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Vibrational Spectral Studies of 1,4-Dihydroxy-2,3,5-trimethylbenzene

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Vibrational spectral studies of 1,4-dihydroxy-2,3,5-trimethylbenzene has been carried out by assuming C_S point group symmetry. The FT-IR and FT-Raman spectra are interpreted on the basis of force field calculations and potential energy distributions.

Key Words: Spectral studies, 1,4-Dihydroxy-2,3,5-trimethylbenzene.

INTRODUCTION

The vibraional spectra of methylbenzene derivatives have been analyzed on the basis of group frequency approach by Rao *et al.*[1]. The normal coordinate analysis and force field calculations are useful tool for interpreting the vibrational spectra. In the present study, an effort has been made to record the FT-IR and FT-Raman spectra of 1,4-dihydroxy-2,3,5-trimethylbenzene and to assign the observed fundamental modes of vibrations. Essentially all the functional frequencies have been assigned. The assignment is supported by normal coordinate analysis with a simplified general valence force field. The interaction force constants have been transferred intact from the *ab initio* force fields of structurally related compounds. The calculated frequencies are in good agreement with experiment. The potential energy distribution obtained in the analysis provides some insight into the nature of normal modes of 1,4-dihydroxy-2,3,5-trimethylbenzene (Fig. 1) having m.f. $C_9H_{12}O_2$.

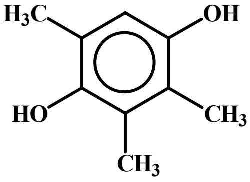

Fig. 1. Molecular structure of 1,4-dihydroxy-2,3,5-trimethylbenzene

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EXPERIMENTAL

The fine sample of 1,4-dihydroxy-2,3,5-trimethylbenzene was obtained from Lancaster Chemical Company, UK and used as such for the spectral measurements. The FT-Raman spectra was recorded on a computer interfaced Bruker IFS model interferometer equipped with FRA 106 FT-Raman accessories. The spectra was recorded in the region 3500-100 cm^{-1} using Nd: YAG laser operating at 200 mW power continuously with 1064 nm excitation. The room temperature mid infrared spectrum of the experimental compound was measured in the region 4000-400 cm^{-1} at a resolution of ± 1 cm^{-1} using Perkin-Elmer FTIR spectrum RX1 model spectrometer equipped with an MCT detector, a KBr beam splitter and globar source. Boxcar apodization was used for the 250 averaged interferogrames collected for the samples.

Molecular symmetry: From the structural point of view the molecule is belonging to C_S point group symmetry. The experimental compound has 63 normal mode vibrations, these can be classified into 43 A' and 20 A" according to symmetry species of C_S point group symmetry. The A' and A" species represent the in-plane and out-of-plane vibrations, respectively.

Normal coordinate analysis: The normal coordinate analysis has been performed by applying Wilson's F-G Matrix mechanism[2] on the basis of general valence force field (GVFF). The structural parameters required for the computation of G-matrix are taken from Sutton's table[3]. The initial set of force constants required to solve the secular equation $[FG - E\lambda] = 0$ was taken from literature. All possible internal coordinates were included in the calculation of potential energy constants. The chief problem posed by this method lies in eliminating redundancies made in defining all the internal coordinates in the molecule. Branching redundancies can be readily eliminated by analytical procedures. However the occurrence of a ring gives rise to cyclic redundancies that cannot be readily eliminated analytically and usually call for numerical methods. Therefore the final set of force constants observed in this study are refined by least square fit technique and also by successive approximation method by using the software developed by Schachtschneider[4] with suitable modifications. To check whether the chosen set of assignments contributes maximum to the potential energy associated with normal coordinates of the molecule, the potential energy distribution calculation was made using the final set of force constants.

Force constants: The best fit force constants obtained in the study for the experimental compound is listed in the Table-1. The objective of this investigation is to find out the stretching, bending and interaction force constants corresponding to each substitutent and its position in the ring. The stretching force constants observed in the study for f_t (C-C) atoms are found to be 3.781 m dyne A^{-1}. The potential energy constants between carbon and oxygen f_r (C-O) is found to be 2.633 m dyne A^{-1} for the experimental compound. The interaction force constants are slowly introduced in force constant refinement process in order to minimize the difference between the observed and calculated frequencies. In general, the values of principal and

TABLE-1
POTENTAIL ENERGY CONSTANTS OF 1,4-DIHYDROXY-2,3,5-TRIMETHYLBENZENE
(In the units of m dyne Å, m dyne rad^{-1} and m dyne rad^{-2})

Type of constants	Parameters	Coordinates involved	Values
Stretching	f_t	C-C	3.781
	f_s	C-H	5.214
	f_r	C-O	2.633
	f_p	O-H	3.008
	f_q	C=C	9.363
Bending	f_α	CCC	0.594
	f_β	CCH	0.278
	f_γ	CCO	0.361
	f_ψ	COH	0.470
	f_θ	HCH	0.235
Stretching – Stretching	f_{tt}	CC CC	0.211
	f_{ts}	CC CH	0.271
	f_{tp}	CC OH	0.363
	f_{rp}	CO OH	0.301
	f_{qr}	CC CO	0.281
Stretch-Bend	$f_{t\alpha}$	CC CCC	0.201
	$f_{r\beta}$	CO CCH	0.195
	$f_{r\alpha}$	CO CCC	0.186
	$f_{t\psi}$	CC COH	0.201
	$f_{t\beta}$	CC CCH	0.176
	$f_{t\gamma}$	CC CCO	0.216
Bend-Bend	$f_{\alpha\alpha}$	CCC CCC	0.019
	$f_{\beta\alpha}$	CCH CCC	0.024
	$f_{\alpha\gamma}$	CCC CCO	0.052
	$f_{\alpha\psi}$	CCC COH	0.041
	$f_{\beta\psi}$	CCH COH	0.031
	$f_{\gamma\beta}$	CCO CCH	0.041

interaction force constants obtained in the present investigation are fairly in agreement with the literature. The set of force constants reported here reproduces the observed frequency fairly well.

RESULTS AND DISCUSSION

The FT-IR and FT-Raman spectra of 1,4-dihydroxy-2,3,5-trimethylbenzene together with relative intensities, probable assignments, calculated frequencies and potential energy distributions (PEDs) are presented in Table-2. The vibrational assignments are discussed below:

C-H Vibrations: The aromatic structure shows the presence of CH stretching vibrations in the region 3100-3000 cm^{-1} which is the characteristic region for the ready identification of CH stretching vibrations[5]. Accordingly, the Raman band

TABLE-2
VIBRATIONAL ASSIGNMENTS (cm^{-1}) OF
1,4-DIHYDROXY-2,3,5-TRIMETHYLBENZENE

Species	Observed frequencies		Calculated frequencies	Assignment (PED %)
	FT-IR	FT-Raman		
A'	3371	-	3360	OH stretching (99)
A'	3352	-	3345	OH stretching (98)
A'	-	3051	3041	CH stretching (99)
A'	-	2940	2933	CH_3 symmetric stretching (88)
A'	2931	2928	2921	CH_3 symmetric stretching (88)
A'	-	2862	2858	CH_3 symmetric stretching (88)
A'	2840	-	2834	CH_3 asymmetric stretching (88)
A'	2815	-	2808	CH_3 asymmetric stretching (85)
A'	2730	-	2728	CH_3 asymmetric stretching (88)
A'	-	1621	1613	CO stretching (95)
A'	1594	1594	1590	CO stretching (95)
A'	-	1580	1578	CC stretching (95)
A'	-	1544	1540	CC stretching (92)
A'	-	1538	1534	CC stretching (95))
A'	-	1524	1521	CC stretching (95)
A'	1465	-	1463	OH in plane bending (87)
A'	-	1456	1452	OH in plane bending (87)
A'	1345	1340	1343	CH_3 asymmetric deformation (85)
A'	-	1325	1326	CH_3 asymmetric deformation (85)
A'	-	1304	1304	CH_3 asymmetric deformation (85)
A'	-	1250	1253	C-C stretching (90)
A'	-	1224	1221	C-C stretching (90)
A'	1210	-	1208	C-C stretching (90)
A'	1074	-	1073	C-C stretching (90)
A'	1019	-	1017	CH in-plane bending (68)
A'	950	-	953	C-C stretching (90)
A'	-	926	929	CH_3 symmetric deformation (85)
A'	-	912	906	CH_3 symmetric deformation (85)
A'	-	888	881	CH_3 symmetric deformation (85)
A'	763	-	757	CH_3 in plane rocking (87)
A'	697	-	690	CH_3 in plane rocking (87)
A'	-	680	678	CH_3 in plane rocking (87)
A'	-	578	572	CO in plane bending (84)
A'	570	-	563	CO in plane bending (84)
A'	-	522	522	CC in plane bending (84)
A'	-	488	489	CC in plane bending (84)
A'	-	475	474	CC in plane bending (84)
A'	-	449	448	Ring in plane bending (85)
A'	-	392	393	Ring in plane bending (83)
A'	-	380	380	Ring in plane bending (83)

Species	Observed frequencies		Calculated frequencies	Assignment (PED %)
	FT-IR	FT-Raman		
A"	-	3005	2996	CH_3 asymmetric stretching (89)
A"	-	2980	2974	CH_3 asymmetric stretching (89)
A"	-	2965	2960	CH_3 asymmetric stretching (89)
A"	-	1440	1436	CH_3 asymmetric deformation (85)
A"	1409	-	1407	CH_3 asymmetric deformation (85)
A"	-	1379	1378	CH_3 asymmetric deformation (85)
A"	837	-	830	OH out plane bending (78)
A"	-	830	825	OH out plane bending (78)
A"	-	712	706	CH_3 out plane rocking (78)
A"	-	688	681	CH_3 out plane rocking (78)
A"	-	668	665	CH_3 out plane rocking (78)
A"	-	653	651	CH out plane bending (78)
A"	-	366	364	CO out plane bending (75)
A"	-	356	352	CO out plane bending (76)
A"	-	340	342	CC out plane bending (75)
A"	-	315	316	CC out plane bending (78)
A"	-	302	302	CC out plane bending (78)
A"	-	150	148	CH_3 torsion(55)
A"	-	138	139	CH_3 torsion(55)
A"	-	130	130	CH_3 torsion(55)
A"	-	115	112	Ring out plane bending (66)
A"	-	108	107	Ring out plane bending (66)
A"	-	103	101	Ring out plane bending (69)

observed in this study at 3051 cm^{-1} is assigned to CH stretching modes of vibration for the title compound. The frequency shift is due to inclusion of methyl group in the benzene ring[6,7]. The in-plane and out-of plane bending vibration are listed in the Table-2.

O-H Vibrations: The precise position of the O-H bond is dependent on the strength of the hydrogen bond. In some samples, intra-molecular hydrogen bonding may occur, the resulting hydroxyl group band which appears at 3590-3400 cm^{-1} being sharp and unaffected by concentration changes[6]. Accordingly in 1,4-dihydroxy-2,3,5-trimethylbenzene the O-H hydrogen bond is longer and the absorption is found at 3371 and 3352 cm^{-1} in the measured FT-IR spectrum. The in-plane and out-of-plane deformation modes of hydroxyl group in the experimental compound are found at 1465 cm^{-1} in IR and 1456 cm^{-1} in Raman and 837 cm^{-1} in IR and 830 cm^{-1} Raman, respectively.

C-O Vbrations: The non-linearity of hydrogen bond in 1,4-dihydroxy-2,3,5-trimethylbenzene has an impact over the carbonyl group frequency. The FT-Raman band formed at 1621 cm^{-1} in infrared and 1594 cm^{-1} in Raman are assigned to CO stretching vibrations. The FT-IR bands observed at 578, 570 and 366, 356 cm^{-1} are due to in-plane and out-of-plane of carbon and oxygen vibrations, respectively.

CH_3 Group vibration: The C-CH_3 stretching and bending modes appear to be quite pure group vibrations. Considering the assignment of CH^3 group frequencies, one can expect that nine fundamentals and can be associated to each CH_3 group, namely the CH_3 symmetrical stretching and asymmetrical CH_3 stretching in-plane stretching asymmetrical; in-plane stretching modes; the symmetrical CH_3 deformation and asymmetrical CH_3 deformation modes; the in-plane rocking and out-of-plane rocking and twisting bending modes. The asymmetric stretching and asymmetric deformation modes of the methyl group is expected to be depolarized for A″ symmetry species[6,8]. In this present investigation there are three methyl groups are attached in the positions 2nd, 3rd and 5th places, there are 27 normal modes of CH_3 group vibrations occur[7]. The entire fundamental vibrations were depicted in Table-2.

Vibrational coupling with neighboring carbon atoms may resulted into a shift in the absorption frequencies of the respective compounds. The predominant values of PED obtained for other groups of vibrations listed in Table-2 are also supporting the assignments proposed in this study.

Conclusion

A complete vibrational analysis of 1,4-dihydroxy-2,3,5-trimethylbenzene have been carried out. A normal coordinate analysis has been performed that supports the assignments and reveals the mixing of the symmetric bending vibration of this molecule. Force constants in internal coordinate representation is compared well with their characteristic values. The assignment of most of the fundamentals provided in this work is believed to be unambiguous. The calculated and observed frequencies agrees well with the better frequency fit. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the 1,4-dihydroxy-2,3,5-trimethylbenzene in the solid phase.

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