Samples were admitted by a calibrated micropipet, using the technique described by Taylor and Young.[8] Sample pressures were computed to be between 5 and 50 × 10^{-3} mm. at the capillary leak, which was located inside the ion source.

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(8) R. C. Taylor and W. S. Young, *Ind. Eng. Chem., Anal. Ed.*, **17**, 811 (1945).

Samples of the acids used had boiling points and refractive indices as shown in Table III. The formic acid was Eastman Kodak Co. white label material, not further purified. We are indebted to C. F. H. Allen and L. B. Genung, for arranging for the other purifications and syntheses.

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[CONTRIBUTION FROM THE NATIONAL RESEARCH COUNCIL (CANADA)]

The Infrared and Raman Spectra of *p*-Dioxane

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The infrared spectrum of liquid *p*-dioxane has been obtained from 2.5–37 μ and three new fundamentals were observed. Reinvestigation of the Raman spectrum gave one new fundamental. A tentative assignment of all vibrational modes has been made and the specific heat calculated at several temperatures.

In the course of investigating complex formation with *p*-dioxane by spectroscopic methods we obtained the infrared spectrum of *p*-dioxane in the liquid, solid and gas phase and the Raman spectrum of the liquid. The infrared spectrum of the liquid and gas had been obtained previously[2,3] from

TABLE I

ASSIGNMENT OF THE FUNDAMENTALS IN *p*-DIOXANE

		Description of vibration	This work	Burket[a] and Badger	Ramsay[b]
A_g	ν_1	CH stretching	2966		
	ν_2		2855		
	ν_3	Deformation	1443		
	ν_4	Twisting	1303	1305	
	ν_5	Wagging	1127		
	ν_6	Rocking	852		
	ν_7	Ring stretching	1015	1014	1111
	ν_8		834	835	835
	ν_9	Ring bending	433		485
	ν_{10}		422		(390)[c]
B_u	ν_{11}	CH stretching	2967		
	ν_{12}		2860		
	ν_{13}	Deformation	1446		
	ν_{14}	Twisting	1368		
	ν_{15}	Wagging	1251	1253	
	ν_{16}	Rocking	887		
	ν_{17}	Ring stretching	1120	1122	1020
	ν_{18}	Ring bending	610		740[d]
	ν_{19}		273		233[c]
A_u	ν_{20}	CH stretching	2921		
	ν_{21}		2899		
	ν_{22}	Deformation	1446		
	ν_{23}	Twisting	1318		
	ν_{24}	Wagging	1286	1285	
	ν_{25}	Rocking	1046		
	ν_{26}	Ring stretching	1081	1086	1136
	ν_{27}		874	874	879 or 889
	ν_{28}	Ring bending	283		
B_g	ν_{29}	CH stretching			
	ν_{30}				
	ν_{31}	Deformation	1461		
	ν_{32}	Twisting	1396		
	ν_{33}	Wagging	1216		
	ν_{34}	Rocking	946		
	ν_{35}	Ring stretching	1109	1109	1125
	ν_{36}	Ring bending	486		433

[a] Reference (3). [b] Reference (2). [c] Calculated in reference (2) from a normal coördinate treatment of the skeleton. [d] Observed as weak band and matched with the calculated value of 742 cm.$^{-1}$. The observed band is very strong, however, and is at 610 cm.$^{-1}$.

TABLE II

RAMAN SPECTRUM OF LIQUID *p*-DIOXANE

νcm.$^{-1}$[a]	Relative[a] intensity	Polarization[b]	This research νcm.$^{-1}$	Int.	Assignment[c]
178[d]	0				
241[e]	1				
			422	1	ν_{10} A_g
433[f]	2	p	433	2	ν_9 A_g
486	4	d	486	4	ν_{38} B_g
835	8	p	834	8	ν_8 A_g
850	1	d	852[h]	1	ν_6 A_g
946	1	d	946	1	ν_{34} B_g
1014	6	p	1015	6	ν_7 A_g
1109	3	d	1109	3	ν_{35} B_g
1125	3	p	1127	3	ν_5 A_g
1209[g]	1	d			
1222	5	d	1216	5	ν_{33} B_g
1305	8	p	1303	8	ν_4 A_g
1330	2	p	1334	2	$\nu_{25} + \nu_{28}$ A_g
			1396	1	ν_{32} B_g
1448	8	p	1443	8	ν_3 A_g
1455	2	d	1461	2	ν_{31} B_g
2662	0	p	2662	1	$\nu_3 + \nu_{33}$ A_g
2720	1	p	2720	1	$\nu_{22} + \nu_{24}$ A_g
2748	3	p	2748	2	$\nu_3 + \nu_4$ A_g
2854	8	p	2855	8	ν_2 A_g
2890	2	p	2889	2	$2\nu_3$ A_g
2966	10	p	2966	10	ν_1 A_g
3064	1	p			ν_{29} B_g ?

[a] Summary of results of eight authors given by K. W. F. Kohlrausch in "Ramanspektren." [b] Polarization measurements are by B. Saksena, *Proc. Ind. Acad. Sci.*, 12, 321 (1940). [c] This work. [d] Obtained only by J. Lecomte, *J. chim. phys.*, **33**, 626 (1936). [e] Obtained by Venkateswaran, *Proc. Ind. Acad. Sci.*, **2**, 279 (1935), and Saksena, reference (b). [f] Observed as double; A. Simon and F. Feher, *Ber.*, **69**, 214 (1936). [g] Our Raman spectrum contains a band at ∼ 1200 cm.$^{-1}$ corresponding to the band at 1209 cm.$^{-1}$ which we are certain is ν_1 excited by λ 4047. [h] This band is assigned as of species A_g although it is given as depolarized. However, it is not impossible that the depolarization of such a weak band has been estimated incorrectly.

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[1] National Research Council Post doctorate Fellow, 1951.

(2) D. A. Ramsay, *Proc. Roy. Soc.* (*London*), **A190**, 562 (1947).

(3) S. C. Burket and R. M. Badger, THIS JOURNAL, **72**, 4397 (1950).

700 to 3500 cm.$^{-1}$ and assignments made for the ring frequencies[2] and also for some of the hydrogen modes.[3] The Raman spectrum has been obtained by several investigators and the results summarized by Kohlrausch.[4]

We had decided to reinvestigate the infrared and Raman spectra of *p*-dioxane since: (1) the region from 265 – 700 cm.$^{-1}$ had not been covered in the infrared, (2) two low lying lines below 300 cm.$^{-1}$ were reported in the Raman spectrum by some authors and not by others (see Table II), (3) only one of the eight independent Raman spectra previously obtained reported the band 433 cm.$^{-1}$ to be double (see footnote *f* to Table II).

The infrared spectra were obtained on a Perkin-Elmer Spectrometer (Model 12c) with electronic recording and LiF, NaCl, KBr and KRS-5 prisms. The results are shown in Fig. 1 and Table III. In Fig. 2 the infrared spectrum of solid *p*-dioxane is shown only in the spectral regions where marked changes from that of the liquid were observed.

TABLE III

INFRARED SPECTRUM OF LIQUID *p*-DIOXANE

νcm.$^{-1}$	Intensity	Assignment	νcm.$^{-1}$	Intensity	Assignment
273	m	ν_{19} B$_u$	2193	w	$\nu_{35} + \nu_{26}$ B$_u$
283	m	ν_{28} A$_u$	2212	w	$\nu_{35} + \nu_{17}$ A$_u$
610	s	ν_{18} B$_u$	2225	w	$\nu_{34} + \nu_{24}$ B$_u$
708	w	$\nu_9 + \nu_{19}$ A$_u$	2260	w	$\nu_7 + \nu_{15}$ B$_u$
733	w	$\nu_7 - \nu_{28}$ A$_u$	2273	w	$\nu_8 + \nu_{22}$ A$_u$
750	w	$\nu_{36} + \nu_{19}$ A$_u$	2283	w	$\nu_7 + \nu_{24}$ A$_u$
874	s	ν_{27} A$_u$	2340	w	$\nu_4 + \nu_{25}$ A$_u$
887	s	ν_{16} B$_u$	2391	w	$\nu_{35} + \nu_{24}$ B$_u$
1046	m	ν_{25} A$_u$	2470	w	$\nu_{33} + \nu_{15}$ A$_u$
1081	s	ν_{26} A$_u$	2582	w	$\nu_4 + \nu_{24}$ A$_u$
1110	w	$\nu_8 + \nu_{28}$ A$_u$	2695	w	$\nu_3 + \nu_{15}$ B$_u$
1120	s	ν_{17} B$_u$	2760	w	$\nu_4 + \nu_{22}$ A$_u$
1251	s	ν_{15} B$_u$	2860	s	ν_{12} B$_u$
1286	s	ν_{24} A$_u$	2899	w	ν_{21} A$_u$
1318	w	ν_{23} A$_u$	2921	w	ν_{20} A$_u$
1368	m	ν_{14} B$_u$	2967	s	ν_{11} B$_u$
1400	w	$\nu_5 + \nu_{19}$ B$_u$	3133	w	$\nu_2 + \nu_{28}$ A$_u$
1446	s	ν_{13}, ν_{22}	3250	w	$\nu_1 + \nu_{28}$ A$_u$
1500	w	$\nu_{26} + \nu_{10}$ A$_u$	3299	w	$\nu_{10} + \nu_{12}$ B$_u$
1707	w	$\nu_8 + \nu_{27}$ A$_u$	3336	w	$\nu_{36} + \nu_{12}$ A$_u$
1729	w	$\nu_{19} + \nu_{31}$ A$_u$	3407	w	$\nu_9 + \nu_{11}$ B$_u$
1855	w	$\nu_{13} + \nu_{10}$ B$_u$	3479	w	$\nu_2 + \nu_{18}$ B$_u$
1901	w	$\nu_7 + \nu_{16}$ B$_u$	3534	w	$\nu_1 + \nu_{18}$ B$_u$
1917	w	$\nu_4 + \nu_{18}$ B$_u$	3610	w	
1956	w	$\nu_8 + \nu_{17}$ B$_u$	3910	w	
1990	w	$\nu_{35} + \nu_{16}$ A$_u$	4143	w	$\nu_4 + \nu_{12}$ B$_u$
2072	w	$\nu_3 + \nu_{15}$ B$_u$	4340	w	$\nu_3 + \nu_{12}$ B$_u$
2089	w	$\nu_7 + \nu_{26}$ A$_u$	4410	w	$\nu_3 + \nu_{11}$ B$_u$
2131	w	$\nu_8 + \nu_{24}$ A$_u$	4470	w	
2177	w	$\nu_4 + \nu_{27}$ A$_u$	4850	w	

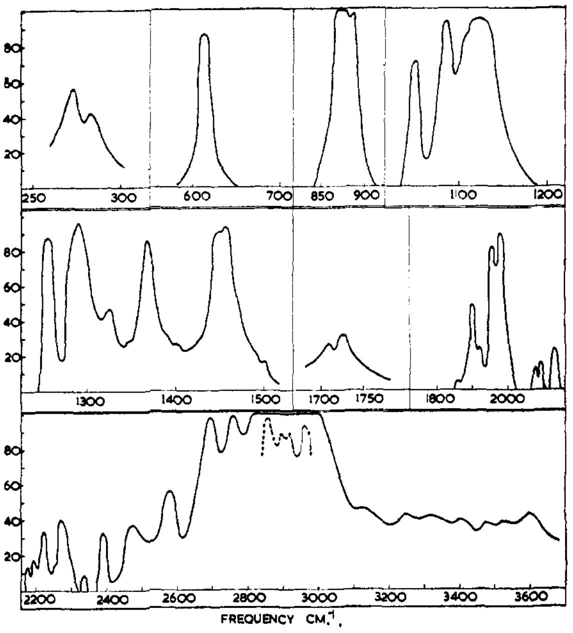

Fig. 1.—The infrared spectrum of liquid *p*-dioxane: —, 0.10 mm. cell; ----, pressed plates; the bands at ~280 cm.$^{-1}$ were obtained in a 1.5-mm. cell.

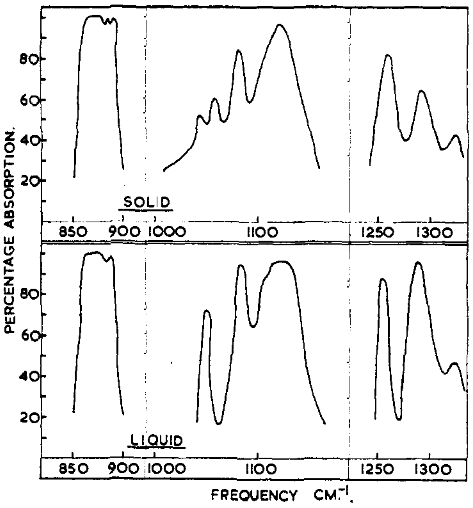

Fig. 2.

The Raman spectrum was obtained with a two-prism glass spectrograph (camera f/7.7, linear dispersion 11 Å./mm. at λ 4358) on an Eastman Kodak 103a-J plate after 9 and 30 hours exposure. Three thicknesses of Wratten 2B gelatin filter and a solution of praseodymium nitrate were used to reduce λ4047 excitation and mercury continuum near the exciting line. Two Lane-Wells type Hg arcs run at 25 amperes were used as sources. The results are shown in Table II along with the summary of the previous work done.

In the Raman spectrum we have not found anything below 300 cm.$^{-1}$ even on long exposures whereas the two lines at 422 and 433 cm.$^{-1}$ were very readily resolved. There can be no doubt that the three low lying fundamentals which are to be expected in the Raman spectrum are at 422, 433 and 486 cm.$^{-1}$.

In the infrared spectrum a very strong band has been observed at 610 cm.$^{-1}$ and two others at 273 and 283 cm.$^{-1}$. Thus the complete spectrum due to the skeletal vibrations has been observed.

The assignment for *p*-dioxane is made on the basis of the point group C_{2h} since it seems well established that in *p*-dioxane those molecules with the

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[4] K. W. F. Kohlrausch "Ramanspektren," Edwards Bros., Ann Arbor, Michigan, 1945, p. 342.

boat configuration (C_{2v}) are present in an almost negligible amount.[5a,5b] The thirty-six modes of vibration are divided among the four symmetry types in the following manner: 10 A_g (Raman active, Infrared inactive), 9 B_u (Raman inactive, Infrared active), 9 A_u (Raman inactive, Infrared active), and 8 B_g (Raman active, infrared inactive).[6]

A_g Vibrations.—From the intensity in the Raman spectrum and state of depolarization it seems probable that the skeletal modes ν_{10}, ν_9, ν_8 and ν_7 are 422, 433, 834 and 1015 cm.$^{-1}$, respectively. By comparison with the assignment of the modes in cyclohexane[7] one may expect to find the hydrogen bending frequencies separated roughly into the following spectral regions: (a) deformation vibrations giving rise to bands around 1450 cm.$^{-1}$; (b) twisting vibrations giving rise to bands around 1300–1390 cm.$^{-1}$; (c) wagging vibrations giving rise to bands around 1150–1270 cm.$^{-1}$; and (d) rocking vibrations giving rise to bands around 800–1050 cm.$^{-1}$.

Accordingly, it seems probable that the strong polarized lines at 1443, 1303 and 1127 cm.$^{-1}$ are the hydrogen deformation, twisting and wagging modes, respectively. The two strong polarized lines at 2966 and 2855 are presumably the CH stretching vibrations ν_1 and ν_2.

The assignment of the rocking vibration ν_6 is made in conjunction with the identification of the B_g type rocking vibration and thought to be 852 cm.$^{-1}$. The magnitude of this frequency is about right but the band is given as depolarized (see Table II). It is not improbable, however, that the depolarization of such a weak band has been estimated incorrectly.

B_g Vibrations.—No depolarized bands have been reported in the CH stretching region of the Raman spectrum. The four strong depolarized Raman lines at 1461, 1216, 1109 and 486 are presumably the hydrogen deformation and wagging vibrations, and the stretching and bending of the ring, respectively. The line at 1396 cm.$^{-1}$ might very well be the twisting vibration whereas the line at 946 cm.$^{-1}$ is probably due to the rocking vibration.

It is possible that ν_{34} and ν_6 may be interchanged; however, antisymmetrical frequencies are usually higher than totally symmetrical ones. In order to keep the Raman active rocking frequencies ν_6 and ν_{34} in the same spectral region, the fairly weak polarized line at 1334 cm.$^{-1}$ in the Raman spectrum is interpreted as a combination tone of the lines at 1046 and 283 cm.$^{-1}$.

A_u and B_u Vibrations.—The intensities of the infrared bands make a reasonable selection of fundamentals possible since all weak bands can be explained by at least one binary combination (see Table III). There are no compelling reasons why most of these bands belonging to corresponding vibrations cannot be interchanged. The assignment as given (see Table I) is consistent with the data but must be regarded as tentative. It is believed however that all fundamentals of thermodynamic significance have been observed.

The specific heat (C_p^0) of the gas at 300, 350 and 400°K. has been calculated by the well known methods of statistical thermodynamics[8] and found to be 22.56, 26.58 and 30.48 cal./deg./mole, respectively.

Acknowledgment.—The authors are indebted to A. D. E. Pullin for obtaining the Raman spectrum.

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(5) (a) See reference (1) for a summary of the supporting dipole moment and electron diffraction results. (b) Recently (J. H. Gibbs, *Trans. Faraday Soc. Disc.* #**10**, 1951, p. 122) it has been suggested that a small amount of the antisymmetrical *cis* form of point group C_2 may be present.

(6) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 134.

(7) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2188 (1947).

(8) See reference (6) p. 501 *et seq.*