IR, Raman and *ab-initio* calcualtions of 2,6-dimethoxyphenol

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ABSTRACT

IR and Raman spectra of 2,6-dimethoxyphenol were recorded and analyzed. The vibrational wavenumbers of the compound have been computed using the Hartree-Fock/6-31G* basis and compared with the experimental values. Predicted infrared intensities and Raman activities are reported.

INTRODUCTION

Natural methoxyphenols are used in perfumes, soaps, detergents, air fresheners and cosmetics[1]. Lignin is a relatively resistant cell wall constituent of all vascular plants and consists of ether- and carbon-linked methoxyphenols[2]. Photoinduced yellowing of papers manufactured from ultra high yield pulps limits their use to low grade paper products, such as newsprint, catalog, and advertising products. The yellowing process results largely from photoinduced reactions involving the chromophores in lignin; among these, mono- and dimethoxypheonols are believed to play an important role[3]. Laccases, part of a large group of enzymes among the multicopper enzymes, widely occur in higher plants and fungi and these enzymes constitute a very prospective class of enzymes for physiological development and industrial utility, such as bioremediation, organic catalyzed synthesis, pulp and paper biobleaching, and analytical uses. 2,6-dimethoxyphenol was widely used as a substrate of laccases catalysis and activity determination in aqueous solution[4]. Ab initio quantum mechanical method is at present widely used for simulating IR spectra. Such simulations are indispensable tools to perform normal coordinate analysis, so that modern spectroscopy is unimaginable without involving them. In this work, we have calculated the vibrational wavenumbers of the title compound by using Hartree-Fock method and compared it with IR and Raman bands. These calculations are valuable for providing insight into the vibrational spectrum and related molecular parameters.

EXPERIMENTAL

The FT-IR spectrum was recorded on a DR/Jasco FT/IR-6300 spectrometer with KBr pellets. The FT-Raman spectrum was obtained on a Bruker RFS 100/S, Germany**.** For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, resolution 4 cm^{-1}, measurement on solid sample.

Computational details

Calculations of the title compound were carried out with Gaussian03 software package[5] using the HF/6-31G* basis set to predict the molecular structure and vibrational wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavaenumber were calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wavenumber values computed at the HF level contain known systematic

errors due to the negligence of electron correlation[6]. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set. The absence of imaginary wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The observed IR and Raman bands with the relative intensities and calculated wavenumbers and assignments are given in Table. The wavenumbers of the vibrational modes of the methoxy group are known to be influenced by a variety of interesting interactions such as electronic effects, inter-molecular hydrogen bonding and Fermi resonance[7]. Electronic effects such as back-donation and induction, mainly caused by the presence of oxygen atom adjacent to CH_3 group, can shift the position of CH stretching and bending modes[8,9]. In aromatic methoxy compounds, $\upsilon_{as}CH_3$ are expected in the region[10] 2985 ± 20 and 2955 ± 20 cm^{-1}. The computed wavenumbers of modes corresponding to the $\upsilon_{as}CH_3$ group are 3003, 2984, 2962 and 2934 cm^{-1}. The bands observed at 2982, 2930 cm^{-1} in the IR spectrum and at 2985, 2945 cm^{-1} in the Raman spectrum are assigned as asymmetric CH_3 stretching modes. In this mode two C-H bonds of the methyl group are extending while the third one is contracting.

The symmetrical stretching mode $\upsilon_s CH_3$ is expected in the range 2845 ± 15 cm^{-1} in which all the three C-H bonds extend and contract in phase[10]. Theoretical calculations give values of 2875 and 2867 cm^{-1} for the symmetric methyl group stretching modes and the bands at 2881, 2860 (IR), 2855 cm^{-1} (Raman) areassigned as these modes. Two bending vibrations can occur within a methyl group. The first of these, the symmetrical bending vibration $\delta_s CH_3$ involves the in-phase bending of the C-H bonds. The second, the asymmetrical bending mode $\delta_{as}CH_3$ involves out-of-phase bending of the C-H bonds[11]. With methyl esters the overlap of the regions in methyl asymmetric deformations are active (1465 ± 10 and 1460 ± 15 cm^{-1}) is quite strong, which leads to many coinciding wavenumbers[10]. This is obvious, not only for the asymmetric deformation, but also for the symmetric deformations[10] mostly displayed in the

range 1450 ± 20 cm^{-1}. The intensity of these absorptions is only weak to moderate. The HF calculations give 1492, 1489, 1481, 1474 cm^{-1} and 1453, 1447 cm^{-1} as $\delta_{as}CH_3$ and $\delta_s CH_3$ respectively, for the title compound. The bands observed at 1488, 1480, 1469 (IR) and 1445 (IR), 1454 cm^{-1} (Raman) are assigned as asymmetric and symmetric deformations of the methyl group, respectively. The methyl rock ρCH_3 has been observed at 1190 ± 45 cm^{-1} [10]. The second methyl rock[10] absorbs at 1150 ± 30 cm^{-1}. The bands calculated at 1163, 1152, 1140 and 1133 cm^{-1} are assigned as rocking modes of the methyl group. These modes are observed at 1153, 1126 cm^{-1} in the IR spectrum and at 1159, 1127 cm^{-1} in the Raman spectrum. A methoxy group attached to an aromatic ring gives υ_{as}C-O-C in the range 1310-1210 cm^{-1} and υ_sC-O-C in the range[12] 1050-1010 cm^{-1}. The ab initio calculations give 1254, 1185 and 1061, 1014 cm^{-1} as asymmetric and symmetric C-O-C stretching vibrations, respectively. The skeletal C-O- deformation can be found in the region[10] 320 ± 50 cm^{-1}.

The hydroxyl OH group provides three normal vibrations υOH, δOH and γOH, of which not only the stretching vibration but also the out-of-plane deformation are good group vibrations[10]. The hydroxyl stretching vibrations are generally observed in the region[8,12] around 3500 cm^{-1}. The band in the IR spectrum at 3489 cm^{-1} and at 3493 cm^{-1} in the Raman spectrum is assigned as the OH stretching vibration. The results of computation give the wavenumber of this mode as 3577 cm^{-1}. The moderate to strong absorption at 1350 ± 40 cm^{-1} in the spectra of phenols is assigned to δOH mode. The band at 1321 (IR), 1330 (Raman) and 1322
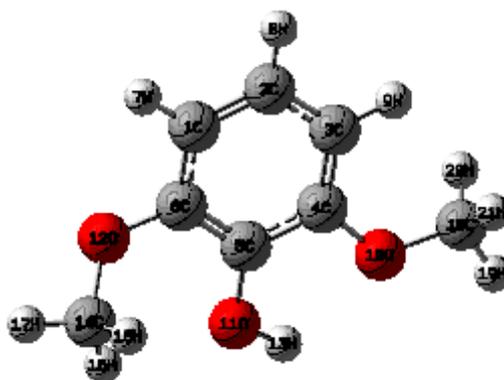
Table 1: Calculated vibrational wavenumbers, measured Infrared and Raman band positions and assignments

$\upsilon_{(HF)}$ (cm^{-1})	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	IR intensity (KM/Mol)	Raman activity (A**4/AMU)	Assignments
3577	3489 sbr	3493 w	135.01	58.28	υOH
3046	3095 w	3094 w	7.01	162.77	υCH
3038	3024 w	3078 w	11.88	59.32	υCH
3013		3016 w	8.89	65.95	υCH
3003			13.45	60.25	υ_{as}Me
2984	2982 w	2985 w	24.93	109.75	υ_{as}Me
2962			48.63	104.72	υ_{as}Me
2934	2939 w	2945 w	42.12	47.76	υ_{as}Me
2875	2881 w		54.87	110.36	υ_{s}Me
2867	2860 w	2855 m	38.18	114.67	υ_{s}Me
1628	1622 s		94.76	16.92	υPh
1608	1598 w	1595 s	3.07	18.75	υPh
1503	1508s	1509 w	78.84	2.62	υPh
1492			15.83	19.84	δ_{as}Me
1489	1488 s		18.64	14.07	δ_{as}Me
1481			95.57	3.19	υPh
1481	1480 s		9.13	28.20	δ_{as}Me
1474	1469 s		8.59	24.05	δ_{as}Me
1453		1454 m	19.21	6.72	δ_{s}Me
1447	1445 s		21.93	7.78	δ_{s}Me
1322	1321 w	1330 s	27.71	12.22	δOH
1283	1288 s	1295 w	187.63	3.27	δCH, υPh
1254	1240 s	1242 w	217.34	0.80	υ_{as}C-O-C
1222	1220 s		23.85	0.89	υC-O
1185		1192 w	173.61	2.30	υ_{as}C-O-C
1177	1174 w	1178 w	41.47	10.28	δCH
1163		1159 w	9.99	3.19	ρMe
1152	1153 w		50.54	8.73	ρMe
1140			2.58	6.60	ρMe
1133	1126 s	1127 w	1.02	4.88	ρMe
1077		1080 s	181.57	1.31	δCH
1061	1057 w	1053 m	47.18	18.33	υ_{s}C-O-C
1014		1017 m	3.71	0.36	υ_{s}C-O-C
992		984 w	33.01	11.65	γCH
927	930 w		0.33	2.11	γCH
868	873 w	880 w	59.51	3.84	δPh(X)
814	813 w	820 s	10.86	3.55	υPh(X)
806	798 s	800 w	97.45	1.36	γCH
727	727 m	727 s	8.97	0.73	γPh
663			9.17	25.25	γOH
613	612 w	609 w	5.74	2.07	γPh(X)
576	570 w		11.89	2.27	δPh(X)
550			1.20	0.41	δPh(X)
514	529 w	523 m	8.53	4.38	δPh(X)
458		465 m	16.60	5.05	γPh(X)
435			193.71	3.12	γPh(X)
379			13.17	1.04	δC-O-
331		338 s	7.17	2.57	δC-O-
297			1.90	1.59	γPh(X)
272			0.09	1.78	tMe
238		244 m	0.73	1.13	tMe
201			1.97	0.94	tMeO
183		180 m	3.14	0.92	tMeO
156			6.27	0.31	tPh
120			0.92	1.05	tPh
61			5.24	0.21	tPh
36			8.67	0.58	tPh

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ -rocking; t-torsion; s-strong; b-broad; v-very; w-weak; Ph-phenyl; Me –methyl; X-substituent sensitive; subscript : as-asymmetric; s-symmetric

cm^{-1} (HF) is assigned as δOH mode. The OH out-of-plane deformations in the spectra of phenols[10] take up the whole region 685 ± 115 cm^{-1}. The band at 663 cm^{-1} given by ab initio calculations is assigned as γOH mode and experimentally no band is observed.

For tri-substituted benzenes, the aromatic CH stretching vibrations[10] absorb weakly to moderately between 3110 and 3000 cm^{-1}. For the title compound, the bands observed at 3095, 3024 cm^{-1} in the IR spectrum and at 3094, 3078, 3016 cm^{-1} in the Raman spectrum are assigned as νCH modes of the phenyl ring. The theoretically calculated values are 3046, 3038 and 3013 cm^{-1}. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and 1440 cm^{-1} are good group vibrations[10]. The fifth ring stretching vibration is active near 1315 ± 65 cm^{-1}, a region that overlaps strongly with that of the CH in-plane deformation[10]. The sixth

ring stretching vibration, the ring breathing mode, appears as a weak band near 1000 cm in mono, 1,3-di- and1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from other modes. For the title compound, the νPh modes are observed at 1622, 1598, 1508, 1288 cm^{-1} in the IR spectrum and at 1595, 1509, 1295 cm^{-1} in the Raman spectrum. The HF calculations showed this modes at 1628, 1608, 1503, 1481, 1288 cm^{-1}. For the title compound, the ring breathing mode is observed at 813 cm in the IR spectrum and at 820 cm^{-1} in the Raman spectrum. The ab initio calculations give this mode at 814 cm^{-1}. The aromatic in-plane and out-of-plane CH deformations are observed in the range 1050-1305 and 700 – 1000 cm^{-1}, respectively[10]. For 1,2,3-trisubstituted benzenes, strong νCH and νPh are respectively observed[13] at 790 ± 40 and 710 ± 30 cm^{-1} and in the present case, these modes are observed at 798 and 727 cm^{-1} in the IR spectrum, respectively.

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