

Vibrational Spectra of 2,2-Dimethylpropanal

By Gene A. Crowder, Department of Chemistry and Killgore Research Center, West Texas State University, Canyon, Texas 79015

I.r. and Raman spectra were obtained for 2,2-dimethylpropanal, and a vibrational assignment has been suggested.

VIBRATIONAL spectra have been reported for several compounds that contain the tertiary butyl group bonded to a carbon atom. Included in this list are *t*-butyl cyanide,¹ 2,2-dimethylbutane,^{2,3} 3,3-dimethylbut-1-ene,³ and 3,3-dimethylbut-1-yne.³ Vibrational assignments have been discussed for all these compounds. The Raman spectrum was also reported for pivalaldehyde (2,2-dimethylpropanal)⁴ almost forty years ago, but there has apparently been no i.r. work reported, nor has a vibrational assignment been attempted. Such a study is of interest because of the similarity in structure between this compound, $\text{Me}_3\text{CCH}=\text{O}$, and that of 3,3-dimethylbut-1-ene, $\text{Me}_3\text{CCH}=\text{CH}_2$. Therefore, i.r. spec-

tra have been obtained and the Raman spectrum has been redetermined, resulting in the observation of several bands not reported in the previous work.

EXPERIMENTAL

I.r. spectra were obtained with a Beckman IR-12 spectrophotometer which was calibrated against atmospheric water vapour and carbon dioxide bands. The wavenumbers were read from the instrument at the band peaks and should be accurate to $\pm 1 \text{ cm}^{-1}$ for the sharp bands. Raman spectra were obtained with a Jarrell-Ash 25-100 dual monochromator photon-counting spectrometer equipped with an Argon laser by Dr. P. Devlin. The wavenumbers of the Raman bands were read from the spectra and are not expected to

¹ G. A. Crowder, *J. Phys. Chem.*, 1971, **75**, 2806.

² R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, 1965, **21**, 169.

³ N. Sheppard, *J. Chem. Phys.*, 1949, **17**, 455.

⁴ K. W. F. Kohlrausch and F. Koppel, *Z. Phys. Chem.*, 1934, **834**, 370.

be as accurate as the i.r. wavenumbers. The sample of pivalaldehyde was from Chemical Samples Co., and was stated to be 99% pure. No appreciable amounts of impurity were detected by g.l.c.

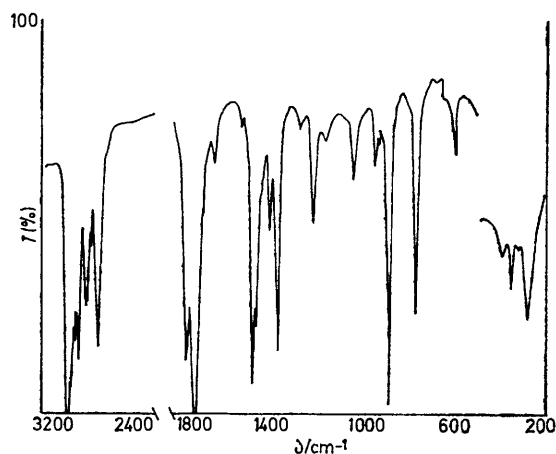


FIGURE 1 I.r. spectrum for liquid pivalaldehyde. Pathlength, 0.015 mm above 500 cm^{-1} , 0.1 mm below 500 cm^{-1} . Background transmittance below 500 cm^{-1} is 50–60%.

RESULTS AND DISCUSSION

I.r. spectra for pivalaldehyde liquid and vapour are shown in Figures 1 and 2, and the liquid-state Raman spectrum is shown in Figure 3. The observed wavenumbers are listed in the Table, along with the band assignments. These conventional descriptions are only approximate because most of the normal modes are mixtures of group vibrations.

In its most symmetrical configuration, a molecule of pivalaldehyde belongs to the C_{3v} point group and will have Raman polarized (a') and depolarized (a'') bands. However, nearly all the a'' bands are coincident with a'

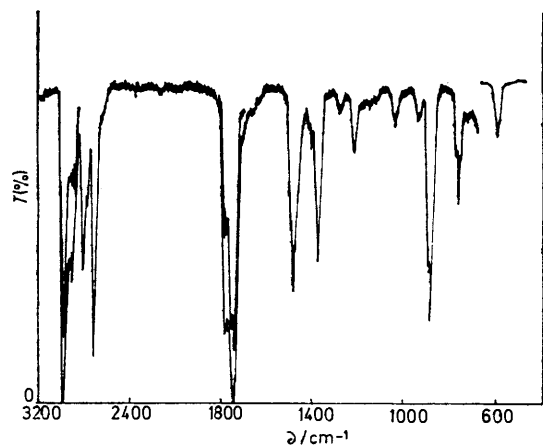


FIGURE 2 I.r. spectrum for pivalaldehyde vapour

bands, and therefore nearly all bands are polarized to some extent.

Vibrational Assignment.—*Carbon-hydrogen stretching vibrations.* Several bands were observed in the C-H

⁵ G. Sbrana and V. Schettino, *J. Mol. Spectroscopy*, 1970, **33**, 100.

stretching region. The three methyl groups will have $5a' + 4a''$ vibrations, but only one Raman band in this region, at 2978 cm^{-1} , is depolarized. This band must be assigned to the three a'' antisymmetric stretches and the Raman band at 2932 cm^{-1} is assigned to all three a' antisymmetric stretches. The three methyl symmetric stretches are distributed as $2a' + a''$, and there is no depolarized Raman band that can be assigned to the a'' mode.

The C-H stretch of the aldehyde group apparently is in Fermi resonance with the overtone of the in-plane C-H bend, which is common for aldehydes,⁵ but the two frequencies for pivalaldehyde are a little lower than normal.

Carbonyl stretching vibration. There is a very strong band and a weaker band (although still intense) in the region 1700–1800 cm^{-1} . The 1770 cm^{-1} i.r. band seems to be too strong to be due to an overtone or combination mode, and therefore probably arises from Fermi resonance of the overtone of the 885 cm^{-1} band with the carbonyl stretch. The low-frequency band is much the

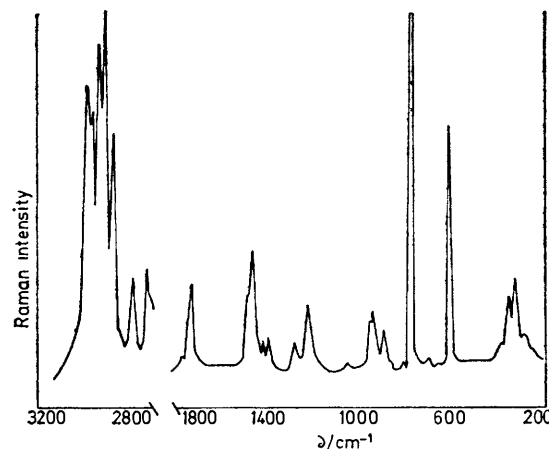


FIGURE 3 Raman spectrum for liquid pivalaldehyde

stronger of the two and therefore has the most $\nu(\text{C}=\text{O})$ character. A similar observation was made for propionaldehyde and butyraldehyde,⁵ although for those two compounds, the doublet is 1690, 1720 cm^{-1} , with the high-frequency band being the more intense and therefore possessing more carbonyl character. The observation of the Fermi doublet in pivalaldehyde at 1730, 1770 cm^{-1} is therefore similar to that observed for the other aldehydes.

Carbon-hydrogen bending vibrations. The CH_3 deformations are easily assigned as given in the Table. The C-H in-plane bend of the aldehyde group is assigned to the 1380 cm^{-1} Raman band, which appears only as a shoulder of the 1367 cm^{-1} i.r. band. This assignment fits the Fermi resonance doublet involving the overtone of the C-H bend better than would assignment of the C-H bend to 1367 cm^{-1} .

The C-H out-of-plane wag of the aldehyde group is generally quite weak,⁶ and can be assigned to the very

⁶ N. B. Colthup, L. H. Daly, and S. E. Wiberly, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964.

I.r. and Raman spectral data ^a for pivalaldehyde (cm⁻¹)

I.r. vapour	I.r. liquid	Raman liquid	Assignment
~3470vw	3442vw		2 × ν(C=O)
2969 } vs	2972vs	2978s (d)	ν(CH ₃), asym a'' (3)
2980 } vs		2960w	2 × δ(CH ₃)
	2939	2932s (p)	ν(CH ₃), asym a' (3)
2919m	2912m	2910vs (p)	ν(CH ₃), sym a'
2883ms	2874s	2872s (p)	ν(CH ₃), sym a'
	2813m	~2820sh,vw	
2803 } ms	2794m	2795m (0.15)	Fermi doublet a'
2791 } ms			
~2779 } ms	2767w	2720m (0.2)	2 × 1380 + ν(C-H)
2768w	2702s	1770w (0.15)	Fermi doublet
2696s	1770s		
1774s	1730vs	1726m (0.15)	2 × 885 + ν(C=O) a'
1752 } vs			
1742 } vs			
~1735 } vs			
	1693		
1656vw	1648w		885 + 765
1493 } s	1479s		δ(CH ₃), asym a', a''
1484 } s			
1476 } s	1466m	~1466sh	δ(CH ₃), asym a', a''
		1451m (0.3)	δ(CH ₃), asym a', a''
1457sh	1405m	1404w (0.15)	δ(CH ₃), sym a'
1417 } w	~1380	1380w (0.15)	δ(C-H), in-plane a'
1406 } w	1367s		δ(CH ₃), sym a', a''
	~1275w	1275w (0.3)	ν(C-C) a'
1371s	1213m	1214m (0.3)	ν(CC ₃), asym a', a''
~1277w	~1165w		
1217m			
1180vs			
~1150vw			
1122vw	1093vvw		
1047 } mw	1041m	1042w (0.5)	ρ(CH ₃) a', a''
1041 } mw			
1035 } mw	943mw	942mw (0.5)	ρ(CH ₃) a'
	930w	927mw (0.5)	ρ(CH ₃) a', a''
942mw	885s	884mw (0.5)	ρ(CH ₃) a'
930w			
892 } s	~800vvw	798vvw	γ(C-H) a''
884 } s			
~878sh } s			
	773 } m	763vs (p)	ν(CC ₃), sym a'
773 } m	765ms		
764 } m			
757 } m			
726w			
		689vw (p)	2 × 350
		647vvw	2 × 321
593m	595m	591s (0.1)	δ(CCO) a'
	393vvw	389w (0.65)	} Skeletal bends
	355vw	350mw (0.5)	
	~325vvw	321m (0.65)	
	279w	282w (0.65)	
		~243sh,vvw (d)	

^a s = Strong, m = medium, w = weak, v = very, sh = shoulder. Depolarization ratios, ±0.05, are given in parentheses for the Raman bands, or are labelled as d for depolarized, or p for ρ < 0.1.

weak 800 cm⁻¹ band. The corresponding wavenumber in propionaldehyde is 805 cm⁻¹.⁵

Carbon-carbon stretching vibrations. By comparison with other t-butyl compounds, the C-C stretch involving the aldehydic carbon atom can be assigned to the band at 1277 cm⁻¹. The value for Me₃CCH=CH₂ is 1271 cm⁻¹.³ The CBut group will have two antisymmetric (a' + a'') and one symmetric (a') CC₃ stretches. The antisymmetric CC₃ stretch in Me₃CCN is doubly degenerate and was assigned to a depolarized Raman band at 1209 cm⁻¹. For pivalaldehyde, the i.r. band at 1220 cm⁻¹ can be assigned to both antisymmetric stretches. The Raman band is partially polarized, indicating an overlapping of the a' and a'' bands.

The symmetric CC₃ stretch can undoubtedly be assigned to the intense Raman band at 763 cm⁻¹. This value is higher than has been observed previously for this vibration in other compounds, probably because of mixing with δ(C-C=O).

Methyl rocking vibrations. The four bands observed at 885, 930, 943, and 1041 cm⁻¹ in the i.r. spectrum can confidently be assigned to methyl rocking modes. However, there are six such vibrations, distributed as 3a' + 3a''. The 885 cm⁻¹ band can be assigned solely to an a' rock and the 1041 cm⁻¹ band is assigned to an a', a'' pair by comparison with t-butyl cyanide, whose corresponding values are 880 (a₁) and 1033 cm⁻¹ (e). One of the 930, 943 cm⁻¹ pair must represent both an a' and a'' rock,

corresponding to the other type *e* rock in Me₃CCN at 939 cm⁻¹. This pair is assigned to the 930 cm⁻¹ band by analogy with Me₃CCH=CH₂. Although these bands are discussed here as being due to methyl rocking modes, there is normally mixing between methyl rocking and C-C stretching co-ordinates.^{2,7}

Skeletal bending vibrations. The skeletal bending modes consist of the CCO bend (*a'*), which can be assigned to the intense highly polarized Raman band at 591 cm⁻¹, two CC₃ rocks (*a' + a''*), and the three CC₃ deformations (*2a' + a''*). These last five modes must be assigned to the last five bands listed in the Table, but the order is uncertain. For t-butyl cyanide, the type *e* CC₃ rock was assigned as 578 cm⁻¹ and the CC₃ deformations were assigned as 375 (*a₁*) and 360 cm⁻¹ (*e*). How-

⁷ J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 1963, **19**, 117.

ever, for t-butyl fluoride,⁸ the C-F rock (*e*) was assigned as 335 cm⁻¹ and the CC₃ deformations as 461 (*e*) and 409 (*a₁*). The main difference lies in the rocking frequencies, and both assignments were supported by normal co-ordinate calculations.

There is a very weak depolarized Raman band, observed as a shoulder at *ca.* 245 cm⁻¹, that may be a methyl torsion, or two overlapping torsions, as predicted by Ronn and Woods⁹ from their microwave studies.

This work was supported by The Robert A. Welch Foundation, Houston, Texas. I am grateful to Dr. P. Devlin for obtaining the Raman spectra.

[2/2839 Received, 18th December, 1972]

⁸ W. Huttner and W. Zeil, *Spectrochim. Acta*, 1966, **22**, 1007.

⁹ A. M. Ronn and R. C. Woods, *tert.*, *J. Chem. Phys.*, 1966, **45**, 3831.