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DENSITY FUNCTIONAL THEORY CALCULATIONS AND VIBRATIONAL ASSIGNMENT OF TRIMETHYLHYDROQUINONE (TMHQ)

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Abstract

The spectroscopic techniques are very effective and sensitive tool for study of atomic and molecular structure and also used for qualitative and quantitative analysis of compounds. The Fourier transform infrared and Fourier transform Raman spectra of Trimethyl hydroquinone have been recorded in the region 4000-400 cm^{-1} and 3500-50 cm^{-1} respectively. The equilibrium geometry harmonic vibrational frequencies, infrared intensities and Raman scattering activities were calculated with Density Functional B3LYP method with 6-31+G(d,p) and 6-311++G(d,p) basis set combination. A detailed interpretation of the infrared and Raman spectra of Trimethylhydroquinone is reported. Our calculated vibrational frequencies are in good agreement with experimental wavenumbers.

Keywords: Trimethylhydroquinone, Fourier transform, Infrared spectrum, Raman spectrum, Density Functional Theory, molecular geometries, vibrational analysis.

Introduction

Hydroquinone has been a widely studied molecular system because of its diverse commercial and technological applications [1-10]. It is one of the three isomers of the dihydroxy benzene the para-hydroquinone the other two being, ortho hydroquinone (Pyrocalechhol) and meta-hydroquinone (resorcinol). Consideration of these factors motivated to study the vibrational aspects of the Trimethylhydroquinone. For that, the FTIR and FT Raman spectra of Trimethylhydroquinone were recorded and a complete vibrational analysis is proposed for the better understanding of physical and chemical properties of the title compound.

For the proper understanding of IR and Raman spectra, a reliable assignment of all vibrational bands is essential. For this purpose, the quantum chemical methods, ranging from semi empirical to DFT approaches, are invaluable tools [11-13], each method having its own advantages. The semi empirical calculations provide very fast and in certain circumstances fairly good theoretical results, being applicable to large molecular systems. The Hartree-Fock, *ab-initio* methods are able to give good results provided a reasonable basis set and an appropriate correlation treatment are taken into account. On the other hand, DFT methods have evolved to a powerful quantum chemical tool for the determination of the electronic structure of molecules. In the frame work of DFT approach, different exchange and correlation

functions are routinely used. Among these, the B3LYP combination [14, 15] is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. In the present work, we apply the density functional theory to study the vibrational spectra and structure of Trimethylhydroquinone.

Experimental details

Spectroscopically pure sample of Trimethylhydroquinone was purchased from Lancaster Chemical Company, UK and used as such without any further purification.

The FT-Raman spectrum of TMHQ was recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50-3500 cm^{-1} on the BRUCKER IFS-66 V spectrophotometer equipped with FRA 106 Raman module.

The room temperature FTIR spectrum of the title compound was recorded in the 400-4000 cm^{-1} region at a resolution of $\pm \text{cm}^{-1}$ using a BRUCKER IFS-66 spectrometer using KBr pellet.

Computational details

Quantum chemical density functional calculations, the molecular geometry optimizations, energy and vibrational frequency calculations were carried out for Trimethyl hydroquinone with the GAUSSIAN 2003 window software package [16] using the Becke-3-Lee-Yang-Parr functions [14,15] supplemented with the

standard 6-31+G and 6-311+G basis sets. All the parameters were allowed to relax and all the calculations converged to an optimized geometry, which corresponds to a true energy minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming C_s point group symmetry. The transformation of force field from Cartesian to internal local symmetry coordinates the scaling, the subsequent normal coordinate analysis (NCA), and calculation of prediction of IR and Raman intensities were done on a PC with the MOLVIE program (version V7.0-G77) written by Sundius [17-19]

The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational mode were determined by using the standard procedure [20] of decomposing the traces of the symmetry operation into the irreducible representations. The symmetry analysis for the vibrational modes of Trimethylhydroquinone is presented in some details to describe the basis for the assignments.

Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 2003 program and adjusted during the scaling procedure with MOLVIB were subsequently

converted to relative Raman intensities (I_i) using the following relationship derived from the basis theory of Raman scattering [21, 22]

$$I_i = \frac{f(\gamma_0 - \gamma_i)^4 S_i}{V_i \left[1 - \exp\left(\frac{hc\gamma_i}{kT}\right) \right]}$$

(1)

where γ_0 is the exciting frequency (in cm^{-1} units), γ_i is the vibrational wavenumber if the i^{th} normal modes, h, c, k are fundamental constants and f is a suitable chosen common normalization factor for all peak intensities.

Result and Discussions

Molecular geometry

The molecular structure of the Trimethylhydroquinone is shown in Fig 1. The global minimum energy obtained by the DFT structure optimization for the Trimethylhydroquinone is calculated using B3LYP as -500.67415822 Hartrees for 6-31+G(d, p) and -500.78100621 Hartrees for 6-311++G(d, p). The calculated optimized geometrical parameters obtained in this study are presented in Table-1.

Fig. 1

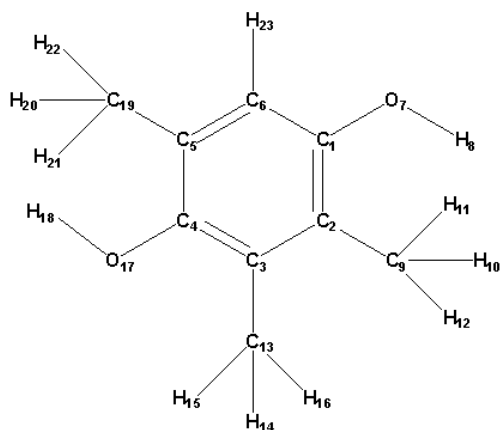


Table 1. Optimized geometrical parameters of Trimethylhydroquinone obtained by B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d,p) density functional calculations

	Value (Å)			Value (Å)	
Bond length	B3LYP/	B3LYP/	Bond angle	B3LYP/	B3LYP/
	6-31+G	6-311++G		6-31+G	6-311++G

C ₁ - C ₂	1.4051	1.4003	C ₁ - C ₂ - C ₃	118.2179	118.3296
C ₂ - C ₃	1.4151	1.4120	C ₂ - C ₃ - C ₄	119.0742	119.3293
C ₃ - C ₄	1.4056	1.4004	C ₃ - C ₄ - C ₅	122.4663	122.1090
C ₄ - C ₅	1.4024	1.4007	C ₄ - C ₅ - C ₆	117.6995	117.8039
C ₅ - C ₆	1.3935	1.3891	C ₅ - C ₆ - C ₁	120.9459	121.1443
C ₆ - C ₁	1.3938	1.3923	C ₆ - C ₁ - C ₂	121.5954	121.2415
C ₁ - O ₇	1.3800	1.3787	C ₁ - O ₇ - H ₈	110.4402	110.0772
O ₇ - H ₈	0.9645	0.9612	C ₂ - C ₉ - H ₁₀	110.4016	112.4929
C ₂ - C ₉	1.5144	1.5136	C ₂ - C ₉ - H ₁₁	113.1099	111.4527
C ₉ - H ₁₀	0.9643	1.0972	C ₂ - C ₉ - H ₁₂	111.4636	112.0923
C ₉ - H ₁₁	1.0892	1.0956	H ₁₀ - C ₉ - H ₁₁	111.6929	107.5343
C ₉ - H ₁₂	1.0991	1.0894	H ₁₁ - C ₉ - H ₁₂	106.4264	105.5410
C ₃ - C ₁₃	1.5150	1.5140	H ₁₀ - C ₉ - H ₁₂	106.2193	107.3453
C ₁₃ - H ₁₄	1.0993	1.0965	C ₃ - C ₁₃ - H ₁₄	107.5562	111.2997
C ₁₃ - H ₁₅	1.0992	1.0974	C ₃ - C ₁₃ - H ₁₅	111.6875	112.2655
C ₁₃ - H ₁₆	1.0889	1.0884	C ₃ - C ₁₃ - H ₁₆	112.9768	112.3279
C ₄ - O ₁₇	1.3823	1.3804	H ₁₄ - C ₁₃ - H ₁₅	111.5011	107.5771
C ₁₇ - H ₁₈	1.0991	0.9613	H ₁₅ - C ₁₃ - H ₁₆	107.6180	107.2396
C ₅ - C ₁₉	1.5075	1.5061	H ₁₄ - C ₁₃ - H ₁₆	106.4675	105.7706
C ₁₉ - H ₂₀	1.0958	1.0940	C ₄ - O ₁₇ - H ₁₈	106.2264	110.0874
C ₁₉ - H ₂₁	1.0933	1.0939	C ₅ - C ₁₉ - H ₂₀	111.2429	111.1577
C ₁₉ - H ₂₂	1.0958	1.0913	C ₅ - C ₁₉ - H ₂₁	110.7439	111.2214
C ₆ - H ₂₃	1.0857	1.0839	C ₅ - C ₁₉ - H ₂₂	111.2491	110.7513
			H ₂₀ - C ₁₉ - H ₂₁	108.4615	106.5560
			H ₂₁ - C ₁₉ - H ₂₂	108.4606	108.5034
			H ₂₀ - C ₁₉ - H ₂₂	107.5283	108.5013
			C ₁ - C ₂ - C ₉	117.8891	119.4357
			C ₃ - C ₂ - C ₉	123.8929	122.2347
			C ₂ - C ₃ - H ₁₃	123.3415	122.0967
			C ₄ - C ₃ - C ₁₃	117.5843	118.5739
			C ₃ - C ₄ - O ₁₇	121.8275	122.0828
			C ₅ - C ₄ - O ₁₇	115.7062	115.8080
			C ₄ - C ₅ - C ₁₉	120.4088	120.3274
			C ₆ - C ₅ - C ₁₉	121.8917	120.8683

	$C_5 - C_6 - H_{23}$	120.4661	120.4268
	$C_1 - C_6 - H_{23}$	118.5871	118.4290
	$C_6 - C_1 - O_7$	116.1080	115.9877
	$C_2 - C_1 - O_7$	122.2965	122.7698

For numbering of an atom refer Fig. 1

Table 2. Definition of internal co-ordinates of Trimethylhydroquinone

No. (i)	Symbol	Type	Definition
Stretching			
1	r_i	C - H	$C_5 - H_{23}$
2-10	r_i	C - H (Methyl)	$C_9 - H_{10}, C_9 - H_{11}, C_9 - H_{12}, C_{13} - H_{14}, C_{13} - H_{15}, C_{13} - H_{16},$ $C_{19} - H_{20}, C_{19} - H_{21}, C_{19} - H_{22},$
11-19	R_i	C - C	$C_1 - C_2, C_2 - C_3, C_3 - C_4, C_4 - C_5, C_5 - C_6, C_6 - C_1, C_2 - C_9,$ $C_3 - C_{13}, C_5 - C_{19}.$
20,21	Q_i	C - O	$C_1 - O_7, C_4 - O_{17}.$
22,23	P_i	O - H	$O_7 - H_8, O_{17} - H_{18}$
Bending			
24 - 29	β_i	Ring 1	$C_1 - C_2 - C_3, C_2 - C_3 - C_4, C_3 - C_4 - C_5,$ $C_4 - C_5 - C_6, C_5 - C_6 - C_1, C_6 - C_1 - C_2$
30 - 31	α_i	C - C - H	$C_1 - C_6 - H_{23}, C_5 - C_6 - H_{23}.$
32 - 40	α_i	C - C - H (Methyl)	$C_2 - C_9 - H_{10}, C_2 - C_9 - H_{11}, C_2 - C_9 - H_{12}, C_3 - C_{13} - H_{14},$ $C_3 - C_{13} - H_{15}, C_3 - C_{13} - H_{16}, C_5 - C_{19} - H_{20}, C_5 - C_{19} - H_{21},$ $C_5 - C_{19} - H_{22}$
41 - 49	σ_i	H - C - H	$H_{10} - C_9 - H_{11}, H_{11} - C_9 - H_{12}, H_{10} - C_9 - H_{12}, H_{14} - C_{13} - H_{15},$ $H_{15} - C_{13} - H_{16}, H_{14} - C_{13} - H_{16}, H_{20} - C_{19} - H_{21}, H_{21} - C_{19} - H_{22},$ $H_{20} - C_{19} - H_{22}.$
50 - 53	θ_i	C - C - O	$C_2 - C_1 - O_7, C_6 - C_1 - O_7, C_3 - C_4 - O_{17}, C_5 - C_4 - O_{17},$
54 - 57	ε_i	C - O - H	$C_1 - O_7 - H_8, C_4 - O_{17} - H_{18}, H_8 - O_7 - C_1, H_{18} - O_{17} - C_4,$
58 - 63	φ_i	C - C - C	$C_1 - C_2 - C_9, C_3 - C_2 - C_9, C_2 - C_3 - C_{13},$ $C_4 - C_3 - C_{13}, C_4 - C_5 - C_{19}, C_6 - C_5 - C_{19}.$
Out-of-plane bending			
64	ω_i	C - H	$H_{23} - C_6 - C_1 - C_5,$
65 - 67	π_i	C - C	$C_9 - C_2 - C_1 - C_3, C_{13} - C_3 - C_2 - C_4, C_{19} - C_5 - C_4 - C_6.$
68,69	ρ_i	O - C	$O_7 - C_1 - C_2 - C_6, O_{17} - C_4 - C_3 - C_5$
70,71	γ_i	O - H	$H_8 - O_7 - C_1 - (C_2, C_6), H_{18} - O_{17} - C_4 - (C_3, C_5).$
Torsion			
72 - 77	τ_i	τ Ring 1	$C_1 - C_2 - C_3 - C_4, C_2 - C_3 - C_4 - C_5, C_3 - C_4 - C_5 - C_6,$ $C_4 - C_5 - C_6 - C_1, C_5 - C_6 - C_1 - C_2, C_6 - C_1 - C_2 - C_3.$

78 - 80	τ	τ C - CH ₃	(C ₁ , C ₃)- C ₂ - C ₄ - (H ₁₀ , H ₁₁ H ₁₂) (C ₂ , C ₄)- C ₃ - C ₁₃ - (H ₁₄ , H ₁₅ H ₁₆) (C ₄ , C ₆)- C ₅ - C ₁₉ - (H ₂₀ , H ₂₁ H ₂₂)
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For numbering of an atom refer Fig. 1

Table 3. Definition of local symmetry co-ordinates of Trimethyl-Hydroquinone

No. (i)	Symbol	Definition
1	CH	r_1
2 - 4	CH ₃ SS	$(r_1 + r_3 + r_4)/\sqrt{3}, (r_5 + r_6 + r_7)/\sqrt{3}, (r_8 + r_9 + r_{10})/\sqrt{3},$
5 - 7	CH ₃ ips	$(2r_1 + r_3 + r_4)/\sqrt{6}, (2r_5 + r_6 + r_7)/\sqrt{6}, (2r_8 + r_9 + r_{10})/\sqrt{6},$
8 - 10	CH ₃ ops	$(r_3 - r_4)/\sqrt{2}, (r_6 - r_7)/\sqrt{2}, (r_9 - r_{10})/\sqrt{2}$
11 - 19	CC	R ₁₁ , R ₁₂ , R ₁₃ , R ₁₄ , R ₁₅ , R ₁₆ , R ₁₇ , R ₁₈ , R ₁₉ .
20,21	CO	Q ₂₀ , Q ₂₁
22,23	OH	P ₂₂ , P ₂₃
24	R trigd	$(\beta_{24} - \beta_{25} + \beta_{26} - \beta_{27} + \beta_{28} - \beta_{29})/\sqrt{6}$
25	R symd	$(-\beta_{24} - \beta_{25} + 2\beta_{26} - \beta_{27} - \beta_{28} + 2\beta_{29})/\sqrt{12}$
26	R asymd	$(\beta_{24} - \beta_{25} + \beta_{27} - \beta_{28})/2$
27	bCH	$(\alpha_{30} - \alpha_{31})/\sqrt{2}$
28 - 30	CH ₃ Sb	$(-\alpha_{32} - \alpha_{33} - \alpha_{34} + \sigma_{35} + \sigma_{36} + \sigma_{37})/\sqrt{6}$ $(-\alpha_{38} - \alpha_{39} - \alpha_{40} + \sigma_{41} + \sigma_{42} + \sigma_{43})/\sqrt{6}$ $(-\alpha_{44} - \alpha_{45} - \alpha_{46} + \sigma_{47} + \sigma_{48} + \sigma_{49})/\sqrt{6}$
31 - 33	CH ₃ ipb	$(-\sigma_{35} - \sigma_{36} - 2\sigma_{37})/\sqrt{6}, (-\sigma_{41} - \sigma_{42} - 2\sigma_{43})/\sqrt{6},$ $(-\sigma_{47} - \sigma_{48} - 2\sigma_{49})/\sqrt{6}$
34 - 36	CH ₃ opb	$(\sigma_{35} - \sigma_{36})/\sqrt{2}, (\sigma_{41} - \sigma_{42})/\sqrt{2}, (\sigma_{47} - \sigma_{48})/\sqrt{2}$
37 - 39	CH ₃ ipr	$(2\alpha_{32} - \alpha_{33} - \alpha_{34})/\sqrt{6}, (2\alpha_{38} - \alpha_{39} - \alpha_{40})/\sqrt{6},$ $(2\alpha_{44} - \alpha_{45} - \alpha_{46})/\sqrt{6},$
40 - 42	CH ₃ opr	$(\alpha_{33} - \alpha_{34})/\sqrt{2}, (\alpha_{39} - \alpha_{40})/\sqrt{2}, (\alpha_{45} - \alpha_{46})/\sqrt{2}$
43,44	b CO	$(\theta_{50} - \theta_{51})/\sqrt{2}, (\theta_{52} - \theta_{53})/\sqrt{2}$
45,46	b OH	$(\epsilon_{54} - \epsilon_{55})/\sqrt{2}, (\epsilon_{56} - \epsilon_{57})/\sqrt{2}$
47 - 49	b CC	$(\phi_{58} - \phi_{59})/\sqrt{2}, (\phi_{60} - \phi_{61})/\sqrt{2}, (\phi_{62} - \phi_{63})/\sqrt{2}$
50	ω CH	ω_{64}
51 - 53	ω CC	$\pi_{65}, \pi_{66}, \pi_{67}$
54,55	ω OC	ρ_{68}, ρ_{69}
56,57	ω OH	γ_{70}, γ_{71}
58	t R trigd	$(\tau_{72} - \tau_{73} + \tau_{74} - \tau_{75} + \tau_{76} - \tau_{77})/\sqrt{6}$
59	t R symd	$(\tau_{72} - \tau_{74} + \tau_{75} - \tau_{77})/\sqrt{2}$
60	t R asymd	$(-\tau_{72} + 2\tau_{73} - \tau_{74} - \tau_{75} + 2\tau_{76} - \tau_{77})/\sqrt{12}$
61 - 63	t CH ₃	$\tau_{78}, \tau_{79}, \tau_{80}$

Table 4. Assignment of fundamental vibrational of Trimethylhydroquinone by normal mode analysis based on SQM force field calculations using selectively scaled B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d,p) force field

Symmetry species C _s	Observed frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹) (Unscaled)		Scaling frequency (cm ⁻¹)	Reduced mass (AMU)		Force constant (mDyne/A)		IR intensity (KM/Mole)		Raman activity (A ⁴ /AMU)		Assignment
	FTIR	FT-Raman	B3LYP/6-31+G	B3LYP/6-311++G		B3LYP/6-31+G	B3LYP/6-311++G	B3LYP/6-31+G	B3LYP/6-311++G	B3LYP/6-31+G	B3LYP/6-311++G	B3LYP/6-31+G	B3LYP/6-311++G	
A'	3250(s)	-	3852	3856	3252	1.0657	1.0657	9.3179	9.3339	55.0564	62.6128	93.6224	120.4833	v OH
A'	-	3025(w)	3850	3854	3029	1.0656	1.0655	9.3042	9.3261	52.6901	52.5072	54.6937	23.0075	v OH
A'	-	2950(s)	3199	3182	2945	1.0911	1.0908	6.5796	6.5069	6.6659	5.8606	109.8671	107.5332	v CH
A'	2912(w)	-	3168	3132	2908	1.0869	1.0897	6.4271	6.2967	26.3040	15.7891	87.1636	71.5464	CH ₃ ips
A'	-	2875(vw)	3150	3113	2780	1.0926	1.0926	6.3877	6.2371	4.6042	10.7156	29.3814	52.3648	CH ₃ ips
A'	2853(vw)	-	3124	3108	2852	1.1026	1.1020	6.3398	6.2708	18.7900	18.0624	68.8376	66.5514	CH ₃ ips
A'	2815(w)	-	3093	3076	2813	1.1003	1.0998	6.2018	6.1292	15.6699	15.9571	94.8621	96.5916	CH ₃ ss
A'	2785(w)	2784(vw)	3052	3049	2785	1.1009	1.0977	6.0412	6.0111	32.0968	22.0517	70.6946	94.0486	CH ₃ ss
A'	-	2750(w)	3051	3040	2743	1.1009	1.0996	6.0375	5.9886	9.8690	21.2161	129.3076	89.6446	CH ₃ ss
A'	-	1625(m)	3039	3028	1624	1.0362	1.0360	5.6397	5.5966	35.8575	32.4899	257.6737	280.6312	v CC
A'	1600(s)	-	3011	3005	1597	1.0463	1.0460	5.5884	5.5643	30.9900	40.2583	382.2802	297.5690	v CC
A'	-	1585(m)	3009	3001	1580	1.0449	1.0453	5.5737	5.5459	51.2448	36.9836	75.8294	204.9852	v CC
A'	1572(vw)	-	1672	1664	1576	6.8559	6.7365	11.2861	10.9878	1.8422	2.3779	28.9709	29.7357	v CC
A'	1554(vw)	-	1639	1632	1557	6.0656	6.1422	9.6022	9.6407	11.8979	14.2879	13.2063	12.9735	v CC
A'	-	1529(vw)	1538	1537	1526	1.7139	1.3187	2.3880	1.8355	20.5745	15.7864	2.6017	3.1897	v CC
A'	1522(m)	-	1512	1515	1524	1.3583	1.5509	1.8436	2.0968	96.1175	67.7410	1.1390	2.2357	v CC
A'	-	1515(vw)	1506	1508	1515	1.0459	1.3712	1.3973	1.8366	12.4593	39.8992	16.7789	2.6050	v CC
A'	-	1487(w)	1497	1500	1494	1.2323	1.0542	1.6279	1.3973	3.6097	15.0197	10.6831	12.2786	v CC
A'	-	1480(vw)	149	1491	1483	1.0896	1.1273	1.4342	1.4768	13.8709	15.9029	4.9669	7.4902	CH ₃ ipb
A'	1425(m)	-	149	1480	1430	1.3566	1.2862	1.7798	1.6603	12.0340	4.8037	4.6582	10.1754	CH ₃ ipb
A'	-	1415(s)	148	1478	1418	1.0439	1.0437	1.3517	1.3437	7.5811	7.6969	8.9590	9.1067	CH ₃ ipb
A'	1390(vw)	-	145	1352	1392	2.4764	2.4631	3.0919	3.0579	93.9295	82.8989	0.5914	0.6985	CH ₃ sb
A'	-	1385(s)	143	1420	1383	1.2020	1.1942	1.4501	1.4196	0.1971	0.0842	19.5828	24.8603	CH ₃ sb
A'	1375(ms)	-	142	1415	1375	1.2872	1.2900	1.5293	1.5216	3.6930	3.7615	11.8093	5.8734	CH ₃ sb

A'	-	1350(vw)	1409	1410	1354	1.3133	1.2724	1.5359	1.4900	1.8705	1.3477	15.1647	13.0046	v CO
A'	-	1235(vw)	1366	1350	1230	3.8956	5.7821	4.2797	6.2043	2.1716	1.6201	9.9089	41.1187	v CO
A'	1087(vw)	-	1353	1348	1095	8.2788	4.3398	8.9239	4.6473	7.5582	6.9404	39.6777	12.6598	b OH
A'	1025(m)	-	1279	1283	1030	1.3826	1.3769	1.3323	1.3355	60.0167	84.4358	0.3017	0.5585	b OH
A'	-	1015(vw)	1267	1265	1012	4.2446	4.2216	4.0167	3.9811	127.4822	107.6440	2.2143	2.2001	b CH
A'	948(vw)	-	1205	1206	954	1.6187	1.6860	1.3853	1.4448	115.9033	121.3581	2.5863	3.2303	CH ₃ ipr
A'	-	935(vw)	1177	1178	937	1.4188	1.4592	1.1616	1.1921	87.7719	80.4260	2.5841	3.1036	CH ₃ ipr
A'	924(vw)	-	1114	1109	927	4.3402	4.4120	3.1711	3.1967	0.2027	0.0094	4.3867	2.3887	CH ₃ ipr
A'	867(vw)	-	1095	1092	872	2.1413	2.0585	1.5127	1.4474	77.4760	66.5647	0.1781	0.0999	b CC
A'	858(s)	-	1061	1060	856	1.4906	1.4964	0.9881	0.9907	1.2792	1.6535	0.0694	0.3651	b CC
A'	-	825(vw)	1049	1052	826	1.4785	1.5092	0.9594	0.9845	0.1891	1.9004	0.2879	1.8178	b CC
A'	765(w)	-	1043	1038	760	1.4150	1.5251	0.9068	0.9684	0.5850	23.5945	0.1957	0.5929	b CO
A'	-	745(w)	1039	1035	748	1.5420	1.4474	0.9312	0.9142	39.6428	20.1897	0.4562	0.0278	b CO
A'	-	715(s)	1010	1011	715	1.7141	1.6872	1.0295	1.0157	1.6598	2.2585	3.7741	1.9703	R trigd
A'	-	710(vw)	926	929	711	2.2313	2.3184	1.1269	1.1789	2.5661	1.8562	2.5063	3.7664	R symd
A'	694(m)	-	881	882	699	1.3594	1.3804	0.6215	0.6325	17.1875	16.0948	0.0919	0.0481	R asym d
A''	-	2552(vw)	839	840	2555	2.6194	2.6908	1.0869	1.1176	16.5557	21.3786	0.2225	0.1657	CH ₃ ops
A''	2518(vw)	2520(vw)	701	722	2520	5.0274	4.7143	1.4554	1.4497	12.4839	1.4498	9.0957	0.2628	CH ₃ ops
A''	-	2412(w)	697	702	2417	5.3498	5.1086	1.5302	1.4849	0.7819	13.2508	0.1896	8.4702	CH ₃ ops

A ^u	1215(s)	-	641	638	1210	4.5556	4.6755	1.1015	1.1229	0.1700	0.5754	0.4072	0.2613	CH ₃ opb
A ^u	-	1128(vw)	602	606	1134	2.8037	2.8246	0.5982	0.6110	23.4638	21.0604	2.2881	1.5686	CH ₃ opb
A ^u	1115(s)	-	578	577	1113	4.9665	4.9636	0.9779	0.9749	5.8963	6.0917	25.2201	24.6465	CH ₃ opb
A ^u	965(vw)	-	520	521	970	3.4394	3.3898	0.5473	0.5428	0.3587	0.7359	0.0132	0.1383	CH ₃ opr
A ^u	953(vw)	-	489	490	948	6.3102	6.2944	0.8883	0.8921	0.5346	0.6290	7.9947	7.9108	CH ₃ opr
A ^u	-	915(w)	451	452	910	5.4771	5.5034	0.6558	0.6632	1.3593	1.2406	6.1328	5.6768	CH ₃ opr
A ^u	-	815(w)	383	403	822	5.6302	2.2808	0.4870	0.2181	0.1364	0.2487	1.0550	0.2450	ω CH
A ^u	634(vw)	-	380	386	635	2.7691	5.2906	0.2378	0.4638	0.1448	0.3903	0.1166	0.9896	t R trigd
A ^u	-	625(vw)	356	352	633	4.8914	4.1794	0.3646	0.3056	0.0823	1.2576	0.3935	0.2853	t R symd
A ^u	-	610(s)	323	344	606	3.3531	2.9221	0.2056	0.2043	2.9168	7.8913	0.0482	0.1929	t R asymd
A ^u	575(vw)	-	304	302	572	2.7459	2.7186	0.1493	0.1457	22.1077	25.5333	1.1358	1.0833	ω CC
A ^u	-	505(m)	279	281	503	2.6939	2.7238	0.1234	0.1264	4.1896	4.5540	0.4080	0.4075	ω CC
A ^u	-	495(s)	219	229	500	1.2880	1.2263	0.0364	0.0379	53.0537	12.5832	1.9312	1.8178	ω CC
A ^u	-	480(s)	200	217	485	1.6649	1.1518	0.0391	0.0320	58.6382	140.5508	0.5180	1.4361	ω OH
A ^u	-	462(vw)	189	191	467	1.8223	4.6166	0.0385	0.0988	59.0961	0.2297	1.1369	0.1731	ω OH
A ^u	-	405(m)	142	141	400	1.9230	2.2826	0.0227	0.0266	0.1835	0.1543	0.1666	0.1986	ω CO
A ^u	-	394(vw)	127	125	393	1.0739	1.1038	0.0101	0.0100	0.8771	0.2304	0.4519	0.5234	ω CO
A ^u	-	250(vw)	122	116	256	2.0920	3.0616	0.0182	0.0242	0.6037	2.1478	0.0945	0.0702	t CH ₃
A ^u	-	242(vw)	91	86	242	1.2082	1.1274	0.0059	0.0049	1.5375	3.2845	0.7253	0.7188	t CH ₃
A ^u	-	230(vw)	23	67	238	1.2090	1.1428	0.0004	0.0030	0.1738	0.6494	0.1146	1.5856	t CH ₃

Abbreviations: v - stretching; b - in-plane bending; ω - out-of-plane bending; asymd - asymmetric; symd - symmetric; t - torsion; trig - trigonal; w - weak; vw - very weak; vs - very strong; s - strong; ms - medium strong; ss - symmetric stretching; ass - asymmetric stretching; ips - in-plane stretching; ops - out-of-plane stretching; sb - symmetric bending; ipr - in-plane rocking; opr - out-of-plane rocking; opb - out-of-plane bending

Vibrational spectra

The 63 normal modes of Trimethylhydroquinone are distributed amongst the symmetry species as

$\overline{3N} - 6 = 43A'$ (in-plane) + 20 A^u (out-of-plane, in agreement with C_s symmetry. All the vibrations are active both in the Raman scattering and infrared absorption.

The observed and calculated frequencies of Trimethylhydroquinone are compared with B3LYP/6-

31+G (d,p) and B3LYP/6-311++G(d,p) are summarized in Table 4. The detailed vibrational assignments of fundamental modes of Trimethylhydroquinone along with the calculated IR and Raman intensities and normal mode descriptions are reported in Table.4

The FTIR and FT Raman spectra of the Trimethylhydroquinone are shown in Figs. 2 and 3.

Fig. 2 - FTIR Spectrum of Trimethylhydroquinone

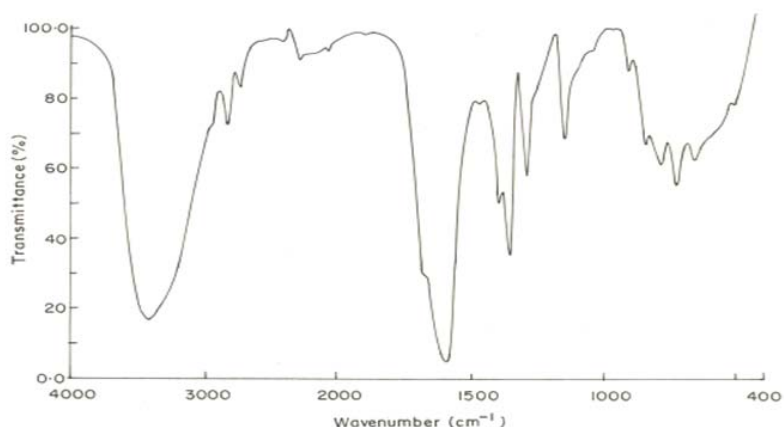
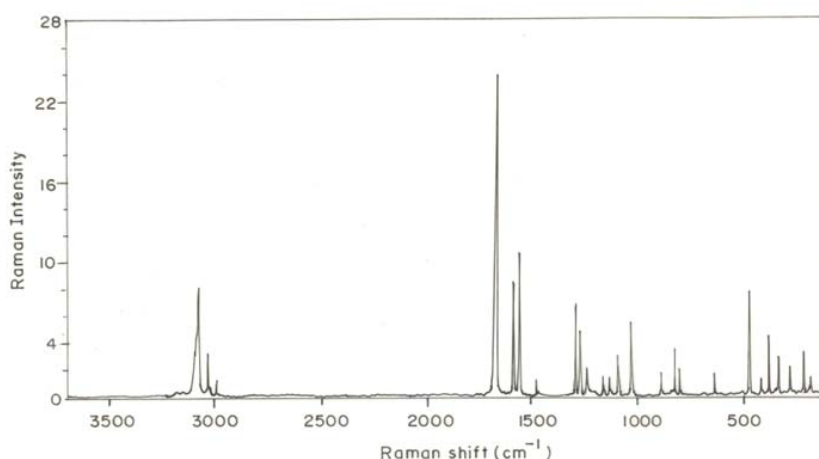


Fig. 3.- FT-Raman Spectrum of Trimethylhydroquinone



C-H vibrations

The substituted benzene gives rise to C-H stretching. C-H in-plane bending and C-H out-of-plane deformations. The heteromatic structure shows the presence of C-H stretching vibrations in the region 3000 – 3100 cm^{-1} which is the characteristic region for the ready identification of such stretching vibrations [23, 24]. Accordingly in this study the C-H vibrations of the Trimethylhydroquinone are observed at 2950 cm^{-1} in FT-Raman. The C-H in-plane and out-of-plane bending vibrations have also identified and listed in Table 4.

C-C vibrations

The bands between 1400 and 1650 cm^{-1} in the aromatic and hetero aromatic compounds are assigned to C-C stretching vibrations [25, 26]. Therefore, the C-C stretching vibrations of the Trimethylhydroquinone these vibrations are found at 1600, 1572, 1554, 1522 cm^{-1} in the FTIR and 1625, 1585, 1529, 1515, 1487 cm^{-1} in the FT-Raman spectrum. In the present study the ring in-plane and out-of-plane bending vibrations are

made for the title compound by careful consideration of their qualitative descriptions.

C-O vibrations

The presence of the carbonyl group in a molecule often gives rise to the appearance of the medium intensity band in the single bonded stretching region 1350-1200 cm^{-1} . Hence in this study the FT-Raman bands observed at 1350, 1235 cm^{-1} in Trimethylhydroquinone have been assigned C-O stretching modes of vibrations. The in-plane and out-of-plane vibrations of C-O group are in very good agreement with the assignment of chithambarathanu et al [27].

CH₃ vibrations

For the assignments of CH₃ group frequencies, nine fundamental vibrations can be associated to each CH₃ group. Three stretching, three bending, two rocking modes and a single torsional mode describe the motion of the CH₃ group. CH₃ group frequencies

are present in the Trimethylhydroquinone compound and the above modes defined in Table.

The CH₃ symmetric stretching frequency is established at 2815, 2785 cm⁻¹ in FTIR and 2784, 2750 cm⁻¹ FT-Raman. The CH₃ symmetric bending frequencies are attributed at 1390, 1375 cm⁻¹ and 1385 cm⁻¹ in FTIR and FT-Raman respectively. The in-plane rocking found at 948, 924 cm⁻¹ in FTIR and 935 cm⁻¹ in FT-Raman. The out-of-plane rocking modes of CH₃ group are found at 965, 953 cm⁻¹ in FTIR and 915 cm⁻¹ in FT-Raman. The bands obtained at 2518 cm⁻¹ in FTIR and 2552, 2520, 2412 cm⁻¹ in FT-Raman are assigned to CH₃ out-of-plane stretching. The out-of-plane bending modes are assigned at 1215, 1115 cm⁻¹ in FT-IR and 1128 cm⁻¹ in FT-Raman respectively. The assignment of band at 250, 242, and 230 cm⁻¹ in FT-Raman are attributed to CH₃ twisting mode.

Conclusions

The optimized geometries, harmonic vibrational wave numbers and intensities of vibrational bands of Trimethylhydroquinone have been determined using Density Functional Theory -B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d,p) level calculations. This DFT based quantum mechanical approach provides the most reliable theoretical information on the vibrational properties of the molecule. In the present investigations, normal modes of Trimethylhydroquinone have been studied by FTIR and FT-Raman spectroscopies on the basis of Cs point group symmetry. The assignments of most of the fundamentals provided in the present work are believed to be unambiguous.

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