

A note on the vibrational assignments of 1,3,5-triethyl- and 1,3,5-trihydroxy benzene

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In this note are presented assignments of the vibrational frequencies of 1,3,5-triethyl, and 1,3,5-trihydroxy benzene. The Raman and infrared spectra of the first compound and the infrared spectrum of the second compound were recorded. The Raman data of Kohlrausch & Pongratz (1934) for the trihydroxy benzene were utilized and normal coordinate calculations of out-of-plane vibrations reported by Nonnenmacher & Mecke (1961) were considered.

Chemically pure samples of 1,3,5-triethyl benzene and 1,3,5-trihydroxy benzene from original packings of Schuchardt (Munich) and Fluka (Switzerland) respectively were used without further purification. Experimental arrangements were as described previously (Mallik 1974). The infrared spectrum of 1,3,5-trihydroxy benzene was studied in nujol mull and care was taken to ascertain absorption bands due to nujol.

Treating the substituent groups as point mass X , the symmetric 1,3,5- $C_6H_3X_3$ molecules may be assumed to have D_{3h} symmetry and the thirty phenyl ring vibrations in each molecule may be divided into

$$4a_1'(R, p) + 3a_2' + 7e'((1r : R, dp) | 3a_2''(1r) | 3e''(R, dp))$$

The assignments of the phenyl ring vibrations are given in table 1 and those of the vibrations of the substituent groups are given in table 2.

1,3,5-Triethyl benzene

The totally symmetric a_1' vibrations are readily identified from the intensity and polarization character of the Raman lines. No attempt has been made to propose definite assignments for a_2' vibrations which are inactive in both Raman and infrared.

Two weak Raman lines at 637 and 440 cm^{-1} are observed in this work. These two could not be definitely assigned. But it may be mentioned that Bogomolov (1962) assigned a frequency 617 cm^{-1} to a $\gamma(C_2H_6)$ mode in the case of *m*-diethylbenzene. Further a frequency in the region 430-500 cm^{-1} observed in the spectra of a few 1,3,5- $C_6H_3X_3$ molecules has been assigned to a_2' mode ν_9 by Green *et al* (1971).

Table 1 Fundamental frequencies of 1, 3, 5-C₅H₃X₃ (in cm⁻¹)

X = Symmetry	C ₂ H ₅		OH	
	R	IR*	R ^a	IR**
α_1'	ν_1 3003 (1)
$R(p), -$	ν_2 1263 (2)p	.	1306 ($\frac{1}{2}$)	.
	ν_3 1001 (10p)	.	994 (4)	..
	ν_4 544 (3)p	.	598 (2b)	...
α_2' ---, -;	ν_5
	ν_6
	ν_7
e'	ν_8 3040 (1)
	$R(dp), I R: \nu_9$ 1602 (4)dp	1604 (vs)	1601 (1)	1611 (s)
	ν_{10} 1457 (1)	1465 (vs)	.	1493 (s)
	ν_{11} 1168 (5)	1167 (w)	.	1198 (m)
	ν_{12} 960 (3)	.	.	1006 (s)
	ν_{13} 517 (4b)	.	.	535 (m)
	ν_{14} 270 (1)	..	291 (0)	..
	ν_{15} ..	866 (vs)	..	810 (s)
-, IR.	ν_{16} 712 (1)	707 (vs)	.	660 (m)
	ν_{17}	(187 $\frac{1}{2}$)
e''	ν_{18} 889 (2b)dp	889 (w)	...	885 (vw)
	$R(dp), -$, ν_{19} 577 (1)	..	566 (0)	...
	169 (9b)dp	..	249 (2)	...

^aKohlrausch & Pongratz (1934)^bCalculated (Nonnenmacher & Moock 1961)

*liquid.

**in nujol mull

The frequencies of vibrations associated with the stretching and the bending modes of CH₃ and CH₂ groups are generally accepted. Following Versanyi (1969), the frequency 371 cm⁻¹ is assigned to C-C-C bending vibration. The very weak infrared band at 783 cm⁻¹ is proposed to have arisen from CH₂ rocking vibration (Green 1962).

Table 2. Internal vibrations of the substituent groups of 1, 3, 5- $C_6H_3X_3$ molecules

(Frequencies cm^{-1})

X =	C_2H_5		OH	
	R	IR	R	IR
ν_{as} (CH_3)	2966 (3)	--	--	--
ν_s (CH_3)	2940 (3P)	--	--	--
ν_{as} (CH_2)	2894 (2b)	--	--	--
ν_s (CH_2)	2850 (2bP)	--	--	--
δ_{as} (CH_3)	1436 (6dp)	--	--	--
δ_s (CH_3)	1385 (1)	1380 (s)	--	--
CH_2 wag	1336 (3P)	1325 (s)	--	--
CH_2 twist	1245 (2)	--	--	--
CH_3 rock	1064 (1bP)	1060 (s)	--	--
	--	1072 (s)	--	--
CH_2 rock	790 (1)	783 (w)	--	--
$\delta(CCC)$	317 (1b)			
$\delta(OH)$	--	--	--	1291 (s) 1150 (s) } --

1, 3, 5-Trihydroxy benzene

The strong infrared band at 1006 cm^{-1} has been assigned at $\nu_{12}(e')$. On the basis of calculations of frequencies, Nonnenmacher & Mecke (1961) assigned the frequencies 566 and 249 cm^{-1} to e'' modes ν_{19} and ν_{20} respectively. These assignments are retained. In regard to the assignment of the 566 cm^{-1} Raman line it may be noted that the e'' mode ν_{19} has been reported to have frequency 577, 955, 530, 509 cm^{-1} in the case of symmetrictriethyl-, trifluoro-, trichloro- and tribromobenzene respectively. In accord with the results of Nonnenmacher and Mecke, the infrared bands at 810 and 660 cm^{-1} are identified as ν_{15} and ν_{16} respectively. In view of the analysis of the vibrational frequencies of 1, 3, 5-trimethyl benzene reported by Pitzer & Scott (1943) these two bands 10 cm^{-1} and 660 cm^{-1} may be considered to have originated from modes derived from b_{2g} mode 5 and b_{2g} mode 4 of benzene respectively. The former is an X-sensitive $\gamma(CH)$ mode and the latter a $\phi(CC)$ mode. These bands of low frequency arising from such out-of-plane vibrations are not expected to exhibit any marked solvent effect and actually the frequencies observed in nujol mull are in good agreement with

those in KBr reported by Nonnenmacher & Mecke (1961). A very weak infrared band is observed at 895 cm^{-1} and this has been assigned to e'' mode ν_{18} . The calculated frequency is 923 cm^{-1} .

The assignments of 1291 and 1158 cm^{-1} (table 2) are made following Wilson (1974).

REFERENCES

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ERRATA

RACAH PARAMETERS AND AVERAGE MOMENTS OF THE SECOND AND THIRD SERIES TRANSITION METAL IONS" by Ibha De, V. P. Desai and A. S. Chakravarty *Ind. J. Phys.* **48**, 1133-1138 (1974)

Table 1. : Row 12, column 12 should read 640(B) instead of 740(B).
Row 16, column 7 should read 484 instead of 474.
Row 18, column 5 should read 507 instead of 5.7.

Table 2. . Row 2, column 12 should read 0.678 instead of 2.869
Row 5, column 14 should read 33.142 instead of 3.142.
In the same row, values in the column 15 and 16 should be interchanged.
Row 12, column 14 should read 18.941 instead of 19.941
Row 16, column 5 and 6 should read 3.529 and 18.266 instead of 3.539 and 18.286 respectively.
Row 17, column 16 should read 0.924 instead of 0.925
Row 19, column 10 should read 12.867 instead of 2.867

Table 3. : Row 2, column 6, should read 3.662 instead of 3.664.
Row 15, column 7 should read 720 instead of 820.
The following line should be inserted between rows 16 and 17 :
5D(4) Re(3+) 1.299 0.978 1.380 2.626 656 4.27

"CHARGE TRANSPORT IN A VAN DE GRAAFF GENERATOR" by Ashim Kumar Ganguly and Asok Saha published in *Ind. J. Phys.* **49**, 287-295 (1975) :

1. Page 288 : Caption to fig. 1 : Line 6 (from the bottom) : "...d V_{C_1} : distance comb....." should read "...d V_{C_1} : distance of the comb.....".
2. Page 290 : Caption to fig. 3 : Line 2 (from the bottom) : " $g^V_{R= \frac{1}{2}}$ " "should read ' $g^V_a = \frac{1}{2}$ '".
3. Page 293 : Line 6 : "...from about 120 μA as the comb C^V_1 " should read ".....from about 120 μA in the configuration IV. 2a to a value of about 60 μA as the comb C^V_1 ".
4. Page 293 : Line 8 : "roller from the...." should read "onto the roller from the....".
5. Page 293 : Caption to fig. 6 . "configurations" should read "configurations".
6. Page 294 : Line 11 (from the bottom) : "configuration IV. 2" should read "configuration IV. 2a".
7. Page 295 : Line 9 (from the bottom) : "Craggs J. D." should read "Craggs J. D.".
8. Page 295 : Last line : "Van de Graff R. J." should read "Van de Graaff R. J.".