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Vibrational Assignments of FT-IR and FT-Raman Spectra of Pyrogallol

R. Ramasamy
Department of physics, National College (Autonomous), Trichy-620 001, Tamil Nadu, India

ABSTRACT
The molecular vibrations of pyrogallol was investigated by FT-IR and FT-Raman spectroscopies. Normal co-ordinate calculations of pyrogallol have been carried out Wilson's FG matrix mechanism on the basis of General Valence Force Field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in this study are refined using numerical methods.

Keywords: FT-IR, FT-Raman, pyrogallol, normal co-ordinate analysis, potential energy distribution.

I. INTRODUCTION

Pyrogallol is an organic compound with the formula $C_6H_3(OH)_3$. It is a white solid although because of its sensitivity toward oxygen, samples are typically brownish. Pyrogallol is a trihydroxybenzene that can be prepared by heating gallic acid. One can find its uses in hair dying, dying of suturing materials and for oxygen absorption in gas analysis. It also has antiseptic properties. Pyrogallol was also used as a developing agent in black-and-white developers.

In the present paper, an effort has been made to record the spectra and to assign the fundamental modes of vibrations. The evaluation of potential energy constant has been made on the basis of General Valence Force Field (GVFF) by applying Wilson's FG matrix mechanism [1].

II. EXPERIMENTAL METHODS

Pure chemical of pyrogallol is obtained from Lancaster chemical company and used as such without any further purification.

The FT-IR spectrum of the title compound was recorded in the region 4000-400 cm^{-1} using KBr pellet. The Bruker IFS 66v model FT-IR spectrometer was used for the spectral measurements. The globar and mercury arc sources, KBr beam splitters are used while recording FT-IR spectrum of the title compound.

The FT-Raman spectrum was recorded on Bruker IFS 66v model interferometer equipped with an FRA-106 FT-Raman accessory. The spectrum was recorded in the stoke's region (4000-100 cm^{-1}) using the 1064 nm line of a Nd: YAG laser for excitation operating at 200mW of power.

III. RESULTS AND DISCUSSION

3.1. Structure and symmetry

The molecular structure of pyrogallol is shown in Fig.1.

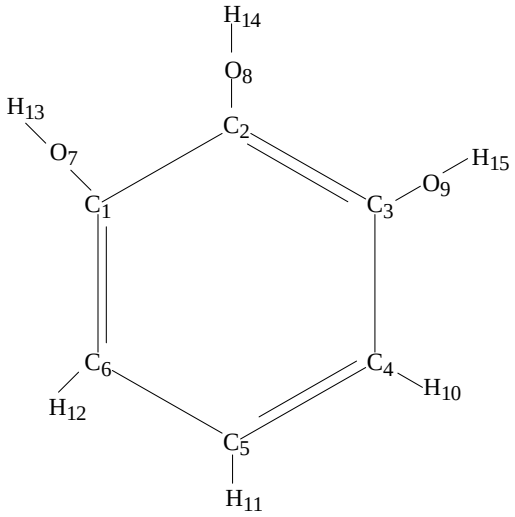

Fig. 1 - Molecular structure of pyrogallol

From the structural point of view the molecule is assumed to have C_s point group symmetry. The 39 fundamental modes of vibrations arising for this molecule are distributed into 27A' and 12A" species. The A' and A" species represent the in-plane and out-of-plane vibrations.

3.2. Normal Coordinate Analysis

The evaluation of potential energy constants are made on the basis of GVFF by applying Wilson's FG matrix mechanism. The structural parameters were taken from the Sutton's table [2]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure [3]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [4]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

3.3 Symmetry Coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 51 standard internal valence coordinates (containing 12 redundancies) were defined in Table 1. From these a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [5, 6]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

Table 1: Definition of internal coordinates of pyrogallol

No (i)	Symbol	Type	Definition
Stretching			
1-6	r_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1
7-9	R_i	C-H	C4-H10, C5-H11, C6-H12
10-12	q_i	C-O	C1-O7, C2-O8, C3-O9
13-15	Q_i	O-H	O7-H13, O8-H14, O9-H15
In-plane bending			
16-21	α_i	C-C-H	C3-C4-H10, C5-C4-H10, C4-C5-H11, C6-C5-H11, C5-C6-H12, C1-C6-H12
22-27	γ_i	C-C-O	C4-C3-O9, C2-C3-O9, C3-C2-O8, C1-C2-O8, C6-C1-O7, C2-C1-O7
28-30	θ_i	C-O-H	C1-O7-H13, C2-O8-H14, C3-O9-H15
31-36	β_i	Ring	C5-C4-C3, C4-C3-C2, C3-C2-C1, C2-C1-C6, C1-C6-C5, C6-C5-C4
Out-of-plane-bending			
37-39	ω_i	C-H	H10-C4-C5-C3, H11-C5-C6-C4, H12-C6-C1-C5
40-42	σi	C-O	O9-C3-C4-C2, O8-C2-C3-C1, O7-C1-C2-C6
43-45	ψ_i	O-H	H15-O9-C3-(C4,C2), H14-O8-C2-(C3,C1), H13-O7-C1-(C2,C6)
Torsion			
46-51	t_i	τRing	C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3, C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6

For numbering of atoms refer Fig. 1.

Table 2: Definition of local symmetry coordinates of pyrogallol

No.(i)	Type	Definition
1-6	CC	r_1, r_2, r_3, r_4, r_5, r_6
7-9	CH	R_7, R_8, R_9
10-12	CO	q_{10}, q_{11}, q_{12}
13-15	OH	Q_{13}, Q_{14}, Q_{15}
16-18	bCH	$(\alpha_{16}-\alpha_{17})/\sqrt{2}$, $(\alpha_{18}-\alpha_{19})/\sqrt{2}$, $(\alpha_{20}-\alpha_{21})/\sqrt{2}$
19-21	bCO	$(\gamma_{22}-\gamma_{23})/\sqrt{2}$, $(\gamma_{24}-\gamma_{25})/\sqrt{2}$, $(\gamma_{26}-\gamma_{27})/\sqrt{2}$
22-24	bOH	θ_{28}, θ_{29}, θ_{30}
25	Rtrigd	$(\beta_{31}-\beta_{32}+\beta_{33}-\beta_{34}+\beta_{35}-\beta_{36})/\sqrt{6}$

26	Rsymd	$(-\beta_{31}-\beta_{32}+\beta_{33}-\beta_{34}-\beta_{35}+2\beta_{36})/\sqrt{6}$
27	Rasymd	$(\beta_{31}-\beta_{32}+\beta_{33}-\beta_{34})/\sqrt{2}$
28-30	ωCH	ω_{37}, ω_{38}, ω_{39}
31-33	σCO	σ_{40}, σ_{41}, σ_{42}
34-36	ψOH	ψ_{43}, ψ_{44}, ψ_{45}
37	tRtrig	$(\tau_{46}-\tau_{47}+\tau_{48}-\tau_{49}+\tau_{50}-\tau_{51})/\sqrt{6}$
38	tRsym	$(\tau_{46}-\tau_{48}+\tau_{49}-\tau_{51})/\sqrt{2}$
39	tRasy	$(-\tau_{46}+2\tau_{47}-\tau_{48}-\tau_{49}+2\tau_{50}-\tau_{51})/\sqrt{12}$

3.4. Vibrational Band Assignments

The FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2-3.

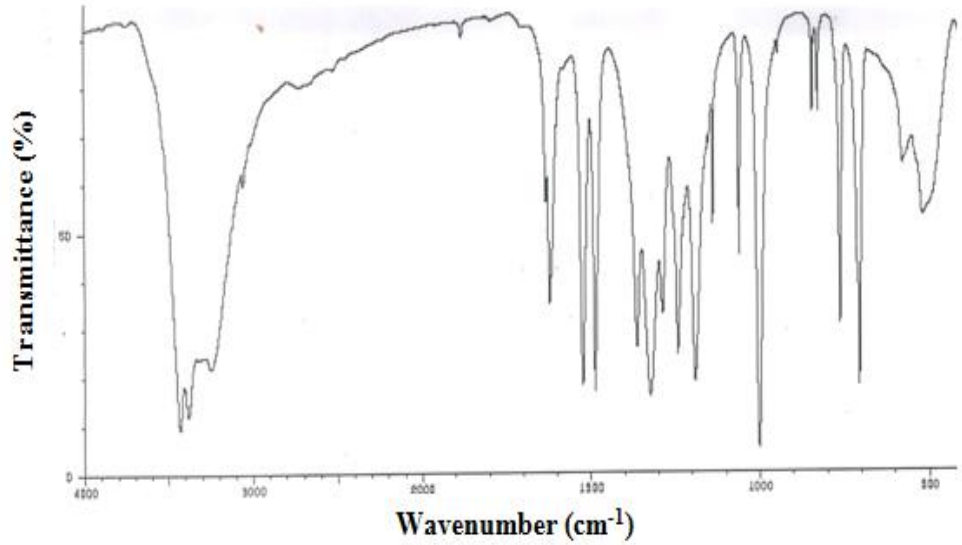

Fig. 2 - FT-IR spectrum of Pyrogallol

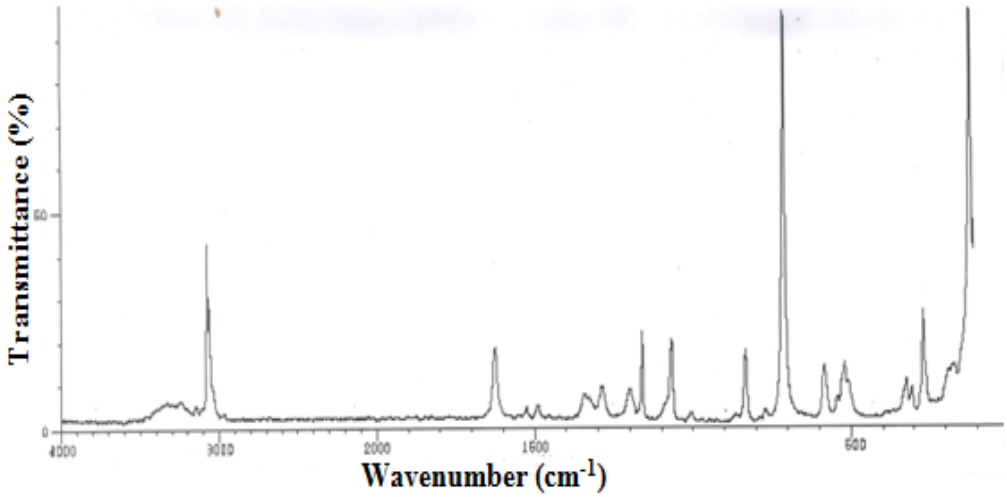

Fig. 3 – FT-Raman spectrum of Pyrogallol

The observed frequencies of the title compound together with probable assignment, calculated frequencies and PEDS are presented in Table 3.

Table 3: Vibrational frequencies and assignments of pyrogallol

S.No.	Species	observed frequency (cm^{-1})		Calculated frequency (cm^{-1})	Assignment (% PED)
		FT-IR	FT-Raman		
1	A′	3589	-	3578	O-H stretching (96)
2	A′	3431	-	3422	O-H stretching (95)
3	A′	3401	-	3391	O-H stretching (97)
4	A′	-	3077	3069	C-H stretching (99)
5	A′	3069	-	3059	C-H stretching (97)
6	A′	-	3060	3048	C-H stretching (98)
7	A′	1633	-	1624	C-C stretching (70)
8	A′	-	1627	1617	C-C stretching (72)
9	A′	1621	-	1610	C-C stretching (71)
10	A′	-	1540	1530	C-C stretching (72)
11	A′	1524	-	1513	C-C stretching (70)
12	A′	-	1493	1485	C-C stretching (71)
13	A′	1488	-	1478	O-H in-plane bending (53)
14	A′	1461	-	1452	O-H in-plane bending (52)
15	A′	-	1437	1429	O-H in-plane bending (51)
16	A′	1323	-	1331	C-O stretching (82)
17	A′	1289	-	1298	C-O stretching (83)
18	A′	1243	-	1253	C-O stretching (81)
19	A′	1192	-	1203	C-H in-plane bending (70)
20	A′	1163	-	1153	C-H in-plane bending (72)
21	A′	1141	-	1132	C-H in-plane bending (71)
22	A′	-	1070	1059	Ring deformation in-plane bending (53)
23	A′	1061	-	1053	Ring deformation in-plane bending (51)
24	A′	1002	-	1011	Ring deformation in-plane bending (52)
25	A″	949	-	960	C-H out-of-plane bending (65)
26	A″	848	-	857	O-H out-of-plane bending (62)
27	A″	840	-	832	O-H out-of-plane bending (65)
28	A″	-	836	825	O-H out-of-plane bending (64)
29	A′	764	-	754	C-O in-plane bending (64)
30	A′	-	714	704	C-O in-plane bending (63)
31	A′	707	-	695	C-O in-plane bending (65)
32	A″	-	587	578	C-O out-of-plane bending (55)
33	A″	571	-	560	C-H out-of-plane bending (66)
34	A″	-	526	534	C-O out-of-plane bending (56)
35	A″	519	-	528	C-H out-of-plane bending (64)
36	A″	507	-	518	C-O out-of-plane bending (57)
37	A″	-	327	318	Ring deformation out-of-plane bending (57)
38	A″	-	273	262	Ring deformation out-of-plane bending (58)
39	A″	-	124	116	Ring deformation out-of-plane bending (59)

O-H vibrations

The precised 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 [7]. Hence the FT-IR bands at 3589, 3431 and 3401 cm^{-1} have been designated to O-H vibrations.

C-H vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100cm^{-1}, which is the characteristic region for the ready identification of C-H stretching vibrations [8]. In this region the bands are not affected appreciably by the nature of the constituents. Hence, in the present investigation, C-H vibrations have found at 3069 cm^{-1} in IR and 3077, 3060 cm^{-1} in Raman.

C-C vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are due to C-C stretching vibrations [9]. Therefore, the C-C stretching vibrations of the title compound are observed at 1633, 1621, 1524 cm^{-1} in IR and 1627, 1540, 1493 cm^{-1} in Raman.

C-O vibrations

If a compound contains a carbonyl group, the absorption caused by C-O stretching is generally strongest [10]. Consideration of these factors lead to assign the very strong FT-IR band at 1323, 1289 and 1243 cm^{-1} to C-O stretching vibrations for the title compound.

IV. CONCLUSION

Based on the normal coordinate analysis a complete vibrational analysis was performed on pyrogallol. A systematic set of symmetric coordinates have been constructed. The closer agreement obtained between the calculated and the observed frequencies and the PED calculations are also supporting the assignments made for various functional groups present in the molecule.

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