The Molecular Structure and Thermodynamics of Propane The Vibration Frequencies, Barrier to Internal Rotation, Entropy, and Heat Capacity

Kenneth S. Pitzer

The Molecular Structure and Thermodynamics of Propane

The Vibration Frequencies, Barrier to Internal Rotation, Entropy, and Heat Capacity

KENNETH S. PITZER[1]

Department of Chemistry, University of California, Berkeley, California

(Received April 17, 1944)

A substantially complete picture is proposed for the vibrational and torsional motions of the propane molecule. The vibrational assignment of Wu and Barker is extended and slightly revised so that definite values are assigned to all normal modes. It is believed that, with possibly one exception, all are correct within 2 percent. Comparison with the experimental entropy and heat capacity shows excellent agreement. The free energy, heat content, and heat capacity functions are then calculated over the range 180 to 1500°K. By obtaining the fundamental frequency of one torsional mode from a combination band in the infra-red spectrum, it was possible to evaluate the other from the entropy. The force constants calculable therefrom indicate that the apparent increase of potential barrier from ethane to propane arises from interaction of methyl group hydrogen atoms. For that mode in propane where these distances remain larger the torsional force constant is the same as that for ethane.

A LTHOUGH the existence of an appreciable barrier resisting rotation in propane is well known, it has not been possible previously to obtain various details of the forces within that molecule. In the present paper is presented a reasonably complete, but by no means absolutely proven, picture. It involves first a complete assignment of ordinary vibrational modes, second a calculation of the usual thermodynamic quantities based on a simplified rotational potential scheme, and finally a more detailed internal rotational analysis making use of both the infra-red spectrum and the entropy data.

VIBRATION FREQUENCIES

A number of partial or statistical assignments of vibration frequencies of propane[2–4] have been made, but in all cases some frequencies have been either missing or mere guesses. The most detailed assignment was that of Wu and Barker[4] based on their excellent infra-red absorption spectrum. By extending the Wu and Barker data with dynamical considerations and taking account of the work of Edgell and Glockler[5] and of Wagner[6] on the CH_2X_2 series of molecules, an assignment has been worked out which gives a definite value (within 2 percent) to all frequencies, accounts for the spectra, and agrees with the thermodynamic data for propane. This assignment is presented in Table I. It will be discussed according to types of motion below. Data for ethane,[7] methylene fluoride,[5,8] and methylene chloride[5,6] are given for comparison. While the CH_3 group is lighter than a fluorine atom, the greater distances, particularly to the hydrogen atoms, give it a greater effective moment of inertia for all vibrations of interest.

The data for these related molecules indicate that the carbon-hydrogen stretching modes are so close together in frequency that complete segregation is out of the question. The values given are certainly close to the correct ones for the same reason and a few are definitely identified from the spectra. Likewise the unsymmetrical bending or deformation motions within the methyl group all lie so close to 1460 cm^{-1} that separate identification is impossible. As in ethane, the two modes arising from symmetrical bending of the methyl group are close to 1375 cm^{-1}. The selection of 375 cm^{-1} for the skeletal bending

[1] Now on leave. Temporary address, Maryland Research Laboratories, Box 2706, Washington 13, D. C.

[2] G. B. Kistiakowsky and O. K. Rice, J. Chem. Phys. **8**, 610 (1940) (includes references to earlier work).

[3] K. S. Pitzer, Chem. Rev. **27**, 39 (1940).

[4] V. L. Wu and E. F. Barker, J. Chem. Phys. **9**, 487 (1941). G. B. Kistiakowsky and A. G. Nickel, *ibid.* **10**, 78 (1942) have offered apparently arbitrary values for those frequencies not included by Wu and Barker.

[5] G. Glockler and W. F. Edgell, private communica-
tions; see also G. Glockler, Rev. Mod. Phys. **15**, 111 (1943); W. F. Edgell, Thesis for Degree of Master of Science, State University of Iowa (1941).

[6] J. Wagner, Zeits. f. physik. Chemie **B45**, 69 (1939).

[7] F. Stitt, J. Chem. Phys. **7**, 297 (1939).

[8] G. Glockler and G. R. Leader, J. Chem. Phys. **7**, 382 (1939).

TABLE I. Vibration frequencies in cm^{-1}.

Molecule sym.	Sym. class	Allowed activity	C—C—C bending	C—C str.	CH₃, CH₂ wagging	CH₃ sym. bend.	CH₃ unsym. bending	CH₂ twisting	CH₂ sym. bending	CH₃ sym. str.	CH₃ unsym. str.	CH₂ str.
C_2H_6 (D_{3d})	A_{1g}	R—		993		1375				2925		
	A_{2u}	—IR				1380				2925		
	E_u	—IR			827		1465				2980	
	E_g	R—			1170		1460				2960	
C_3H_8 (C_{2v})	A_1	R, IR	375	868	1155	1370	1468		1460	2914	2966	2960
	A_2	R—			940		1450	1278			(2970)	
	B_1	R, IR		1053	922, 1338	1375	1470			2942	2968	
	B_2	R, IR			748, 1179		1450				2968	2980
CH_2F_2 (C_{2v})	A_1	R, IR							1508			2963
	A_2	R—						1294				
	B_1	R, IR			1487							
	B_2	R, IR			1262							3030
CH_2Cl_2 (C_{2v})	A_1	R, IR							1425			2985
	A_2	R—						1149				
	B_1	R, IR			1266							
	B_2	R, IR			896							3046

mode and 868 cm^{-1} and 1053 cm^{-1} for the skeletal stretching modes has been made by various authors already.

Of the remaining modes the symmetrical bending and the twisting of the CH_2 group are expected to be distinct enough in propane to be identified from the spectra of the CH_2X_2 series of molecules. From the pertinent values for CH_2F_2 and CH_2Cl_2 listed in Table I, the selection of the 1278 cm^{-1} Raman line is quite definite, particularly since it should be and is absent from the infra-red spectrum. The sym. bending motion is merely limited to the 1450 to 1500 cm^{-1} region already crowded with four methyl group motions. Probably the best indication of the value for this vibration is found in the spectra of cyclohexane and cyclopentane, neither of which contain any methyl groups. They show one or more lines in the 1440 to 1480 cm^{-1} range in both the infra-red and Raman spectra. The value 1460 may be adopted as probably correct within 2 percent.

Besides internal rotational modes which will be discussed later, there remain only the wagging motions of both CH_2 and CH_3 groups. The latter might be expected to have lower frequencies but serious interactions cannot be ruled out when the two wagging frequencies in ethane differ so greatly. The selections by Wu and Barker[4] of 922 cm^{-1} for class B_1, and 748 and 1179 for B_2 seem reasonably certain on the basis of band contours. The contour of the infra-red band near 1150 cm^{-1} is very much like that of the 867 cm^{-1} class A_1 band provided one takes the center at 1158 cm^{-1}. Therefore, with a Raman line reported at 1155 cm^{-1} assigned to class A_1, it seems best to classify that infra-red band as A_1 rather than B_1 as shown by Wu and Barker. Furthermore, the CH_2X_2 data suggest the range 1300 to 1400 cm^{-1} for the remaining mode of B_1 symmetry which is well above the 1150 cm^{-1} value and is far enough above the 922 cm^{-1} mode to make serious interaction unlikely. The 1338 cm^{-1} band has a sharper and more prominent Q branch than the 922 cm^{-1} B_1 class band which presumably led to the B_2 assignment by Wu and Barker. However, the 1338 cm^{-1} band has more prominent P and R branches than the class B_2 bands. This together with its similarity of P, Q, R spacing with the remaining B_1 bands and its location in the expected range lead to the assignment shown in Table I.

The final wagging motion is that of A_2 symmetry which is forbidden in the infra-red but is Raman active. In this motion one methyl wags up from the plane of the three carbons while the other goes down. In the 748 cm^{-1} class B_2 mode both methyls go up and down together. These modes are analogous to the 1170 and 827 cm^{-1} modes of ethane, respectively. The increased mass and moment of inertia of the propane skeleton and interaction with the higher CH_2

frequencies would be expected to decrease both of these frequencies and to decrease the higher one by a larger amount. The only unassigned Raman line in this region is that reported by Daure[9] at 940 cm^{-1} but not found by either Bhagavantam[10] or Kohlrausch and Köppl.[11] This value is adopted, but without any sense of certainty. The true value must be not far different in any case.

Before discussing the internal rotational motions the thermodynamic data on propane will be considered. This will be shown to support strongly the vibrational assignment of Table I.

It is interesting to note that where the CH$_3$ wagging frequencies are greatly reduced from ethane to propane, i.e., classes A_2 and B_2, the CH$_2$ frequencies are up near the CH$_2$F$_2$ values while otherwise the CH$_2$ frequencies are about midway between the CH$_2$F$_2$ and CH$_2$Cl$_2$ values. While this is no proof, it strongly suggests considerable interaction in the A_2 and B_2 classes and indicates that the "undisturbed" CH$_3$ frequencies would be higher and the CH$_2$ frequencies lower than the actual values in propane.

It is not yet possible either to show how well characteristic CH$_2$ and CH$_3$ frequencies will agree statistically with the actual frequencies or to select reliable sets of characteristic frequencies. Nevertheless the need for such information for calculation on more complex molecules is such that even highly tentative values are of interest. For the CH$_3$ group one may take the ethane frequencies (slightly rounded): 827, 1170, 1375, 1460 (2), 2950 (3). Then in propane the following

TABLE II. The entropy of propane and the barrier to internal rotation. (Basis: hypothetical ideal gas at 1 atmos. pressure.)

	180.00°K	231.09°K	
Translation and rotation	54.57	56.56	cal./degree mole
Vibration	0.49	1.02	cal./degree mole
Total less internal rotation	55.06 ±0.05	57.58 ±0.05	cal./degree mole
Experimental	57.04 ±0.1	60.46 ±0.1	cal./degree mole
Internal rotation	1.98	2.88	cal./degree mole
Potential barrier to fit entropy (2 degrees of freedom)	3400 ±150	3390 ±150	cal./mole

sets of values are selected to be statistically equivalent to these and may be attributed to

the two CH$_3$ groups: (748, 922), (1155, 1179), (1370, 1375), (1450, 1450, 1468, 1470), (2914, 2942, 2966, 2968, 2970). It will be noted that the 1179 frequency is actually more a CH$_2$ motion while the 940 cm^{-1} CH$_3$ frequency is not in this list. This is another manifestation of the interaction between CH$_2$ and CH$_3$ motions. We then arbitrarily select the remaining frequencies for the CH$_2$ group: 940, 1278, 1338, 1460, 2950 (2).

It will be shown in a paper to be published elsewhere that these frequency sets for the CH$_2$ and CH$_3$ groups actually give good agreement with the heat capacity data for the normal paraffins from butane to heptane.

THERMODYNAMIC PROPERTIES

In Table II calculations of the entropy of propane are compared with experimental values. The experimental data are taken from the work of Kemp and Egan[12] but are corrected to the value 273.16°K, for the ice point. The experimental entropy at 180°K was calculated using the vapor pressure data (together with the Berthelot equation for gas imperfection) to obtain an entropy of vaporization at that temperature.

The uncertainties shown in line three of Table II take account of the possibility that the 940 cm^{-1} Raman line is spurious and would allow for any reasonable assignment. In fact, the principal uncertainty is in the interatomic distances and angles. The following values were used: C—C, 1.54A; C—H, 1.09A; C—C—C angle 111° 30'; other angles tetrahedral.[13] On this basis the over-all moments of inertia are 2.88$_5$, 9.91$_2$, and 11.20$_7$ each×10^{-39} g cm^2. The moment of inertia of a methyl group is 5.30 ×10^{-40} while the effective reduced moment is 4.51×10^{-40}. In these calculations R is taken as 1.98718 cal. per degree and hc/k as 1.43848 cm deg.

The barrier to internal rotation is calculated on the arbitrary assumption that each methyl group rotation is independent, i.e., no potential energy cross terms exist. This assumption will be discussed further below; however, it is not serious for the thermodynamic purposes of this

[9] P. Daure, Ann. de physique 12, 375 (1929).
[10] S. Bhagavantam, Ind. J. Phys. 6, 595 (1932).
[11] K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie B26, 209 (1934).

[12] J. D. Kemp and C. J. Egan, J. Am. Chem. Soc. 60, 1521 (1938).
[13] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 59, 1223 (1937).

TABLE III. The heat capacity of propane in cal. per degree mole.

Experimenter	T, °K	C_p^0 exp.	C_p^0 this research	Difference
Kistiakowsky,	148.2	11.69	11.56	−1.1%
Lacher and	157.8	12.04	11.88	−1.3
Ransom[a]	213.1	14.00	13.86	−1.0
(averaged	219.2	14.17	14.10	−0.5
values)	258.0	15.75	15.73	−0.1
Kistiakowsky and Rice[b]	272.38	16.19	16.38	+1.2
Kistiakowsky and Rice[b]	300.37	17.58	17.67	+0.5
Kistiakowsky and Rice[b]	334.05	19.25	19.30	+0.3
Kistiakowsky and Rice[b]	368.55	20.90	21.00	+0.5
Dailey and Felsing[c]	343.7	19.66	19.77	+0.5
Dailey and Felsing[c]	360.1	20.36	20.58	+1.1
Dailey and Felsing[c]	387.8	21.62	21.94	+1.4
Dailey and Felsing[c]	452.6	25.07	24.99	−0.3
Dailey and Felsing[c]	521.2	27.89	27.91	+0.1
Dailey and Felsing[c]	562.0	29.10	29.48	+1.3
Dailey and Felsing[c]	603.3	30.75	30.96	+0.7
Dailey and Felsing[c]	693.2	33.61	33.93	+1.0

[a] See reference 17.
[b] See reference 2.
[c] Dailey and Felsing, J. Am. Chem. Soc. 65, 42 (1943).

section. The formulas and tables of Gwinn and the writer were used.[14] The potential barrier thus obtained, 3400 cal. per mole, happens to be identical with that originally estimated by the writer[15] in 1937 and is substantially the same as the values obtained by various workers since.[2, 12, 16, 17]

Table III compares the calculated heat capacity with the more recent and accurate experimental data for propane.

While the differences in Table III may slightly exceed the experimental error at certain points, one must consider the agreement excellent for

TABLE IV. Thermodynamic functions for propane. (Basis: hypothetical ideal gas at 1 atmos. pressure.)

T, °K	$\dfrac{(H_0^\circ - F_T^\circ)}{T}$ cal./deg.	$H_T^\circ - H_0^\circ$ kcal.	C_p° cal./deg.
180.00	47.38	1.745₅	12.64
231.09	49.90	2.440	14.57
298.16	52.73	3.512	17.57
400	56.48	5.558	22.54
500	59.81	8.040	27.04
600	62.93	10.92₅	30.84
800	68.74	17.77	37.08
1000	74.10	25.67	41.83
1500	85.85	48.64	49.26

such a complex molecule. It shows that the vibrational assignment must be substantially

[14] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. 10, 428 (1942).
[15] K. S. Pitzer, J. Chem. Phys. 5, 473 (1937).
[16] K. S. Pitzer, Chem. Rev. 27, 39 (1940).
[17] G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, J. Chem. Phys. 8, 970 (1940).

correct. Either the doubtful frequency (here taken as 940 cm⁻¹) or the approximate treatment of internal rotation may be in error enough to account for the 0.1 cal. per degree differences appearing in Table III.

The thermodynamic functions, $(H_0^\circ - F_T^\circ)/T$, $H_T^\circ - H_0^\circ$, and C_p are given in Table IV for a series of temperatures. The entropy is easily calculated from the equation:

$$S = (H_0^\circ - F_T^\circ)/T + (H_T^\circ - H_0^\circ)/T.$$

The heat of formation[18] of propane gas at 298.16°K is $\Delta H^\circ = -24.822 \pm 0.142$ kcal. The standard free energy of formation[19] is therefore $\Delta F^\circ_{298.16} = -5.597$ kcal. and the heat of formation at the absolute zero is $\Delta H_0^\circ = -19.487$ kcal.

INTERNAL ROTATION

Although a value of the potential barrier to internal rotation was obtained on the basis of

TABLE V. Possible values of torsional vibrational level to explain 720 cm⁻¹ band.

Sym. class	Frequency	Difference—combination
A_2	202 cm⁻¹	$922 - 202 = 720$ cm⁻¹
A_2	333	$1053 - 333 = 720$
B_2	148	$868 - 148 = 720$
B_2	435	$1155 - 435 = 720$

certain assumptions in the preceding section, certain other information can be brought to bear on this problem. The data of Wu and Barker[4] show a moderately weak infra-red band at 720 cm⁻¹ whose band contour rather definitely indicates the B_2 symmetry class. Since there is no reasonable explanation of this band as a fundamental, overtone, or sum-combination, it is presumed to be a difference-combination band. Then its intensity is reasonable only if the lower frequency is very low, either an internal rotational (torsional vibration) level or the 375 cm⁻¹ state. The latter would call for a B_2 band at 1095 cm⁻¹ and is thus excluded. Table V lists the various remaining possibilities.

[18] E. J. Prosen and F. D. Rossini, to be published in J. Research Nat. Bur. Stand. (1944).
[19] These calculations involve the thermodynamic functions for graphite from Clayton and Giauque [J. Am. Chem. Soc. 54, 2610 (1932)] and for hydrogen from Giauque [ibid. 52, 4816 (1930)] revised to the present physical constants of Woolley, Brickwedde, and Scott (to be published).
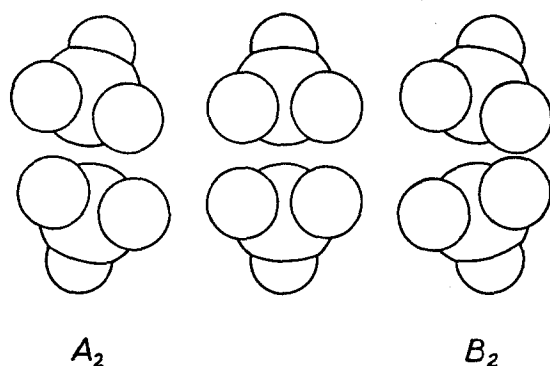
In order to select among the possibilities shown in Table V, the mean frequency (of the two modes) necessary to explain the entropy contribution* of 1.98 cal. per degree at 180°K is calculated to be 238 cm⁻¹. Since no very large separation of the two energy levels is expected, the first line in Table V seems most reasonable. The entropy contribution from the 202 cm⁻¹ mode is 1.24 cal. per degree at 180°K, leaving 0.74 for the class B_2 mode. This gives a frequency value of 283 cm⁻¹ for the B_2 torsional mode.

Having determined both frequencies one can calculate the potential function near the equilibrium position by the usual harmonic oscillator methods. The equations have been presented by Dr. W. D. Gwinn and the writer[14] in a form appropriate to the present problem. In the following analysis reference will be made to this paper as (P. and G.).

The potential energy for the torsional motions of very small amplitude is written, following Eq. (33) (P. and G.),

$$2V = b_{11}(\varphi_1^2 + \varphi_2^2) + 2b_{12}\varphi_1\varphi_2,$$

where φ_1 and φ_2 are the angles of motion of the respective methyl groups from their equilibrium positions. The inertial quantities needed are $A = 5.30 \times 10^{-40}$ the moment of inertia of a methyl group and

$$\Lambda_{11} = \Lambda_{22} = A^2 \sum_{i=1}^{3} \lambda_i^2 / I_i$$

---

* At this low a temperature the difference between a harmonic (torsional) osillator and the restricted rotator is small and will be neglected.

and

$$\Lambda_{12} = A^2 \sum_{i=1}^{3} \lambda_{1i}\lambda_{2i}/I_i,$$

in which the I_i's are over-all rotation moments of inertia and the λ_i's are direction cosines between the methyl axes and the principal axes of the molecule. In these terms $\Lambda_{11} = 0.75_5 \times 10^{-40}$ and $\Lambda_{12} = -0.57_6 \times 10^{-40}$ g cm².

The determinantal equation [(36), P. and G.] can be factored by symmetry into the following:

$$b_{11} + b_{12} - (A - \Lambda_{11} + \Lambda_{12})4\pi^2\nu^2 = 0$$
Class B_2, $\nu c = 283$ cm⁻¹,

$$b_{11} - b_{12} - (A - \Lambda_{11} - \Lambda_{12})4\pi^2\nu^2 = 0$$
Class A_2, $\nu c = 202$ cm⁻¹.

One then finds $b_{11} + b_{12} = 1.12 \times 10^{-12}$ erg per radian² and $b_{11} - b_{12} = 0.74 \times 10^{12}$ erg per radian² or $b_{11} = 0.93 \times 10^{-12}$ and $b_{12} = 0.19 \times 10^{-12}$.

The class A_2 motion would be expected to have the lower force constant since it starts to stagger the hydrogen atoms rather than pressing them close together. This is shown in Fig. 1. It is interesting to compare the torsional force constant from ethane, 0.71×10^{-12}, with the value of $b_{11} - b_{12} = 0.74 \times 10^{-12}$. The difference is hardly significant considering the approximation and many steps involved. Rather, the conclusion may be drawn that the potential function for the A_2 class torsional motion in propane is substantially the same as that for ethane. The increased force for the B_2 class motion may be attributed to interference between methyl group hydrogen atoms.

These results lead to the presumption (not an absolute deduction) that the apparent increase in potential through the series ethane, propane, iso-butane, and neo-pentane is due to interferences of the methyl group hydrogen atoms rather than increase of the potential barrier attributable to a given carbon-carbon bond on substitution of methyl groups at one end. This tentatively answers a question which was studied but not answered in a previous publication.[20] It will be interesting, when circumstances allow the time, to investigate a complete internal rotational potential function consistent with these force constants and other boundary conditions.

---

[20] K. S. Pitzer, J. Chem. Phys. 10, 605 (1942).