

# Ideal Gas Thermodynamic Properties and Isomerization of *n*-Butane and Isobutane

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Reported values of structural parameters, vibrational fundamentals, and potential energy functions for internal rotation of *n*-butane and isobutane are reviewed. The selected values were used to calculate the thermodynamic properties ( $C_p^\circ$ ,  $S^\circ$ ,  $(H^\circ - H_0^\circ)/T$ ,  $(G^\circ - H_0^\circ)/T$ ) in the temperature range of 0 to 1500 K by the usual statistical thermodynamic methods using the rigid-rotor and harmonic-oscillator model. Contributions of internal rotation were evaluated by the direct sum of terms containing energy levels which were calculated with a one-dimensional potential model. For internal rotation about the central C—C bond in *n*-butane, energy levels were approximated by two procedures. A unique potential function was assumed for each methyl rotor of *n*-butane or of isobutane. Top-top interactions in isobutane were approximated by the potential parameter  $V_6$  which was determined empirically by comparison with thermodynamic data. The calculated and observed values of heat capacities and entropies agree well within experimental uncertainties. Standard enthalpies of formation at 298.15 K for the ideal gaseous state were selected from measured values of heats of combustion and third-law enthalpies for isomerization. Corresponding values of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and  $\log K_f$  are tabulated over the same temperature range.

Key words: Equilibrium compositions; heat of isomerization; ideal gas thermodynamic properties; isobutane; *n*-butane; potential barrier to internal rotation.

## 1. Introduction

The thermodynamic properties of *n*-butane and isobutane were measured [1–8]<sup>1</sup> several decades ago. The modified Berthelot equation of state was applied to derive the experimental values of the ideal gas thermal functions. The third law entropies of butanes at their boiling points and/or the standard temperature 298.15 K by Aston et al. [6, 7] were generally chosen as the reference data for comparison with statistical thermodynamic calculations. The theoretical calculations in the temperature range from 0 to 1500 K were made by Pitzer [9, 10], assuming two types of carbon skeletal vibrations, three types of hydrogen vibrations, unique C—C and C—H bond distances, and normal tetrahedral angles for both butanes. Since then, improved techniques and availability of high purity compounds have substantially improved the spectroscopic data [11–29], the molecular structural parameters [30–35] and also the heat capacity measurements [36, 37].

In the present study the following modifications and procedures were used to generate improved values for the ideal gas thermodynamic properties of *n*-butane and isobutane: (a) more reliable vibrational assignments and molecular structural data; (b) correction of the experimental thermodynamic data [1–8] for gas imperfection using the recently established *h*-tables of API Research Project 44 [38]; (c) use of computer programs to generate values of reduced moments of inertia for molecules with compound rotors [39] and to generate energy levels for internal rotation [40]; (d) use of more accurate potential energy functions for internal rotation;

(e) empirical corrections for top-top interactions and other effects in isobutane; (f) use of current values for atomic masses and fundamental constants [41].

## 2. *n*-Butane

The molecular structure of *n*-butane was studied by sector-microphotometer electron diffraction techniques [30–32]. The average structural parameters found were the same for *trans* and *gauche* isomers. Kuchitsu [30] obtained  $67.5 \pm 1.1^\circ$  for the dihedral angle,  $\phi$ , defined as the angle between the two CH<sub>2</sub>—CH<sub>3</sub> bonds as viewed along the central C—C bond, in the *gauche* position while Bonham and Bartell [31] obtained  $63 \pm 8^\circ$ . Bartell and Kohl [42] analyzed their electron diffraction data calculated  $61 \pm 3^\circ$  for the average value of  $\phi$  in several alkanes. They also obtained  $173^\circ$  for the angle between the C—H bond in a methyl group and the C—C—C plane. However, we calculated  $\phi = 62.34^\circ$  for the *gauche* isomer of *n*-butane from the interatomic distances reported by Bartell and Kohl. Their structural parameters have been adopted and are shown in table 1. The principal and reduced moments of inertia for both the *trans* and *gauche* forms were calculated by the method of Kilpatrick and Pitzer [39]. The calculated values are also shown in table 1. The reduced moments are given by the diagonal elements of the Kilpatrick-Pitzer *D* matrix when, as in this case, coupling between overall rotation and internal rotation is small. When the off-diagonal elements are removed by a similarity transformation [43], the resulting diagonal elements correspond to the three torsional modes. These consist of two modes of symmetry species  $a_u$  and one of  $b_g$  for the *trans* conformation, or two of type  $a$  and one of  $b$  for the *gauche* form.

The torsional modes of *n*-butane have not been directly observed. Table 2 lists reported values for the potential barrier to internal rotation of the methyl group

<sup>1</sup> Figures in brackets indicate literature references at the end of this paper.

TABLE 1. Selected values of molecular constants of *n*-butane gas

Property	<i>trans</i> isomer			<i>gauche</i> isomer			Units
Molecular weight	58.124						g mol <sup>-1</sup>
Symmetry number	18						dimensionless
Structural parameters	$r(\text{C}-\text{C}) = 1.533$			$r(\text{C}-\text{H}) = 1.108$			10 <sup>-8</sup> cm
	$\angle \text{CCC} = 112.35^{\text{a}}$		$\angle \text{CCH} = 110.5$	$\angle \text{HCH} = 108.42^{\text{b}}$			degree
Principal moments of inertia	36.865	247.04	230.93	65.890	202.99	170.50	10 <sup>-40</sup> g cm <sup>2</sup>
Reduced moments of inertia	5.2483 (4.7359) <sup>c</sup>	18.602 (18.441) <sup>c</sup>	4.0633 (4.7359) <sup>c</sup>	4.7550 (5.1601) <sup>c</sup>	17.583 (17.175) <sup>c</sup>	5.2531 (5.2553) <sup>c</sup>	10 <sup>-40</sup> g cm <sup>2</sup>
Vibrational fundamentals <sup>d</sup>							cm <sup>-1</sup>
Symmetry species $a_g$	2965	2872	2853	2968	2968	2920	
	1460	1442	1382	2870	2860	1460	
	1361	1151	1059	1460	1450	1380	
	842	432		1350	1281	1168	
Symmetry species $a_u$	2968	2930	1461	1077	980	827	
	1257	948	731	788	320	233 <sup>e</sup>	
	223 <sup>e</sup>	123 <sup>e</sup>		123 <sup>e</sup>			
Symmetry species $b_g$	2965	2912	1460	2968	2968	2920	
	1300	1180	803	2870	2860	1460	
	250 <sup>e</sup>			1460	1450	1380	
Symmetry species $b_u$	2968	2870	2853	1370	1233	1133	
	1461	1461	1379	980	955	747	
	1290	1009	964	469	223 <sup>e</sup>		
	271						
Potential barrier parameters	See tables 2 and 4			See tables 2 and 4			
Heat of formation at 298.15 K	-30.06						kcal mol <sup>-1</sup>

<sup>a</sup> Determined from  $1.533 \times 10^{-8}$  cm for the C—C bond length and  $2.547 \times 10^{-8}$  cm for the nearest nonbonded C—C distance [42]. The previously reported value [32] is  $112.4^\circ$ .

<sup>b</sup> Calculated value by the assumption of an equilateral triangle formed by the hydrogen atoms of a methyl group.

<sup>c</sup> Values in parentheses were obtained before similarity trans-

formation as explained in the text.

<sup>d</sup> The symmetry species  $a_g$  and  $a_u$  of the *trans* isomer correspond to the symmetry species  $a$  of the *gauche* form while  $b_g$  and  $b_u$  of the *trans* correspond to  $b$  of the *gauche*.

<sup>e</sup> Torsional mode.

and the potential energy maximum between *trans* and *gauche* positions as derived from ultrasonic relaxation measurements [44], by fitting of calculated thermodynamic properties to observed data [6, 9, 10, 45, 46], and by theoretical calculations [47–51]. The energy difference between the *gauche* and *trans* isomers listed in table 3 has been obtained by analyses of spectral and thermodynamic data [11, 12, 42, 52–56] or by theoretical calculations [47–50, 57, 58]. The vibrational frequencies of *n*-C<sub>4</sub>H<sub>10</sub> were assigned by analyses of Raman [11, 12, 15] and infrared [11, 13, 14, 16–21] spectra. Shimanouchi [22] reviewed the reported values and selected complete sets of vibrational frequencies for both isomers. These were adopted in the present work except for the C—C stretching mode at  $837 \text{ cm}^{-1}$  (from theoretical calculation) and the C—C—C deformation

mode at  $425 \text{ cm}^{-1}$  (for condensed phase) of the *trans* isomer that are respectively replaced by the most recent values of 842 and  $432 \text{ cm}^{-1}$  from the Raman spectrum of the vapor [56]. The data for the *trans* isomer belonging to C<sub>2h</sub> point group and the *gauche* isomer belonging to C<sub>2</sub> point group are tabulated in table 1.

The usual approximation of assuming that *n*-butane consists of one *trans* and two identical *gauche* conformational isomers in mutual equilibrium for calculating thermodynamic properties has been followed.

The potential energy for internal rotation of each of the two methyl groups contains three equal uniformly spaced minima corresponding to the staggered positions of the hydrogen atoms and three equal maxima at the eclipsed positions. The energy levels were calculated

TABLE 2. Reported potential barriers (cal mol<sup>-1</sup>) in internal rotation in *n*-butane

CH <sub>3</sub> -group	C <sub>2</sub> H <sub>5</sub> -group	Reference
3400 <sup>a</sup>	3800 <sup>b</sup>	[9]
3300	3600	[10]
3300 <sup>a</sup>	30000 <sup>c</sup>	[6]
	3600	[45]
3400	3300	[46]
3400	3720	[47]
	3000	[48]
	3450 <sup>d</sup>	[49]
	4200 <sup>e</sup>	[44]
	4370 <sup>f</sup>	[50]
3280		[51]
3300(2) <sup>g</sup>	3500(1) <sup>g</sup>	This work

<sup>a</sup> The reduced moment  $I_r = 5.0 \times 10^{-40}$  g cm<sup>2</sup> was used. If the value of  $I_r$  is not available, a footnote will not be given.

<sup>b</sup>  $I_r = 18.6 \times 10^{-40}$  g cm<sup>2</sup> was used.

<sup>c</sup>  $I_r = 32.2 \times 10^{-40}$  g cm<sup>2</sup> was used.

<sup>d</sup> Average value of 3390 and 3510 cal mol<sup>-1</sup>.

<sup>e</sup> With an uncertainty of  $\pm 400$  cal mol<sup>-1</sup>.

<sup>f</sup> Average value of 4360 and 4380 cal mol<sup>-1</sup>.

<sup>g</sup> Number in parentheses is degeneracy. The associated values of  $I_r$  are given in table 1.

TABLE 3. The energy difference ( $\Delta E = E_{gauche} - E_{trans}$ ) of the rotational isomers of *n*-butane

$\Delta E$ (cal mol <sup>-1</sup> )	Reference	$\Delta E$ (cal mol <sup>-1</sup> )	Reference
800	[52, 55]	720	[58]
770 $\pm$ 90 <sup>a</sup>	[11]	600	[48]
760 $\pm$ 100 <sup>a</sup>	[12]	490 <sup>b</sup>	[49]
700	[47]	791 <sup>c</sup>	[50]
500	[53]	495	[51]
800 $\pm$ 200	[54]	966 $\pm$ 54 <sup>d</sup>	[56]
610 $\pm$ 200	[42]	760	This work
600	[57]		

<sup>a</sup> Average enthalpy difference in the temperature range of 155 ~ 310 K.

<sup>b</sup> Average value of 390 and 580 cal mol<sup>-1</sup>.

<sup>c</sup> Average value of 761 and 822 cal mol<sup>-1</sup>.

<sup>d</sup> Weighted average of 976  $\pm$  43 and 942  $\pm$  98 cal mol<sup>-1</sup> for the average enthalpy difference in the temperature range of 300 ~ 450 K.

by numerical solution of the Schrodinger equation with the use of the selected values of reduced moments and potential barriers listed in tables 1 and 2, respectively. For internal rotation about the central C—C bond, two approaches were made to evaluate energy levels. Method I: A potential function of three-fold symmetry was assumed for both *trans* and *gauche* isomers similar to that for the methyl groups. One-third of the energy levels were assigned to the *trans* conformer and two-thirds to the *gauche* conformer. Method II: The potential function  $V(\theta) = \frac{1}{2}[V_1(1 - \cos \theta) + V_2(1 - \cos 2\theta) + V_3(1 - \cos 3\theta)]$  simultaneously governing both *trans* and *gauche* forms was used and the variation of the internal rotational constant with the

torsional angle  $\theta$  of the ethyl group,  $F(\theta) = F_0 + F_1 \cos \theta + F_2 \cos 2\theta + F_3 \cos 3\theta$ , was taken into account as well. The potential function also contains three minima and three maxima, but they are not equal and not uniformly spaced. The *trans* position (two methyl groups on opposite sides of the central bond, C<sub>2h</sub> point group) has the lowest minimum,  $V(0^\circ) = 0$ , and the two *gauche* positions have higher minima at  $\theta = \pm 117.66^\circ$ . Two potential energy maxima exist for the eclipsed positions at  $\theta = \pm 61.57^\circ$  between the *trans* and *gauche* positions and the highest maximum,  $V(180^\circ) = V_1 + V_3$ , corresponds to the eclipsed position between the two *gauche* positions. The parameters of  $V_1$ ,  $V_2$  and  $V_3$  listed in table 4 were calculated from the selected values of the potential barrier (table 2) and the energy difference (table 3) between the *trans* and *gauche* isomers and of the dihedral angle of 62.34° for the *gauche* form. These

TABLE 4. Potential and rotational parameters C<sub>2</sub>H<sub>5</sub>-rotation in *n*-C<sub>4</sub>H<sub>10</sub>

Parameter	Approach I		Approach II
	<i>trans</i>	<i>gauche</i>	<i>trans</i> & <i>gauche</i>
Potential function: $V(\theta) = \frac{1}{2}[V_1(1 - \cos \theta) + V_2(1 - \cos 2\theta) + V_3(1 - \cos 3\theta)]$ cal mol <sup>-1</sup>			
Rotational constant: $F(\theta) = F_0 + F_1 \cos \theta + F_2 \cos 2\theta + F_3 \cos 3\theta$ cm <sup>-1</sup>			
$V_1$	0	0	1146.8
$V_2$	0	0	-117.15
$V_3$	3500	2740 <sup>a</sup>	+3295.8
$F_0$	1.5049	1.5921	1.5443
$F_1$	0	0	-0.10258
$F_2$	0	0	+0.06043
$F_3$	0	0	-0.00612

<sup>a</sup> Based on 760 cal mol<sup>-1</sup> in the energy difference between the *trans* and *gauche* forms.

imply that the barrier height between the two *gauche* positions is 943 cal mol<sup>-1</sup> higher than that between the *trans* and *gauche* positions.<sup>2</sup> The use of Kuchitsu's value of 67.5° [30] for the dihedral angle gives 3146 cal mol<sup>-1</sup> for the difference in potential barriers, which seems too large in view of the structural similarity for 2-butene, where 1200 cal mol<sup>-1</sup> was found for the energy difference between the *trans* and *cis* forms [59]. The values of  $F_0$ ,  $F_1$ ,  $F_2$  and  $F_3$  obtained by fitting to directly calculated values of  $F(\theta)$  at several angles are also reported in table 4. The calculated energy levels below the barrier height were assigned to the *trans* and *gauche* isomers by examination of the associated wave functions. However, the energy levels above the barrier height were indistinguishable for both isomers and the proportions of  $\frac{1}{3}$  and  $\frac{2}{3}$  for each level were therefore assumed.

<sup>2</sup> In keeping with the use of cal mol<sup>-1</sup> in much of the literature cited in this paper, the units cal mol<sup>-1</sup> is employed here. One calorie = 4.184 joules.

A number of combinations of potential barriers to internal rotation for the methyl and ethyl groups was used in fitting calculated thermodynamic properties to observed values. It was found that the selected values listed in tables 2-4 led to the best agreement with experimental entropy [6] and heat capacities [8]. As shown in table 5, the calculated  $C_p^\circ$  and  $S^\circ$  in both approaches agree with experimental values well within uncertainties of  $\pm 1$  percent [8] and  $\pm 0.2$  cal K<sup>-1</sup> mol<sup>-1</sup> [6], respectively. The third-law entropy at 272.66 K obtained by Aston and Messerly [6] is believed to be the most reliable. They also used the heat capacity data of Sage and Lacey [2], which appear about 2 percent too low, to calculate  $S_{298.16}^\circ - S_{272.66}^\circ$  and obtained  $S_{298.16}^\circ = 74.00$  cal K<sup>-1</sup> mol<sup>-1</sup>. The use of our  $C_p^\circ$  values leads to 74.09 cal K<sup>-1</sup> mol<sup>-1</sup> which is the same as the  $S^\circ$  at 298.16 K calculated by Method II. It is obvious that Method II is slightly better, particularly for calculated values at elevated temperatures. Therefore, the ideal gas thermodynamic functions calculated by this approach for the temperature range of 0 to 1500 K and at 1 atm are recommended and presented in tables 6, 7 and 8 for the *trans*, *gauche* and their equilibrium mixtures, respectively.

Table 9 summarizes the reported values of the

standard enthalpy of formation for *n*-butane that were derived from experimental measurements [60-63], compilation [64] and correlations [65, 66]. Based on the experimental and correlation values,  $\Delta H_f^\circ$  (298.15, *n*-butane, g) = -30.06 kcal mol<sup>-1</sup> has been selected in this work. From this selected value and  $(H^\circ - H_0^\circ)$  and  $(G^\circ - H_0^\circ)/T$  of reference [38] for C(c) and H<sub>2</sub>(g) and of this work for *n*-butane, the values of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and  $\log K_f$  in the same temperature range have been derived and listed also in table 8.

### 3. Isobutane (2-Methylpropane)

The molecular structural parameters of isobutane were derived from microwave spectra [26, 33] and calculations [34, 35] based on electron diffraction data of alkanes [31, 32] with microwave spectroscopic rotational constants [33]. Of these, the parameters reported by Hilderbrandt and Wieser [35] have been adopted and listed in table 10. The principal moments of inertia were obtained from the rotational constants reported by Lide [33] and the reduced moments were calculated from the adopted structural parameters. These values are also shown in table 10.

TABLE 5. Comparison of calculated  $C_p^\circ$  and  $S^\circ$  with experimental values<sup>a</sup> for *n*-C<sub>4</sub>H<sub>10</sub>

T (K)	$C_p^\circ$ (exptl.) (cal K <sup>-1</sup> mol <sup>-1</sup> )			$C_p^\circ$ (calcd.) (cal K <sup>-1</sup> mol <sup>-1</sup> )	
	[4] 1937	[8] 1943 <sup>b</sup>		Approach I	Approach II
294.3	22.55(22.46)			23.35	23.30
310.9	23.23(23.20)			24.37	24.32
327.6	23.94(23.94)			25.27	25.34
344.3	24.67(24.69)			26.41	26.38
344.9		26.43(26.44)		26.45	26.42
359.6		27.47(27.49)		27.35	27.34
360.9	25.42(25.46)			27.44	27.42
377.6	26.19(26.23)			28.46	28.45
387.5		29.10(29.14)		29.06	29.06
394.3	26.95(27.00)			29.47	29.47
410.9	27.69(27.74)			30.47	30.48
451.6		32.98(33.02)		32.83	32.86
521.0		36.81(36.84)		36.57	36.63
561.3		38.78(38.81)		38.57	38.64
600.8		40.71(40.74)		40.42	40.50
692.6		44.42(44.44)		44.32	44.41
T (K)	$S^\circ$ (exptl.) (cal K <sup>-1</sup> mol <sup>-1</sup> )			$S^\circ$ (calcd.) (cal K <sup>-1</sup> mol <sup>-1</sup> )	
	[1] 1931	[3] 1937 <sup>c</sup>	[6] 1940 <sup>d</sup>	Approach I	Approach II
272.50		73.86(73.90)		72.11	72.03
272.66			72.05(72.10)	72.12	72.04
298.10	74.4	75.76(75.78)		74.16	74.07

<sup>a</sup> Obtained by original investigators using the Berthelot equation for gas imperfection. The values in parentheses were derived by use of h-tables of API Research Project 44 [38] for gas imperfection. Moreover, the API-44 Selected Values for the heat of fusion at the melting point and the heat of vaporization at the boiling point were used for the third-law entropies.

<sup>b</sup> With an experiment uncertainty of  $\pm 1$  percent.

<sup>c</sup> With an experiment uncertainty of  $\pm 0.8$  cal K<sup>-1</sup> mol<sup>-1</sup>.

<sup>d</sup> With an experiment uncertainty of  $\pm 0.2$  cal K<sup>-1</sup> mol<sup>-1</sup>.

TABLE 6. Ideal gas thermodynamic properties for *n*-C<sub>4</sub>H<sub>10</sub> (*trans* form)

<i>T</i>	$H^\circ - H_0^\circ$	$(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	$S^\circ$	$C_p^\circ$
K	cal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>			
0	0	0	0	0	0
50	410	-39.20	8.197	47.39	8.98
100	935	-45.20	9.349	54.55	12.04
150	1604	-49.25	10.692	59.94	14.63
200	2396	-52.50	11.980	64.48	17.10
273.15	3796	-56.51	13.898	70.41	21.33
298.15	4350	-57.76	14.588	72.35	22.93
300	4392	-57.85	14.640	72.49	23.05
400	7023	-62.46	17.558	80.02	29.54
500	10278	-66.70	20.556	87.25	35.42
600	14077	-70.70	23.462	94.17	40.43
700	18339	-74.53	26.198	100.73	44.70
800	22997	-78.20	28.746	106.94	48.38
900	27999	-81.72	31.110	112.83	51.57
1000	33298	-85.11	33.298	118.41	54.35
1100	38857	-88.38	35.324	123.71	56.76
1200	44640	-91.54	37.200	128.74	58.86
1300	50620	-94.58	38.938	133.52	60.69
1400	56770	-97.53	40.550	138.08	62.27
1500	63067	-100.38	42.045	142.42	63.66

TABLE 7. Ideal gas thermodynamic properties for *n*-C<sub>4</sub>H<sub>10</sub> (*gauche* form)

<i>T</i>	$H^\circ - H_0^\circ$	$(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	$S^\circ$	$C_p^\circ$
K	cal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>			
0	0	0	0	0	0
50	411	-40.64	8.218	48.86	8.99
100	933	-46.65	9.329	55.98	11.89
150	1592	-50.67	10.616	61.29	14.42
200	2375	-53.90	11.874	65.77	16.91
273.15	3762	-57.88	13.774	71.65	21.15
298.15	4311	-59.11	14.459	73.57	22.75
300	4353	-59.20	14.511	73.72	22.87
400	6964	-63.77	17.410	81.18	29.31
500	10195	-67.98	20.390	88.37	35.17
600	13970	-71.95	23.284	95.24	40.20
700	18211	-75.75	26.016	101.76	44.50
800	22852	-79.39	28.565	107.96	48.22
900	27839	-82.89	30.932	113.83	51.45
1000	33127	-86.27	33.127	119.40	54.25
1100	38677	-89.52	35.161	124.68	56.69
1200	44454	-92.66	37.045	129.71	58.81
1300	50429	-95.70	38.792	134.49	60.65
1400	56576	-98.63	40.411	139.04	62.25
1500	62873	-101.47	41.915	143.39	63.65

TABLE 8. Ideal gas thermodynamic properties for *n*-C<sub>4</sub>H<sub>10</sub> (mixture of *trans* and *gauche*)

<i>T</i>	Composition	$H^\circ - H_0^\circ$	$(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	$S^\circ$	$C_p^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	log <i>K<sub>f</sub></i>
K	<i>trans</i> %	cal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>			kcal mol <sup>-1</sup>			
0	~ 100	0	0	0	0	0	-23.25	-23.25	∞
50	99.9	411	-39.20	8.212	47.41	9.10	-25.36	-22.58	98.68
100	95.7	968	-45.29	9.677	54.97	13.23	-26.17	-19.48	42.57
150	86.2	1708	-49.54	11.381	60.92	16.09	-27.06	-15.95	23.24
200	77.0	2568	-53.02	12.830	65.85	18.27	-28.05	-12.10	13.22
273.15	67.1	4037	-57.31	14.773	72.08	22.06	-29.56	-6.00	4.80
298.15	64.6	4607	-58.63	15.445	74.07	23.54	-30.06	-3.84	2.81
300	64.4	4651	-58.72	15.496	74.22	23.65	-30.10	-3.67	2.68
400	57.3	7325	-63.56	18.306	81.87	29.82	-31.95	5.43	-2.97
500	53.0	10599	-67.96	21.192	89.15	35.53	-33.48	14.95	-6.53
600	50.2	14405	-72.07	24.004	96.08	40.46	-34.72	24.75	-9.02
700	48.3	18668	-75.97	26.665	102.64	44.70	-35.68	34.75	-10.85
800	46.9	23326	-79.70	29.154	108.85	48.37	-36.41	44.86	-12.26
900	45.9	28326	-83.27	31.471	114.74	51.56	-36.93	55.06	-13.37
1000	45.0	33624	-86.70	33.622	120.32	54.34	-37.25	65.31	-14.27
1100	44.4	39182	-90.00	35.618	125.61	56.76	-37.41	75.53	-15.01
1200	43.8	44965	-93.18	37.469	130.65	58.86	-37.46	85.84	-15.63
1300	43.4	50944	-96.24	39.186	135.43	60.69	-37.42	96.10	-16.16
1400	43.0	57095	-99.21	40.780	139.99	62.28	-37.29	106.43	-16.61
1500	42.7	63393	-102.07	42.261	144.33	63.67	-37.10	116.65	-17.00

TABLE 9. Summary of data on heats (in kcal mol<sup>-1</sup>) of formation and isomerization of gaseous butanes at 298.15 K

$\Delta H_f^\circ(n\text{-C}_4\text{H}_{10})$	$\Delta H_f^\circ(\text{iso-C}_4\text{H}_{10})$	$\Delta H_i$ ( $n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{iso-C}_4\text{H}_{10}$ )	Method	Reference
$-30.36 \pm 0.16$	$-32.41 \pm 0.16$	$-2.05 \pm 0.23$ $-2.12 \pm 0.06^a$	Heat of combustion Equilibrium constants (3rd law calculation)	[52] [61, 62, 70, 73]
$-30.03 \pm 0.16$	$-32.07 \pm 0.15$	$-2.04 \pm 0.22$	Heat of combustion	[63]
$-30.15$	$-32.15$	$-2.00$	Selected values	[64]
$-30.28$	$-32.24$	$-1.96$	Selected values for consistency with butenes	( <sup>b</sup> )
$-30.09$	$-32.05$	$-1.96$	Correlation	[65]
$-30.04 \pm 0.04$	$-32.16 \pm 0.04$	$-2.11 \pm 0.06$	Correlation	[66]
$-30.06$	$-32.23$	$-2.17$	Correlation	( <sup>c</sup> )
$-30.06$	$-32.18$	$-2.12$	Selected values	This work

<sup>a</sup> Derived in this work from the equilibrium constants reported in references [61, 62, 70 and 73].

<sup>b</sup> R. C. Wilhoit, unpublished work of API-44, 1972.

<sup>c</sup> G. R. Somayajulu, new correlation after the publication of [65].

TABLE 10. Selected values of molecular constants of isobutane gas

Property	Quantity	Property	Quantities		
Molecular weight.....	58.124	Principal moments of inertial, 10 <sup>-40</sup> g cm <sup>2</sup> .....	186.48	107.77	107.77
Symmetry number.....	81	Reduced moments of inertial, 10 <sup>-40</sup> g cm <sup>2</sup> .....	5.1364 (5.0306)	5.1364 (5.3479)	5.1364 (5.0306) <sup>b</sup>
Structural parameters <sup>a</sup> :		Vibrational fundamentals, cm <sup>-1</sup> :			
$r_{(\text{C}-\text{C})}$ .....	1.535	Symmetry species $a_1$ .....	2962	2904	2880
$r_{(\text{C}-\text{H in CH}_3)}$ .....	1.113		1477	1394	1177
$r_{(\text{C}-\text{H for tertiary H})}$ .....	1.122		797	433	
$\angle \text{CCC}$ .....	110.8	Symmetry species $a_2$ .....	2958	1450	981
$\angle \text{HCC (for CH}_3)$ .....	111.4		220 <sup>c</sup>		
$\angle \text{HCC (for tertiary H)}$ .....	108.1	Symmetry species $e$ .....	2962	2962	2894
$\angle \text{HCH}$ .....	107.6		1477	1475	1371
			1330	1166	966
			367	256 <sup>c</sup>	
		Potential barrier parameters, cal mol <sup>-1</sup> .....	3851( $V_3$ )		-150( $V_6$ )
		Heat of formation at 298.15 K, kcal mol <sup>-1</sup> .....	-32.18		

<sup>a</sup> Bond lengths in 10<sup>-8</sup> cm and bond angles in degrees.

<sup>b</sup> Values in parentheses were obtained before similarity transformation as explained in the text.

<sup>c</sup> Torsional mode.

Vibrational fundamentals were primarily observed in Raman and infrared spectra [23]. The nontorsional fundamentals assigned by Wilmshurst and Bernstein [24] have been selected, except for the unobservable methyl rocking mode of symmetry species  $a_2$ . The value 981 cm<sup>-1</sup> calculated by Snyder and Schachtschneider [19] was adopted for the remaining one. In fact, the choice of the two sets of vibrational assignments [19, 24] results in very slight differences in the vibrational contributions to ideal gas thermodynamic functions. The selected values of vibrational modes are shown in table 10.

Isobutane has three rotating methyl groups. The

torsional modes give rise to an  $a_2$  fundamental and a doubly degenerate fundamental. The assignments of  $225 \pm 20$  and  $280 \pm 20$  cm<sup>-1</sup>, respectively, obtained from microwave relative intensity measurements [26] are in reasonable accord with the assignments of 220 and 256 cm<sup>-1</sup> from the infrared spectrum [29]. Potential barriers to internal rotation have been obtained from thermodynamic data [7, 9, 10, 68, 69], microwave [26] and infrared [29] spectra, and theoretical calculation [49]. Lide and Mann [26] and Durig, Craven and Bragin [29] based their analyses on the following function for the potential energy of the methyl groups as a function of the three torsional angles,  $\phi_1$ ,  $\phi_2$  and  $\phi_3$ .

$$2V = V_0 - V_1 \sum_{i=1}^3 \cos 3\phi_i - V_2 \sum_{i>j}^3 \cos 3\phi_i \cos 3\phi_j \quad (1)$$

$$- V_3 \cos 3\phi_1 \cos 3\phi_2 \cos 3\phi_3 + V_4 \sum_{i>j}^3 \sin 3\phi_i \sin 3\phi_j$$

$$+ V_5 \sum_{i \neq j \neq k}^3 \cos 3\phi_i \sin 3\phi_j \sin 3\phi_k,$$

where  $V_1$  is the potential barrier to rotation for an "independent" methyl group. The other  $V_i$ 's represent interactions among the methyl groups. However, it is possible to calculate only two parameters from the first two observed rotational transitions. Thus references [26] and [29] report the values of  $V_1 + 2V_2 + V_3$  and  $V_4 + V_5$ . These are listed in table 11. Since  $V_2$  and  $V_3$  are probably small compared to  $V_1$ , the first term is approximately  $V_1$ .

TABLE 11. Reported potential barriers (cal mol<sup>-1</sup>) to internal rotation in isobutane

$V_3$	Top-top interaction	Reference	$V_3$	Top-top interaction	Reference
3800 <sup>a</sup>	0	[9]	3900 <sup>c</sup>	-457 <sup>c</sup>	[26]
3600 <sup>b</sup>	0	[10]	3757	0	[49]
3870 <sup>a</sup>	0	[7]	3390	-270	[29]
3620	0	[69]	3851	-150 <sup>d</sup>	This work
3850	0	[47]			

<sup>a</sup> The reduced moment  $I_r = 5.2 \times 10^{-40}$  g cm<sup>2</sup> was used. If the value of  $I_r$  is not available, a footnote will not be given.

<sup>b</sup>  $I_r = 5.0 \times 10^{-40}$  g cm<sup>2</sup> was used.

<sup>c</sup>  $I_r = 5.20 \times 10^{-40}$  g cm<sup>2</sup> for the singly and  $I_r = 4.91 \times 10^{-40}$  g cm<sup>2</sup> for the doubly degenerate torsional modes were used.

<sup>d</sup> The meaning for this number is different from the others. Refer to the text. The values of  $I_r$  are given in table 10.

If we assume that the methyl groups are independent and thus that the potential function contains  $\cos 3\phi_i$  terms only, we obtain 3280 and 4137 cal mol<sup>-1</sup> for the potential barrier using the two torsional modes observed in the infrared and the reduced moments of inertia in table 2. However, we cannot reproduce the observed heat capacities and entropy of isobutane by assuming independent methyl rotation with any value of  $V_1$ . We conclude that interaction among methyl groups has a significant effect on thermodynamic functions. Although the interaction between the two methyl groups in propane was studied by neutron inelastic scattering measurements [67] and the first five energy levels were calculated by an approximated solution of the Schroedinger equation, a three-dimensional model for the energy levels of internal rotation for isobutane has yet to be solved. We cannot now calculate rotational energy levels for the function (1) because we do not know the values of the  $V_i$ 's and we do not have means of solving the Schroedinger equation including mixed terms. As an empirical approximation we have assumed the methyl rotations to be independent, with the potential energy for each given by

$$2V = V_3(1 - \cos 3\phi) + V_6(1 - \cos 6\phi). \quad (2)$$

We take the value of  $V_3 = 3851$  cal mol<sup>-1</sup> which is the average of 3280 and 4137, obtained from the two torsional modes. The value of  $V_6$  was found empirically by fitting to the observed thermodynamic properties of isobutane [7, 8, 36, 37]. This is shown in table 11. It was found that any value of  $V_6$  in the range of -150 to -100 cal mol<sup>-1</sup> gave a good fit. The most recently observed values of  $C_p^\circ$  [36, 37] with uncertainties of  $\pm 0.1$  percent and  $\pm 0.2$  percent, respectively, are in excellent agreement. The choice of -150 cal mol<sup>-1</sup> for  $V_6$  led to the most striking result that differences between the calculated and observed values of  $C_p^\circ$  in the whole temperature range of 243.15 to 353.15 K are only half of the experimental uncertainty [36, 37], as shown in table 12. At higher temperatures up to 700 K, the calculated  $C_p^\circ$  values also fall within an experimental uncertainty of  $\pm 1$  percent [8]. Table 13 shows the experimental and calculated values of  $S^\circ$ . The third-law entropy at 261.44 K [7] is slightly lower than the calculated value. When the gas imperfection correction calculated from Berthelot equation and heats of fusion and vaporization [7] were replaced by the selected values of API-44 [38], the calculated  $S^\circ$  agreed with the third-law entropy in the experimental limit  $\pm 0.10$  cal K<sup>-1</sup> mol<sup>-1</sup>. Therefore,  $V_3 = 3851$  cal mol<sup>-1</sup> and  $V_6 = -150$  cal mol<sup>-1</sup> have been selected to calculate ideal gas thermodynamic properties. In fact, all possible combinations of potential parameters were tested under the assumption of either a unique or two independent potential functions for the two torsional modes; however, no other selection would result in a better overall fit to experimental data of  $C_p^\circ$  and  $S^\circ$ . It may be interesting to note that the selected value of  $V_6$  for each of the three methyl rotors is equal to one third of the contribution of top-top interactions in isobutane estimated from microwave relative intensity measurements [26]. From the potential function of equation (2) and the calculated reduced moments of inertia we then calculated 225 and 231 cm<sup>-1</sup> for the first transition of the  $a_2$  and  $e$  species respectively. Although this calculation is in poor agreement with the spectroscopic data, we feel the above procedure provides the best values of the thermodynamic properties.

On the basis of the selected values of  $\Delta H_f^\circ$  (298.15, *n*-C<sub>4</sub>H<sub>10</sub>, g) and  $\Delta H_i^\circ$  (298.15, *n*-C<sub>4</sub>H<sub>10</sub>  $\rightleftharpoons$  iso-C<sub>4</sub>H<sub>10</sub>, g) which was derived from equilibrium data [61, 62, 70, 73],  $\Delta H_f^\circ$  (298.15, iso-C<sub>4</sub>H<sub>10</sub>, g) was obtained to be -32.18 kcal mol<sup>-1</sup>. The calculated values of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ ,  $\log K_f$  and other thermodynamic functions in the temperature range of 0 to 1500 K and at 1 atm are shown in table 14.

#### 4. Isomerization

Values of the equilibrium constant  $K_i$  for the isomerization reaction *n*-C<sub>4</sub>H<sub>10</sub>  $\rightleftharpoons$  iso-C<sub>4</sub>H<sub>10</sub> at various tempera-

TABLE 12. Comparison of calculated  $C_p^\circ$  with experimental values <sup>a</sup> for iso-C<sub>4</sub>H<sub>10</sub>

T(K)	$C_p^\circ(\text{exptl.}) (\text{cal K}^{-1} \text{mol}^{-1})$				$C_p^\circ(\text{calcd.})$ (cal K <sup>-1</sup> mol <sup>-1</sup> )
	[4] 1937 & [5] 1938	[8] 1943 <sup>b,c</sup>	[36] 1947 <sup>d</sup>	[37] 1970 <sup>e</sup>	This work
243.15			19.67		19.65
273.15			21.50		21.49
293.15				22.76	22.77
294.3	22.38				22.85
310.9	22.95				23.93
313.15			24.10	24.06	24.08
327.6	23.60				25.03
333.15				25.42	25.39
344.3	24.25				26.13
347.6		26.21(26.23)			26.35
353.15			26.71	26.71	26.71
359.4		26.90(26.93)			27.12
360.9	24.97				27.22
377.6	25.70				28.31
387.5		28.59(28.62)			28.94
394.3	26.49				29.38
410.9	27.40 <sup>b</sup> (27.44)				30.43
427.6	28.27 <sup>b</sup> (28.31)				31.46
444.3	29.15 <sup>b</sup> (29.20)				32.47
452.5		32.75(32.80)			32.96
520.9		36.55(36.60)			36.80
561.7		38.55(38.57)			38.88
605.3		40.56(40.58)			40.96
692.7		44.26(44.28)			44.71

<sup>a</sup> Unless otherwise indicated, values were obtained from extrapolation of  $C_p$  to zero pressure.

<sup>b</sup> Berthelot equation was used for gas imperfection. Values in parentheses were obtained when h-tables of API44 [38] were used for gas imperfection.

<sup>c</sup> With an experimental uncertainty of  $\pm 1$  percent.

<sup>d</sup> With an experimental uncertainty of  $\pm 0.1$  percent.

<sup>e</sup> With an experimental uncertainty of  $\pm 0.2$  percent.

TABLE 13. Comparison of calculated  $S^\circ$  with experimental values <sup>a</sup> for iso-C<sub>4</sub>H<sub>10</sub>

T(K)	$S^\circ(\text{exptl.}) (\text{cal K}^{-1} \text{mol}^{-1})$		$S^\circ(\text{calcd.}) (\text{cal K}^{-1} \text{mol}^{-1})$
	[3] 1937	[7] 1940	This work
260.9	67.20 $\pm$ 1.1 (67.24)		67.68
261.44		67.57 <sup>b</sup> $\pm$ 0.10 (67.63)	67.72
298.1	70.01 $\pm$ 1.1 (70.14)		70.59
298.16		70.48 $\pm$ 0.15 (70.51)	70.60

<sup>a</sup> Refer to footnote a of table 5.

<sup>b</sup> The original value is 67.52 cal K<sup>-1</sup> mol<sup>-1</sup>. However, the correction for gas imperfection should be 0.17 (rather than 0.12) cal K<sup>-1</sup> mol<sup>-1</sup> at 261.44 K, according to Berthelot equation [7].

tures were determined [61, 62, 70, 73]. From plots of  $\log Ki$  against  $1/T$ , the heat of isomerization  $\Delta Hi^\circ$  was derived to be  $-2.32$  kcal mol<sup>-1</sup> [61] or  $-2.03$  kcal mol<sup>-1</sup> [62]. Both values are higher than  $-1.64$  kcal mol<sup>-1</sup> determined from heats of combustion [74]. Different values of  $\Delta Hi^\circ$  obtained from experimental measurements, compilation and correlations were summarized in table 9. From the third-law calculations based on values of the equilibrium constant  $Ki$  [61, 62, 70, 73]

and of  $S^\circ$  and  $H^\circ - H_0^\circ$  of this work,  $\Delta Hi^\circ = -2.12 \pm 0.06$  kcal mol<sup>-1</sup> was obtained and adopted. For convenience, thermodynamic functions of isomerization and equilibrium compositions are tabulated in table 15.

## 5. Discussion

Based on the torsional fundamentals at 254 and 223 cm<sup>-1</sup> for the two methyl groups in solid *n*-C<sub>4</sub>H<sub>10</sub> [25], an average value of  $3343 \pm 33$  cal mol<sup>-1</sup> for the potential



TABLE 14. Ideal gas thermodynamic properties for iso-C<sub>4</sub>H<sub>10</sub>

<i>T</i>	$H^\circ - H_0^\circ$	$(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	$S^\circ$	$C_p^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	log <i>K<sub>f</sub></i>
K	cal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>			kcal mol <sup>-1</sup>			
0	0	0	0	0	0	-25.34	-25.34	∞
50	400	-38.36	8.004	46.37	8.32	-27.46	-24.56	107.34
100	884	-44.11	8.841	52.96	11.30	-28.31	-21.32	46.60
150	1529	-47.95	10.195	58.14	14.41	-29.22	-17.64	25.70
200	2319	-51.07	11.595	62.67	17.17	-30.20	-13.63	14.89
273.15	3729	-54.99	13.653	68.64	21.49	-31.69	-7.31	5.85
298.15	4286	-56.22	14.378	70.60	23.10	-32.18	-5.07	3.72
300	4329	-56.31	14.432	70.74	23.22	-32.22	-4.90	3.57
400	6979	-60.87	17.448	78.32	29.74	-34.03	+4.49	-2.46
500	10257	-65.09	20.513	85.61	35.67	-35.52	14.30	-6.25
600	14083	-69.10	23.472	92.57	40.72	-36.70	24.37	-8.88
700	18375	-72.93	26.250	99.17	45.00	-37.61	34.63	-10.81
800	23063	-76.60	28.829	105.43	48.67	-38.29	45.00	-12.29
900	28093	-80.14	31.214	111.35	51.85	-38.77	55.44	-13.46
1000	33419	-83.54	33.419	116.96	54.60	-39.05	65.94	-14.41
1100	39002	-86.82	35.456	122.28	57.00	-39.18	76.41	-15.18
1200	44808	-89.99	37.340	127.33	59.07	-39.20	86.95	-15.84
1300	50807	-93.05	39.083	132.13	60.88	-39.13	97.45	-16.38
1400	56976	-96.00	40.697	136.70	62.45	-38.99	108.02	-16.86
1500	63291	-98.86	42.194	141.06	63.82	-38.77	118.47	-17.26

TABLE 15. Thermodynamic properties and equilibrium compositions of isomerization for *n*-C<sub>4</sub>H<sub>10</sub> ⇌ iso-C<sub>4</sub>H<sub>10</sub>

<i>T</i>	$\Delta(H^\circ - H_0^\circ)_i$	$\Delta(H^\circ - H_0^\circ)_i/T$	$\Delta(G^\circ - H_0^\circ)_i/T$	$\Delta S_i^\circ$	$\Delta C_{p,i}^\circ$	$\Delta H_i^\circ$	$\Delta G_i^\circ$	log <i>K<sub>i</sub></i>	Mol % <i>n</i> -C <sub>4</sub> H <sub>10</sub>
K	cal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>			kcal mol <sup>-1</sup>				
50	-10	-0.208	0.835	-1.04	-0.78	-2.11	-1.98	8.66	0
100	-84	-0.836	1.164	-2.01	-1.93	-2.15	-1.84	4.02	0
150	-178	-1.186	1.592	-2.78	-1.68	-2.16	-1.69	2.46	0.3
200	-247	-1.235	1.944	-3.18	-1.10	-2.15	-1.53	1.67	2.1
273.15	-306	-1.120	2.315	-3.43	-0.56	-2.13	-1.31	1.05	8.3
298.15	-318	-1.067	2.410	-3.48	-0.44	-2.12	-1.23	0.90	11.1
300	-319	-1.064	2.417	-3.48	-0.43	-2.12	-1.23	0.89	11.3
400	-343	-0.858	2.695	-3.55	-0.08	-2.08	-0.94	0.51	23.6
500	-340	-0.679	2.867	-3.55	+0.14	-2.03	-0.65	0.29	34.1
600	-319	-0.532	2.977	-3.51	0.26	-1.98	-0.38	0.14	42.1
700	-291	-0.415	3.049	-3.47	0.30	-1.93	-0.12	0.037	47.9
800	-260	-0.325	3.098	-3.42	0.31	-1.88	+0.14	-0.037	52.2
900	-231	-0.258	3.133	-3.39	0.29	-1.84	0.39	-0.094	55.4
1000	-203	-0.203	3.157	-3.36	0.27	-1.80	0.63	-0.14	57.9
1100	-178	-0.162	3.174	-3.34	0.24	-1.77	0.87	-0.17	59.9
1200	-155	-0.129	3.187	-3.32	0.21	-1.74	1.11	-0.20	61.5
1300	-135	-0.103	3.197	-3.30	0.19	-1.72	1.35	-0.23	62.8
1400	-117	-0.083	3.203	-3.29	0.17	-1.70	1.59	-0.25	63.9
1500	-101	-0.067	3.208	-3.28	0.15	-1.68	1.82	-0.26	64.8

barrier to internal rotation was derived from eigenvalues of the Mathieu equation. This is in accord with our selected value, 3300 cal mol<sup>-1</sup>. On the other hand, the potential barrier to internal rotation about the central C—C bond was estimated with less certainty. It is likely to be in the range of 3300 to 3800 cal mol<sup>-1</sup>, as shown in table 2. The reported values of the energy difference between *gauche* and *trans* isomers of *n*-C<sub>4</sub>H<sub>10</sub>, summarized in table 3, also scatter widely. Combina-

tions of various values of potential barriers (3300 ~ 3400 cal mol<sup>-1</sup> for the methyl groups and 3400 ~ 3800 cal mol<sup>-1</sup> for the ethyl group) and the energy difference (600 ~ 995 cal mol<sup>-1</sup>) were tested in this study. The most recent value of 966 ± 54 cal mol<sup>-1</sup> for the enthalpy difference at 366 K,  $H_{366}^\circ(\textit{gauche}) - H_{366}^\circ(\textit{trans})$ , derived from intensity ratios of two neighboring pairs of Raman bands [56], leads to 995 cal mol<sup>-1</sup> for  $H_0^\circ(\textit{gauche}) - H_0^\circ(\textit{trans})$ . The use of this value increases the calculated

$C_p^\circ$  by 0.30 ~ 0.32 cal K<sup>-1</sup> mol<sup>-1</sup> and decreases the calculated  $S^\circ$  by 0.45 ~ 0.70 cal K<sup>-1</sup> mol<sup>-1</sup> as compared to the corresponding counterparts in the temperature range of 298.15 ~ 500 K reported in table 8. A satisfactory agreement with experimental data [6, 8] would not be reached, unless barrier heights could be substantially changed. When 600 cal mol<sup>-1</sup> was assumed as the energy difference, the calculated values of  $C_p^\circ$  obtained were too small when compared to the observed values [8] in the low temperature range. Our calculated  $C_p^\circ$  values are in accord with the experimental data [8] and are slightly higher than those derived from a correlation scheme [66].

We found it to be impossible to fit the experimental thermodynamic data for isobutane listed in tables 12 and 13 with values calculated on the assumption that the three methyl rotations are independent. A rigorous solution to this problem of multirotors is beyond our reach at this time, but equation (2) which is valid for a single rotor leads to a good empirical fit. Other phenomena such as anharmonic vibrations, centrifugal stretching and interactions among other internal modes may also have an effect on the thermodynamic properties, but they should be small for the experimental temperature range. We did not find it to be necessary to make separate empirical correction for these various types of phenomena as was done in a recent correlation [66].

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