq 4). Table 3 contains the various estimated,

**Table 3. Temperature-Independent (Average) Experimental Enthalpy Differences for Butane in Gas Phase over Two Disjoint Temperature Ranges Using Various Least-Squares Methods**

ref	parameter estimation <sup>a</sup>	$\Delta H_{\text{tg}}(\text{cal mol}^{-1})$
31	OLLS	663 ± 131
	WLLS	650 ± 128
	ONLS	653 ± 125
32	OLLS	660 ± 21
	WLLS	668 ± 20
	ONLS	668 ± 20

<sup>a</sup>OLLS: ordinary linearized least-squares fit; WLLS: weighted linearized least-squares fit; ONLS: ordinary nonlinear least-squares fit.

temperature-independent (average) experimental  $\Delta H_{\text{tg}}$  values. For the sake of simplicity, the standard errors were taken as two standard deviations. These values are only slightly different from the 95% confidence intervals.

For the raw experimental data of ref 32 the OLLS result (660 ± 21 cal mol<sup>-1</sup>) precisely matches that reported by Balabin (660 ± 22 cal mol<sup>-1</sup>).<sup>32</sup> However, the WLLS and ONLS experimental enthalpy differences are different from the reported value. As the noise in the raw experimental data is not significant, the WLLS and the ONLS fits result in the very same number. Therefore, it can be concluded that, for the temperature interval 133–196 K, the best estimate for the

Table 4. Convergence of the Factors Contributing to  $\Delta H_{\text{tg}}(0)^a$ 

$X^b$	$\Delta E_{\text{HF}}$	$\delta E_{\text{MP2}}$	$\delta E_{\text{CCSD}}$	$\delta E_{\text{(T)}}$	$\delta E_{\text{HO}}$	$\delta E_{\text{DBOC}}^c$	$\delta E_{\text{SR}}^d$	$\delta E_{\text{ZPE}}$
2	1155.7	-438.9	90.1	-39.4	-5.0	-0.7	1.0	84.9 <sup>e</sup>
3	1102.6	-520.9	94.7	-57.6		-0.3	1.4	85.4 <sup>f</sup>
4	1108.9	-534.1	94.9	-58.6			1.4	
5	1108.7	-544.6						
6	1108.9	-544.8						
best <sup>g</sup>	1108.9	-545.2	95.1	-59.4	-5.0	-0.3	1.4	85.4

<sup>a</sup>Equilibrium structures are obtained at the CCSD(T)/cc-pVQZ level of theory; all values are in cal mol<sup>-1</sup>. <sup>b</sup>Cardinal number of the cc-pVXZ basis set. <sup>c</sup>Results are obtained with the cc-pCVXZ basis set. <sup>d</sup>Results are obtained with the aug-cc-pCVXZ-DK basis set. <sup>e</sup>Equilibrium structures are determined at the CCSD(T)/cc-pVDZ level. <sup>f</sup>Equilibrium structures are determined at the CCSD(T)/cc-pVTZ level. <sup>g</sup>Best estimate for the various contributions. The  $\delta E_{\text{MP2}}$  value is obtained from cc-pV(S,6)Z extrapolation; the  $\delta E_{\text{CCSD}}$  and  $\delta E_{\text{(T)}}$  results are taken from cc-pV(T,Q)Z extrapolation.

benchmark (average) experimental enthalpy difference,  $\Delta H_{\text{tg}}$  is  $668 \pm 20$  cal mol<sup>-1</sup> instead of  $660 \pm 22$  cal mol<sup>-1</sup> reported in ref 32.

For the raw experimental data of Herrebout et al.,<sup>31</sup> our OLS result,  $663 \pm 131$  cal mol<sup>-1</sup>, is considerably different from that of  $669 \pm 96$  cal mol<sup>-1</sup> reported in ref 31. In this case, the noise in the raw experimental data is much larger than in the previous case; therefore, the WLS and ONLS fits give different values. Nevertheless, for the temperature interval 223–297 K, the recent benchmark (average) experimental enthalpy difference,  $\Delta H_{\text{tg}}$  is better represented as  $653 \pm 125$  cal mol<sup>-1</sup>, obtained by the ONLS fit.

**Computational Results.** Data in Table 4 show the convergence behavior of the various contributions included in our improved ab initio model chemistry. Obviously, all terms are converged within 1 cal mol<sup>-1</sup>; the differences between the values obtained at the two highest levels are {0.2, -0.4, 0.2, -0.8, 0.4, 0.0, 0.5} cal mol<sup>-1</sup>, respectively, for { $\Delta E_{\text{HF}}$ ,  $\delta E_{\text{MP2}}$ ,  $\delta E_{\text{CCSD}}$ ,  $\delta E_{\text{(T)}}$ ,  $\delta E_{\text{DBOC}}$ ,  $\delta E_{\text{SR}}$ ,  $\delta E_{\text{ZPE}}$ }. It is assumed that the  $\delta E_{\text{HO}}$  contribution is already converged with the double- $\zeta$  basis set. If error cancellation is taken into account, one can say that the value of  $\Delta H_{\text{tg}}$  at 0 K, the sum of the contributions (680.9 cal mol<sup>-1</sup>), is accurate within  $\pm 0.1$  cal mol<sup>-1</sup>; without error cancellation a conservative error bar of  $\pm 2.5$  cal mol<sup>-1</sup> can be deduced for  $\Delta H_{\text{tg}}(0)$ . In passing, we note that the extrapolations of the  $\delta E_{\text{MP2}}$ ,  $\delta E_{\text{CCSD}}$ , and  $\delta E_{\text{(T)}}$  contributions to the CBS limit for  $\Delta H_{\text{tg}}(0)$  were all very small. Without extrapolations a  $\Delta H_{\text{tg}}(0)$  value of 681.9 cal mol<sup>-1</sup> was obtained.

To determine the enthalpy difference at a temperature other than 0 K, the molecular partition function  $\Omega$  needs to be calculated for the conformers and considered for the enthalpy according to eq 3. Therefore, the thermal contributions to the enthalpy difference,  $\Delta H_{\text{tg}}(T) - \Delta H_{\text{tg}}(0)$ , were determined from  $\Omega$  at various temperatures. As a representative example, at 298.15 K, it is equal to -38.0 and -33.5 cal mol<sup>-1</sup> with the cc-pVDZ and cc-pVTZ basis sets, respectively. Using the triple- $\zeta$  value,  $\Delta H_{\text{tg}}(298) = 647.4$  cal mol<sup>-1</sup> can be obtained. Because the triple- $\zeta$  value differs by 4.5 cal mol<sup>-1</sup> from the double- $\zeta$  one, the uncertainty for  $\Delta H_{\text{tg}}(298)$  can be increased by  $\pm 4.5$  cal mol<sup>-1</sup>, relative to  $\Delta H_{\text{tg}}(0)$ , and a conservative error bar of  $\pm 7.0$  cal mol<sup>-1</sup> can be attached to  $\Delta H_{\text{tg}}(298)$ .

To test the quality of our improved ab initio model chemistry for butane over various ranges of temperatures, the intensity ratios of the vibrational bands of the two conformers have been computed via eq 4 using theoretical enthalpy and entropy differences. Tables 5 and 6 list the computed data for the two temperature ranges.

Let us use the same technique as for the raw experimental data to derive temperature-independent (average) theoretical

Table 5. Computed Intensity Ratios Based on Theoretical Enthalpy and Entropy Differences over the Temperature Range of Ref 31

$1/T$ (K <sup>-1</sup> )	$\Delta H_{\text{tg}}$ (cal mol <sup>-1</sup> )	$\Delta S_{\text{tg}}$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\ln(I_{\text{g}}/I_{\text{t}})$
0.00337	647.71	0.00	-1.0984
0.00366	650.10	0.01	-1.1923
0.00380	651.29	0.01	-1.2404
0.00395	652.25	0.02	-1.2864
0.00412	653.68	0.02	-1.3452
0.00429	655.11	0.03	-1.3992
0.00448	656.79	0.04	-1.4606

Table 6. Computed Intensity Ratios Based on Theoretical Enthalpy and Entropy Differences over the Temperature Range of Ref 32

$1/T$ (K <sup>-1</sup> )	$\Delta H_{\text{tg}}$ (cal mol <sup>-1</sup> )	$\Delta S_{\text{tg}}$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\ln(I_{\text{g}}/I_{\text{t}})$
0.00750	675.43	0.15	-2.4737
0.00735	674.71	0.14	-2.4251
0.00720	674.00	0.14	-2.3716
0.00705	673.28	0.13	-2.3232
0.00690	672.56	0.13	-2.2699
0.00675	671.85	0.12	-2.2217
0.00660	670.89	0.12	-2.1678
0.00645	670.41	0.11	-2.1206
0.00630	669.46	0.11	-2.0670
0.00615	668.26	0.10	-2.0178
0.00600	667.54	0.09	-1.9702
0.00585	666.59	0.09	-1.9170
0.00570	665.63	0.08	-1.8690
0.00555	664.68	0.08	-1.8161
0.00540	663.48	0.07	-1.7677
0.00525	662.52	0.07	-1.7151
0.00510	661.57	0.06	-1.6677

$\Delta H_{\text{tg}}$  values. Table 7 shows the results obtained with various LS fits. Comparing the data of Table 7 to those of Table 3, it can be observed that the theoretical enthalpy differences match the best experimental values of Table 3. As to the two temperature ranges, all the LS fits of the theoretical intensity data give the same numbers with very small uncertainties. This means that the noise in the theoretical data is minuscule. It is also worth noting that, based on the computational results, the two benchmark experimental enthalpy differences of Herrebout et al.<sup>31</sup> and Balabin<sup>32</sup> should be different, i.e., the average experimental enthalpy difference  $\Delta H_{\text{tg}}$  does depend on the range of the temperatures considered.

Although this statement is almost evident, it is important to stress, as some practitioners in this field handled the concept of

**Table 7. Temperature-Independent (Average) Theoretical Enthalpy Differences for Butane in Gas Phase over Two Disjoint Temperature Ranges Using Various Least-Squares Methods**

ref	parameter estimation <sup>a</sup>	$\Delta H_{\text{tg}}$ (cal mol <sup>-1</sup> )
31	OLLS	650 ± 6
	WLLS	650 ± 6
	ONLS	650 ± 6
32	OLLS	669 ± 3
	WLLS	668 ± 3
	ONLS	668 ± 3

<sup>a</sup>OLLS: ordinary linearized least-squares fit; WLLS: weighted linearized least-squares fit; ONLS: ordinary nonlinear least-squares fit.

temperature-independence quite generously. The misconception was originated from the fact that during the investigation  $\Delta H_{\text{tg}}$  was assumed to be temperature-independent in the given temperature range. Sometimes the reference for the temperature interval was forgotten, and  $\Delta H_{\text{tg}}$  values obtained for disjoint temperature ranges were compared quantitatively.<sup>32</sup> However, one should not forget that the temperature-independence of  $\Delta H_{\text{tg}}$  is just a necessary supposition that helps to simplify the evaluation of the measured data, or in other words, it is a first-order approximation in the given temperature range.

It was mentioned above that previous computational studies did not result in a definitive value for  $\Delta H_{\text{tg}}$ . A similar statement is valid for  $\Delta E_{\text{tg}}$ . As can be seen in Table 2, the theoretical  $\Delta E_{\text{tg}}$  value determined by Smith and Jaffe,<sup>99</sup> 590 cal mol<sup>-1</sup>, agrees well with that computed by Martin and associates,<sup>102</sup> 596 cal mol<sup>-1</sup>. However, they considerably differ from those reported by Allinger and co-workers,<sup>20</sup> 620 cal mol<sup>-1</sup>, and Klauda and associates,<sup>101</sup> 621 cal mol<sup>-1</sup>. It is likely that much of this 25–30 cal mol<sup>-1</sup> deviation is due to the use of different reference structures; in refs 20 and 101 double- $\zeta$  quality and in refs 99 and 102 triple- $\zeta$  quality basis sets were used in the geometry optimizations.

The protocols used here and in ref 102 are clearly superior to those applied in previous computational studies. It is also noted that due to higher-order CCSDT and CCSDT(Q) electron correlation contributions, the value of 596 cal mol<sup>-1</sup> of ref 102 should be decreased by 4 cal mol<sup>-1</sup> to 592 cal mol<sup>-1</sup>. The latter value is in excellent agreement with that obtained here as the sum of the  $\Delta E_{\text{HF}}$ ,  $\delta E_{\text{MP2}}$ ,  $\delta E_{\text{CCSD}}$ ,  $\delta E_{\text{(T)}}$ , and  $\delta E_{\text{HO}}$  contributions, 594.4 cal mol<sup>-1</sup>. However, our treatment goes beyond the Born–Oppenheimer and nonrelativistic approximations and also includes diagonal Born–Oppenheimer,  $\delta E_{\text{DBOC}} = -0.3$  cal mol<sup>-1</sup>, and scalar relativistic,  $\delta E_{\text{SR}} = 1.4$  cal mol<sup>-1</sup>, corrections. It is obvious that these contributions are of limited importance and need to be included only when peculiar accuracy is sought, since they sum up to 1.1 cal mol<sup>-1</sup>. Nevertheless, our best estimate for  $\Delta E_{\text{tg}}$ , 595.5 cal mol<sup>-1</sup>, includes these corrections in addition to the  $\Delta E_{\text{HF}}$ ,  $\delta E_{\text{MP2}}$ ,  $\delta E_{\text{CCSD}}$ ,  $\delta E_{\text{(T)}}$ , and  $\delta E_{\text{HO}}$  contributions. Furthermore, a well-defined error bar of  $\pm 2.0$  cal mol<sup>-1</sup> can also be attached to our  $\Delta E_{\text{tg}}$  value.

The uncertainty in the experimental  $\Delta H_{\text{tg}}(298)$  value, as mentioned above, is fairly large; as it can be observed in Table 1, the most accurate experimental value with a considerable error bar of  $\pm 100$  cal mol<sup>-1</sup> is  $\Delta H_{\text{tg}}(298) = 690$  cal mol<sup>-1</sup> reported in ref 36. Our data,  $\Delta H_{\text{tg}}(298) = 647.4 \pm 7.0$  cal

mol<sup>-1</sup>, clearly supersedes this, and consequently, all previous results.

## CONCLUSIONS

In this study the raw experimental data of Herrebout et al.<sup>31</sup> and those of Balabin<sup>32</sup> have been re-evaluated avoiding the bias introduced by the OLLS fit in the original papers. Consequently, the benchmark experimental  $\Delta H_{\text{tg}}$  values for the 223–297 and 133–196 K temperature ranges have been revised, from  $669 \pm 96$  and  $660 \pm 22$  to  $653 \pm 125$  and  $668 \pm 20$  cal mol<sup>-1</sup>, respectively. The revised experimental values are in perfect agreement with the computational results,  $650 \pm 6$  and  $668 \pm 3$  cal mol<sup>-1</sup>, determined for the 223–297 and 133–196 K temperature ranges, respectively. This study also presents the most reliable data for  $\Delta E_{\text{tg}}$ ,  $\Delta H_{\text{tg}}(0)$ , and  $\Delta H_{\text{tg}}(298)$ , as  $595.5 \pm 2.0$ ,  $680.9 \pm 2.5$ , and  $647.4 \pm 7.0$  cal mol<sup>-1</sup>. As it has been shown here for energy and enthalpy differences, the thermodynamic features of the conformational space can be determined with exceptional precision using carefully selected quantum chemical techniques and the FPA principle. The reported theoretical values with the associated  $\pm 10$  cal mol<sup>-1</sup> accuracy range might present a great challenge for the available experimental approaches.

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### Notes

The authors declare no competing financial interest.

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