

“Troublesome” Vibrations of Aromatic Molecules in Second-Order Möller–Plesset and Density Functional Theory Calculations: Infrared Spectra of Phenol and Phenol-OD Revisited

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The infrared spectra of phenol and phenol-OD are thoroughly reinvestigated, to resolve the contradictory assignment of some vibrations. The harmonic frequencies, integrated IR intensities, and potential energy distribution (PED) have been calculated by the B3LYP method with the 6-311++G(df,pd) basis set. The Fourier transform infrared (FT-IR) spectra of phenol and phenol-OD have been measured in carbon tetrachloride and cyclohexane solutions, in the frequency range 3700–400 cm⁻¹, and the experimental integrated infrared intensities are reported. On the basis of the results obtained, the detailed assignment of all the fundamental modes of Ph-OH and Ph-OD are presented. The study demonstrates that density functional B3LYP is clearly superior to the ab initio Hartree–Fock (HF) and second-order Möller–Plesset (MP2) methods in reliable prediction of the vibrational spectra of phenol. In particular, it is shown that scaling of the B3LYP-calculated frequencies of the CH and OH(OD) stretching vibrations by the scaling factor, derived by Baker et al. [*J. Phys. Chem. A* **1998**, 102, 1412] gives excellent agreement between theoretical and experimental frequencies of these vibrations. Detailed theoretical investigations are performed for these troublesome normal modes in phenol and benzene, which show the largest deviations between the MP2-predicted frequencies and the experimental ones. It has been demonstrated that these modes have almost identical atomic displacements and potential energy distributions in both the molecules. The electron correlation effects and basis set dependences are examined, and the nature of these problematical vibrations in aromatic molecules is discussed.

Introduction

Despite extensive theoretical studies of the IR spectra of phenol reported in the past few years,^{1–7} the assignment of several vibrations remains contradictory. Furthermore, there are still some controversies in the literature about the ability of the second-order Möller–Plesset (MP2) method to predict reliable molecular properties, vibrational frequencies, and normal coordinates of phenol, phenoxy radical, and their hydrogen-bonded complexes. Recently, we have reported B3LYP/6-311++G(df,pd) calculations of the molecular structures and infrared spectra of *p*-chlorophenol, *p*-bromophenol, and their OD-deuterated derivatives.⁸ Our theoretical results showed very good agreement with the experimental data and allowed us to make a clear-cut assignment of all fundamental transitions in the electronic ground state of these compounds. In particular, it has been demonstrated that the frequencies of the C–H stretching vibrations are significantly affected by the presence of the hydroxy group in phenol, and their assignment is different from that reported for benzene. However, in a number of earlier experimental studies on phenol,^{9–12} the CH stretching vibrations were interpreted in terms of “benzene-like” vibrations. In recent works,^{2,3} the assignments given for the CH stretching vibrations are quite arbitrary; all modes are indeed described as “ ν CH”. Furthermore, Keresztury et al.³ assigned the band near 1200 cm⁻¹ to the OH in-plane bending vibration, which has been contradicted by the recent data obtained from dispersed fluo-

rescence.⁹ The unequivocal assignment of the normal modes involving the vibrations of the OH group is indispensable for understanding the spectral changes resulting from hydrogen-bond formation with proton acceptors.

In the present work, a detailed assignment of all fundamentals of C₆H₅OH (Ph-OH) and C₆H₅OD (Ph-OD) is reported, based on the B3LYP/6-311++G(df,pd)-calculated vibrational frequencies, integrated IR intensities, and potential energy distribution. These are, to date, the largest calculations performed on these molecules (275 contracted basis functions). The theoretical studies are complemented by experimental investigation of the IR spectra of Ph-OH and Ph-OD in inert solvents. The integrated IR intensities of both molecules are reported. It should be noted that these data are lacking in the literature, since Lampert et al.² reported only the absorbances at band maxima for Ph-OH. Most recently,¹³ the anharmonicities for the CH, OH, and OD stretching vibrations were determined from the overtones observed in the near-IR spectra of Ph-OH and Ph-OD. These anharmonicities allowed us to obtain the experimental harmonic frequencies, which show very good agreement with the B3LYP-calculated harmonic frequencies. On the basis of the results obtained, the detailed assignment of all the CH stretching vibrations has been made, and the contradictory assignment of several other vibrations has been clarified.

The second purpose of this work is the detailed investigation of the nature of some vibrations in aromatic molecules, for which the MP2 (and HF) calculations do not reproduce the correct frequencies and the normal coordinates. The electron

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correlation effects and the basis set dependences have been examined for these problematical modes.

Materials and Methods

Theoretical. The optimized equilibrium structure, harmonic frequencies, and IR intensities of phenol and benzene were calculated by the MP2 method¹⁴ and density functional three-parameter hybrid (DFT/B3LYP) method.^{15,16} Three basis sets were employed: 6-31G(df,p), 6-311G(2d,2p), and 6-311++G(df,pd).^{17,18} The latter is the valence triple- ζ basis set, which is augmented by *d* and *f* polarization functions on carbon and oxygen atoms and by *p* and *d* polarization functions on hydrogen atoms. In addition, this basis set is supplemented by diffuse functions on all atoms. For phenol, it consists of 275 contracted basis functions (378 primitives). This basis set has been used in calculations with B3LYP and HF methods but not with the MP2 method. The scaling factors for the calculated frequencies (below 2000 cm⁻¹) were obtained from the least-squares fitting to the experimental values. The B3LYP-calculated CH and OH stretching frequencies have been scaled by different factors derived from the recently reported scaling factors of primitive valence force constants.^{19,20} The nonredundant set of 33 internal coordinates has been derived as recommended by Fogarasi and Pulay.²¹ At each theoretical level, the normal coordinate analyses have been carried out, according to the procedure described in our earlier papers.^{22,23} These yielded the potential energy distributions (PEDs) for the investigated compounds. The PED elements are given in terms of the internal coordinates, which are designated as follows: ν , stretching; δ , in-plane bending; γ , out-of-plane bending; τ , torsional vibration. The symmetry coordinates for the six-membered ring are given in ref 22. All calculations have been carried out with the Gaussian 98 package²⁴ running on Cray SV1 and CSGI Origin 2000 supercomputers.

Experimental. The FT-IR spectra of Ph-OH and Ph-OD were recorded at room temperature, in carbon tetrachloride (3700–850 cm⁻¹) and in cyclohexane (850–400 cm⁻¹) solutions at a concentration of 0.05 mol dm⁻³. The spectra were measured at 2 cm⁻¹ resolution on a Bruker 66 FT-IR spectrometer equipped with a KBr beam splitter, a Globar source, and a DTGS detector, with a KBr liquid cell. The integrated intensities were determined by using the Bruker OPUS software, and overlapping bands were deconvoluted with the same software or with the Galactic GRAMS/386 program. Bands characterized by a very weak IR intensity (ν CH vibrations) were recorded in extended scale.

Ph-OH from Across Chemica was crystallized from a petroleum–ether mixture. Ph-OD was prepared by several exchanges with methanol-OD (99%) from Cambridge Isotope Laboratories and about 90% deuteration was achieved. Carbon tetrachloride from Aldrich was dried on molecular sieves.

Results and Discussion

Infrared Spectra of Ph-OH and Ph-OD. The numbering of atoms in phenol is shown in Figure 1. The harmonic frequencies and IR intensities of Ph-OH, computed by both the B3LYP and MP2 methods, are given in Table 1, together with the experimental frequencies and integrated IR intensities measured in inert solvents. The available literature data from the gas-phase IR and Raman spectra have also been included. In Table 2 are shown the results from similar experimental and theoretical studies of Ph-OD. In both tables, the last column gives the potential energy distribution (PED) matrix, calculated at the B3LYP/6-311++G(df,pd) level. The remaining results

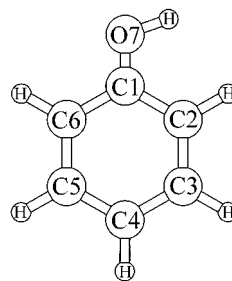


Figure 1. Atom numbering in phenol.

from the B3LYP/6-31G(df,p) and HF/6-311++G(df,pd) calculations for Ph-OH and Ph-OD are given in Tables 1S and 2S of Supporting Information.

The overall agreement between the theoretical frequencies and IR intensities computed at the B3LYP/6-311++G(df,pd) level and the corresponding experimental results is excellent, which indicates that the reported band assignment is correct.

According to the PED, the Q20 mode has a predominant contribution from the OH in-plane bending vibration, δ (OH). The B3LYP-predicted frequency (1173 cm⁻¹) is in very good agreement with our experimental frequency of 1179 cm⁻¹. This assignment is also supported by the fact that this absorption disappears in Ph-OD. In the recently reported dispersed fluorescence (DF) spectrum of Ph-OH, the δ (OH) vibration has been assigned at about the same frequency, 1174 cm⁻¹.⁹ The band at 1197 cm⁻¹, assigned to δ (OH) in ref 3, was not observed in the present work. The same remark also holds for the 1176 cm⁻¹ absorption in Ph-OD. It should be noted that Schiefke et al.,⁷ in their HF/6-31G(d,p) calculations of phenol–ammonia complex, obtained incorrect frequency shifts for the modes involving δ (OH). As follows from the present study, a similar deficiency is noted for the HF/6-311++G(df, pd) level of calculations. Despite the use of such a large basis set, the HF frequency of the mode Q20 is significantly overestimated, by about 75 cm⁻¹, even after scaling (Table 1S in Supporting Information). Apparently, the correlations effects are important for reproducing the frequency of the δ (OH) vibration in phenol.

The normal mode Q23 (Table 1) also involves a significant contribution (18%) from the δ (OH) vibration and is attributed to the absorption at 1341 cm⁻¹. Both the calculated infrared intensity and frequency of this mode agree with the experimental values. It should be noted that when the Ph-OH concentration increases, the two bands at 1179 and 1341 cm⁻¹ decrease in intensity and they are both shifted to higher frequencies, 1221 and 1360 cm⁻¹, respectively. The formation of higher aggregates increases the frequency of the modes involving an important δ (OH) contribution. The normal mode Q23 is sensitive to the *para*-substitution of phenol, since it is shifted to 1320 cm⁻¹ in the spectra of *p*-ClPh and *p*-BrPh.⁸ As revealed by the calculated PEDs for phenol and benzene, this mode *does not* correspond to the “mode 14” in benzene (in Wilson’s notation²⁵). In earlier experimental studies,¹² mode Q23 was interpreted as being similar to mode 14 in benzene, and this interpretation has been followed by many other authors in the literature.

In deuterated Ph-OD, the OD in-plane bending vibration shows a predominant contribution (81%) to the mode Q13, which is assigned at 920 cm⁻¹ in the IR spectrum. The B3LYP-calculated frequency is very close, 914 cm⁻¹.

It should be emphasized that in the low-frequency region our B3LYP results show very good agreement with experiment. The calculated frequency of the mode Q1, 225 cm⁻¹, is identical to the experimental frequency.^{9,26} Thus, the earlier assignment of Q1 to the absorption between 235 and 244 cm⁻¹ 2,3,10–12 seems

TABLE 1: Vibrational Frequencies, IR Intensities, and Assignment for Ph-OH^a

Q	sym	exp					B3LYP [6-311++G(df,pd)]		MP2 [6-31G(df,p)]		PED ^h (%) [B3LYP/6-311++G(df,pd)]
		ν^b	A ^c	I_{rel}^d	ν^e	I_{rel}^e	ω^f	A	ω^g	A	
Q1	A''				225.2 ⁱ		225	1	220	1	$\tau_{\text{ring}}(52)$, $\tau_{\text{ring}}(19)$, $\gamma\text{CO}(16)$
Q2	A''	310 ^j			309.2	47	313	110	326	125	$\tau\text{OH}(99)$
Q3	A'	406	2.9	10	403.1	5	399	10	397	10	$\delta\text{CO}(81)$
Q4	A''	NO			408.5	0	412	1	389 ^k	1	$\tau_{\text{ring}}(75)$, $\tau_{\text{ring}}(25)$
Q5	A''	505	6.5	22	502.8	26	503	14	503	3	$\gamma\text{CO}(46)$, $\tau_{\text{ring}}(29)^l$
Q6	A'	528	2.1	7	526.6	5	529	2	519	1	$\delta_{\text{ring}}(76)$, $\nu(\text{C}-\text{O})(11)$
Q7	A'	618	sh		618.7		624	0	612	0	$\delta_{\text{ring}}(83)$
Q8	A''	689	14.7	49	685.9	50	662	10	452 ^k	4	$\tau_{\text{ring}}(93)^m$
Q9	A''	753	19.8	66	750.6	52	742	86	706	78	$\gamma\text{C}_4\text{H}(35)$, $\gamma\text{CO}(20)$, $\gamma\text{C}_3\text{H}(16)$, $\gamma\text{C}_2\text{H}(16)$
Q10	A''	NO			817.2	0	813	0	780	0	$\gamma\text{C}_2\text{H}(46)$, $\gamma\text{C}_6\text{H}(24)$, $\gamma\text{C}_5\text{H}(20)$
Q11	A'	827	2.1	7	823.2	20	816	22	818	17	$\nu(\text{C}-\text{C})(40)$, $\nu(\text{C}-\text{O})(26)$, $\delta_{\text{ring}}(17)$
Q12	A''	882	3.0	10	881	12	872	5	813 ^k	0	$\gamma\text{C}_6\text{H}(40)$, $\gamma\text{C}_2\text{H}(28)$, $\gamma\text{C}_4\text{H}(20)$, $\gamma\text{C}_3\text{H}(11)$
Q13	A''	NO			958	0	946	0	862	0	$\gamma\text{C}_3\text{H}(60)$, $\gamma\text{C}_4\text{H}(20)$, $\gamma\text{C}_2\text{H}(10)$, $\gamma\text{C}_6\text{H}(10)$
Q14	A''	972	sh		972.5	1	965	0	872	0	$\gamma\text{C}_5\text{H}(60)$, $\gamma\text{C}_4\text{H}(22)$, $\gamma\text{C}_6\text{H}(18)$
Q15	A'	999	1.2	4	999.3	5	999	3	1000	0	$\delta_{\text{ring}}(62)$, $\nu(\text{C}-\text{C})(36)$
Q16	A'	1024	1.8	6	1026.1	8	1027	5	1039	4	$\nu(\text{C}_4-\text{C}_5)(30)$, $\nu(\text{C}_3-\text{C}_4)(24)$
Q17	A'	1069	4.0	13	1072.4	10	1077	15	1087	12	$\nu(\text{C}-\text{C})(53)$, $\delta\text{CH}(40)$
Q18	A'	1151	4.8	16	1150.7	38	1161	36	1166	5	$\delta\text{CH}(66)$, $\nu(\text{C}-\text{C})(22)$, $\delta\text{OH}(10)^n$
Q19	A'	1167	1.8	6	1168.9	70	1175	24	1180	3	$\delta\text{C}_3\text{H}(28)$, $\delta\text{C}_6\text{H}(20)$, $\nu(\text{C}-\text{C})(22)$
Q20	A'	1179	22.7	76	1176.5	80	1173 ^k	100	1189	148	$\delta\text{OH}(45)$, $\delta\text{CH}(33)$, $\nu(\text{C}-\text{C})(21)^o$
Q21	A'	1257	22.3	75	1261.7	62	1260	90	1295	68	$\nu(\text{C}-\text{O})(50)$, $\delta\text{CH}(18)$
Q22	A'	1330	0.6	2			1326	7	1442	13	$\nu(\text{C}-\text{C})(75)$, $\delta\text{CH}(21)^p$
Q23	A'	1341	5.4	18	1343	31	1350	24	1345 ^k	23	$\delta\text{CH}(74)$, $\delta\text{OH}(18)$
Q24	A'	1469	12.3	41	1472	23	1479	23	1489	25	$\delta\text{C}_4\text{H}(26)$, $\delta\text{C}_3\text{H}(13)$, $\nu\text{C}_5-\text{C}_6(12)$, $\nu\text{C}_2-\text{C}_3(12)$
Q25	A'	1499	22.6	76	1501	54	1506	58	1524	60	$\delta\text{C}_3\text{H}(19)$, $\delta\text{C}_2\text{H}(17)$, $\nu\text{C}_3-\text{C}_4(12)$, $\delta\text{C}_3\text{H}(12)$
Q26	A'	1598	20.0	67	1603	70	1609	47	1639	28	$\nu(\text{C}_1-\text{C}_2)(24)$, $\nu(\text{C}_4-\text{C}_5)(21)$
Q27	A'	1606	14.8	49	1610		1620	42	1654	41	$\nu\text{C}_1-\text{C}_6(23)$, $\nu\text{C}_3-\text{C}_4(17)$, $\nu\text{C}_2-\text{C}_3(14)$, $\nu\text{C}_5-\text{C}_6(13)$
Q28	A'	3019	0.7	2	3027 ^q		3019	13	3160	10	$\nu(\text{C}_2-\text{H})(-88)$, $\nu(\text{C}_3-\text{H})(+11)$
Q29	A'	NO					3036	0	3180	0	$\nu(\text{C}_5-\text{H})(+52)$, $\nu(\text{C}_4-\text{H})(-27)$, $\nu(\text{C}_3-\text{H})(+11)$
Q30	A'	3044	4.6	15	3049 ^q		3044	16	3188	13	$\nu(\text{C}_3-\text{H})(+56)$, $\nu(\text{C}_5-\text{H})(-27)$
Q31	A'	3052	0.2	1	3063 ^q		3058	16	3201	11	$\nu(\text{C}_4-\text{H})(+45)$, $\nu(\text{C}_6-\text{H})(-36)$, $\nu(\text{C}_3-\text{H})(+17)$
Q32	A'	3076	0.6	2	3074 ^q		3065	4	3207	4	$\nu(\text{C}_6-\text{H})(+53)$, $\nu(\text{C}_4-\text{H})(+21)$, $\nu(\text{C}_5-\text{H})(+20)$
Q33	A'	3611	45.3	142	3656	50	3654	60	3792	56	$\nu(\text{OH})(100)$

^a Vibrational frequencies are given in reciprocal centimeters; IR intensities are in kilometers per mole. Sh indicates shoulder; NO indicates not observed. ^b From IR spectra of cyclohexane and CCl₄ solutions. ^c Experimental integral absorbances (see text). ^d I_{rel} , integral absorbances normalized in such a way that the observed intensity sum of all bands is equal to the B3LYP-calculated intensity sum of the corresponding modes. ^e IR gas-phase data from ref 10. ^f The scaling factor for frequencies was 0.983, except for Q28–Q32 (0.958) and Q33 (0.953); see text. ^g Scaling factor 0.977. ^h Predominant contributions (those below 10% are summarized and given as a total). Symmetry coordinates are shown in ref 22. ⁱ From dispersed fluorescence (DF), ref 9. ^j From ref 27. ^k Reordered frequencies. ^l Different PED values for MP2: $\gamma\text{CO}(82) + \tau_{\text{ring}}(10)$. ^m MP2: $\tau_{\text{ring}}(80) + \tau_{\text{ring}}(19)$. ⁿ MP2: $\delta\text{CH}(86)$. ^o HF: $\delta\text{CH}(40) + \delta\text{OH}(34) + \nu\text{C}-\text{C}(20)$. ^p HF: $\nu\text{C}-\text{C}(57) + \delta\text{CH}(36)$. MP2: $\nu\text{C}-\text{C}(89)$. ^q The Raman gas-phase data from ref 11.

to be wrong. According to our calculations, the OH torsional vibration in phenol is a “pure” vibration (Q2), and the B3LYP-predicted frequency of this mode, 313 cm⁻¹, is in perfect agreement with the experimental values, 309.2 cm⁻¹ (vapor)¹⁰ and 310 cm⁻¹ (cyclohexane solution).²⁷

Also for Ph-OD, the lowest vibrational frequencies predicted at the B3LYP/6-311++G(df,pd) level are in excellent agreement with experiment, as shown in Table 2. For the modes Q1, Q2, and Q3, the calculated frequencies are 211, 244, and 379 cm⁻¹, while the corresponding experimental frequencies are 211.5, 246.5, and 381.8 cm⁻¹, respectively.²⁶ According to the B3LYP results, the OD torsion vibration mixes with the ring deformation and contributes to two bands of similar infrared intensities. This is in accordance with the experimental results of Larsen and Nicolaisen,²⁶ who have shown that OD torsion contributes to two bands of nearly the same intensity, at 211.5 and 246.5 cm⁻¹ in the IR spectrum of Ph-OD. This important conclusion should be taken into account in the calculation of the rotational barrier of this molecule.

The detailed assignment of the CH stretching vibrations in phenol is presented in Tables 1 and 2. To give a better picture of these normal modes, we have also indicated the relative signs of the contributing internal coordinates. The frequencies of the observed fundamentals were obtained from the deconvolution of the bands in the CH stretching region. The experimental frequencies at 3019, 3044, 3052, and 3076 cm⁻¹ have been assigned to the modes Q28, Q30, Q31, and Q32, respectively.

It should be noted that all the theoretical methods consistently predict zero IR intensity for the mode Q29; therefore, the corresponding band is probably not observed in the spectrum. It is interesting to note that the $\nu(\text{C}_2-\text{H})$ stretching vibration predominates, at 88%, in the mode Q28, and it has the lowest frequency of all the CH stretching modes in phenol. The C₂-H bond is in the vicinity of the O₇-H bond, which causes slight elongation and weakening of the former. Thus, the band at 3019 cm⁻¹ observed in the infrared, and at 3027 cm⁻¹ in the Raman spectra of phenol, are assigned with confidence to the C₂-H stretching vibration. In the Ph-OD derivative, the corresponding $\nu(\text{C}_2-\text{H})$ stretching is observed at 3015 cm⁻¹ in the infrared spectrum.

It has been shown by Pulay and co-workers^{19,20} that the direct scaling of primitive valence force constants (obtained from B3LYP calculations) gives much better agreement between the calculated and experimental frequencies than the use of the same scaling factor for all theoretical frequencies. Thus, we have scaled the B3LYP-calculated frequencies of the CH stretching vibrations by a factor of 0.958. This value corresponds to the scaling factor of 0.918 derived for the valence CH stretching force constant.¹⁹ It is remarkable, indeed, how excellent agreement has been obtained between the B3LYP-calculated frequencies of $\nu(\text{CH})$ modes and experimental data. The use of this scaling factor almost reproduces the experimental frequencies (!), as shown in Tables 1 and 2. The results obtained from these studies support our earlier suggestion¹³ that the weak band at

TABLE 2: Vibrational Frequencies, IR Intensities, and Assignment for Ph-OD

	sym	exp			B3LYP [6-311++G(df,pd)]		MP2 [6-31G(df,p)]		PED ^g (%) [B3LYP/6-311++G(df,pd)]
		ν^b	A ^c	$I_{\text{rel}}^{d,e}$	ω^e	A	ω^f	A	
Q1	A''	211.5 ^h			211	25	210	14	$\tau\text{OD}(42)$, $\tau_3\text{ring}(32)$, $\tau_2\text{ring}(12)^j$
Q2	A''	246.3 ^h			244	35	249	54	$\tau\text{OD}(56)$, $\tau_3\text{ring}(23)$, $\gamma\text{CO}(11)^j$
Q3	A'	381.8 ^h			379	11	377	11	$\delta\text{CO}(79)$
Q4	A''	416	0.1	0	411	0	388	0	$\tau_2\text{ring}(75)$, $\tau_3\text{ring}(25)$
Q5	A''	504	2.7	9	503	12	502	1	$\gamma\text{CO}(46)$, $\tau_3\text{ring}(30)$
Q6	A'	524	0.6	2	523	2	514	1	$\delta_2\text{ring}(75)$, $\nu(\text{C}-\text{O})(12)$
Q7	A'	620	0.2	1	623	0	611	0	$\delta_3\text{ring}(84)$
Q8	A''	689	1.9	6	662	9	452 ^k	4	$\tau_1\text{ring}(100)$
Q9	A''	749	18.4	60	742	89	706	80	$\gamma\text{C}_4\text{H}(35)$, $\gamma\text{CO}(20)$, $\gamma\text{C}_3\text{H}(16)$, $\gamma\text{C}_2\text{H}(15)$
Q10	A''	807	1.0	3	809	10	812	6	$\nu(\text{CO})(24)$, $\nu(\text{C}_1-\text{C}_6)(20)$, $\delta_1\text{ring}(16)$
Q11	A'	827	0.4	1	812	0	779 ^k	1	$\gamma\text{C}_2\text{H}(46)$, $\gamma\text{C}_6\text{H}(25)$, $\gamma\text{C}_5\text{H}(19)$
Q12	A''	882	2.8	9	872	5	813	1	$\gamma\text{C}_6\text{H}(40)$, $\gamma\text{C}_2\text{H}(28)$, $\gamma\text{C}_4\text{H}(21)$, $\gamma\text{C}_3\text{H}(11)$
Q13	A''	920	19.5	64	914	87	923	90	$\delta\text{OD}(81)$, $\nu(\text{C}-\text{C})(14)$
Q14	A''	NO			946	0	862 ^k	0	$\gamma\text{C}_3\text{H}(60)$, $\gamma\text{C}_4\text{H}(20)$, $\gamma\text{C}_2\text{H}(10)$, $\gamma\text{C}_6\text{H}(10)$
Q15	A'	970			965	0	872	0	$\gamma\text{C}_5\text{H}(60)$, $\gamma\text{C}_4\text{H}(22)$, $\gamma\text{C}_6\text{H}(18)$
Q16	A'	999	0.6	2	999	1	1001	0	$\delta_1\text{ring}(62)$, $\nu(\text{C}-\text{C})(37)$
Q17	A'	1024	1.3	4	1027	4	1039	2	$\nu(\text{C}_4-\text{C}_5)(30)$, $\nu(\text{C}_3-\text{C}_4)(25)$, $\delta\text{CH}(24)$
Q18	A'	1075	3.6	12	1085	10	1094	8	$\nu(\text{C}-\text{C})(48)$, $\delta\text{CH}(35)$
Q19	A'	1151	1.1	4	1163	2	1167	1	$\delta\text{CH}(81)$, $\nu(\text{C}-\text{C})(19)$
Q20	A'	1167	2.3	7	1175	13	1180	6	$\delta\text{CH}(78)$, $\nu(\text{CC})(22)$
Q21	A'	1249	47.4	154	1253	131	1289	93	$\nu(\text{C}-\text{O})(52)$, $\delta_1\text{ring}(11)$
Q22	A'	1310	0.6	2	1313	7	1436	6	$\nu(\text{C}-\text{C})(75)$, $\delta\text{CH}(20)^j$
Q23	A'	1332	0.3	1	1335	3	1326 ^k	10	$\delta\text{CH}(80)$, $\nu(\text{C}-\text{C})(16)$
Q24	A'	1470	2.0	7	1469	4	1481	4	$\delta\text{CH}(55)$, $\nu(\text{C}-\text{C})(38)$
Q25	A'	1497	29.9	97	1504	80	1521	83	$\delta\text{CH}(58)$, $\nu(\text{C}-\text{C})(35)$
Q26	A'	1599	sh		1604	18	1635	10	$\nu\text{C}_1-\text{C}_2(23)$, $\nu\text{C}_4-\text{C}_5(22)$, $\nu\text{C}_3-\text{C}_4(11)$, $\nu\text{C}_1-\text{C}_6(10)$
Q27	A'	1603	35.1	114	1617	73	1651	61	$\nu\text{C}_5-\text{C}_6(20)$, $\nu\text{C}_2-\text{C}_3(19)$, $\nu\text{C}_1-\text{C}_6(16)$, $\nu\text{C}_3-\text{C}_4(12)$
Q28	A'	2666	21.9	68	2660	38	2760	36	$\nu(\text{O}-\text{D})(100)$
Q29	A'	3015	0.4	1	3019	14	3160	11	$\nu(\text{C}_2-\text{H})(-88)$, $\nu(\text{C}_3-\text{H})(+11)$
Q30	A'	NO			3036	0	3180	0	$\nu(\text{C}_5-\text{H})(+52)$, $\nu(\text{C}_4-\text{H})(-27)$, $\nu(\text{C}_3-\text{H})(+11)$
Q31	A'	3037	4.2	14	3044	17	3188	13	$\nu(\text{C}_3-\text{H})(+56)$, $\nu(\text{C}_5-\text{H})(-27)$
Q32	A'	3045	3.1	10	3058	16	3201	11	$\nu(\text{C}_4-\text{H})(+45)$, $\nu(\text{C}_6-\text{H})(-36)$, $\nu(\text{C}_3-\text{H})(+17)$
Q33	A'	3072	0.7	3	3065	4	3207	4	$\nu(\text{C}_6-\text{H})(+53)$, $\nu(\text{C}_4-\text{H})(+21)$, $\nu(\text{C}_5-\text{H})(+20)$

^a Vibrational frequencies are given in reciprocal centimeters; IR intensities are in kilometers per mole. NO, not observed. ^b From IR spectra of cyclohexane and CCl₄ solutions (this work); otherwise as indicated. ^c Experimental integral absorbances (see text). ^d I_{rel} , integral absorbances normalized in such a way that the observed intensity sum of all bands is equal to the B3LYP-calculated intensity sum of the corresponding modes. ^e The scaling factor for frequencies was 0.983, except for Q28 (0.953) and Q29–Q33 (0.958); see text. ^f Scaling factor 0.977. ^g Predominant contributions (those below 10% are summarized and given as a total). Symmetry coordinates are shown in ref 22. ^h From gas-phase IR spectrum, ref 26. ⁱ Different PED values for HF: $\tau_3\text{ring}(47) + \gamma\text{CO}(18) + \tau\text{OD}(14)$. MP2: $\tau_3\text{ring}(46) + \tau\text{OD}(23) + \tau_1\text{ring}(18)$. ^j HF: $\tau\text{OD}(87)$. MP2: $\tau\text{OD}(77)$. ^k Reordered frequencies. ^l HF: $\nu\text{C}-\text{C}(57) + \delta\text{CH}(36)$. MP2: $\nu\text{C}-\text{C}(89)$.

3095 cm⁻¹ does not correspond to a fundamental transition, but it should be assigned to a combination: $\nu\text{Q27} + \nu\text{Q25} = (1606 + 1499) \text{ cm}^{-1}$.

We have also compared the unscaled theoretical frequencies of the CH stretching vibrations with the so-called “observed harmonic frequencies”, which were derived from the fundamentals, overtones, and combinations bands observed in the near-IR spectrum of phenol.¹³ The experimental harmonic frequencies, ω^e , can be obtained from the observed fundamental transition frequencies (ω_{01}^{obs}) and the anharmonicity constants (X) by the expression²⁸

$$\omega^e = \omega_{01}^{\text{obs}} + 2X \quad (1)$$

The X values for the $\nu(\text{CH})$ vibrations range between 51 and 72 cm⁻¹.¹³ It follows from this comparison that the experimentally derived harmonic frequencies of the CH stretching vibrations are in very good agreement with the harmonic frequencies calculated at the B3LYP/6-311++G(df,pd) level (Supporting Information). The relative errors between the B3LYP (unscaled) and the experimental harmonic frequencies are as follows: 0.9%, 0.3%, 0.5%, and 0.7% for the modes Q28, Q30, Q31, and Q32, respectively.

The anharmonicity constants for the $\nu(\text{OH})$ and $\nu(\text{OD})$ vibrations of Ph-OH and Ph-OD are 85 and 44 cm⁻¹,¹³ respectively. These constants give ω^e values of 3781 and 2754 cm⁻¹ for $\nu(\text{OH})$ and $\nu(\text{OD})$, respectively. The B3LYP-calculated unscaled harmonic frequencies of these stretching vibrations are

very similar; the relative error is about 1.4% (Supporting Information). However, it should be pointed out that scaling of the B3LYP-calculated frequencies of the $\nu(\text{OH})$ and $\nu(\text{OD})$ stretching vibrations by a factor of 0.953 [very similar to that used for $\nu(\text{CH})$] leads to excellent agreement between theoretical and the experimental results, as shown in Tables 1 and 2.

Troublesome Modes in Phenol and Benzene. In our earlier studies of phenol,¹ we demonstrated that the MP2/6-31G(d,p) level of calculations fails in predicting the frequencies of two vibrations in phenol: the so-called ring puckering and the in-plane ring deformation mode. A very similar effect was noticed by Goodman et al.²⁹ in the MP2/6-311G(d,p) calculations of benzene: the theoretical frequency of mode 4 was too low by about 300 cm⁻¹, whereas that of mode 14 was too high by about 150 cm⁻¹. Handy and co-workers^{30–32} have argued that a large basis set (TZ2P+f) containing an f polarization function on each carbon atom is required to obtain a converged MP2 quadratic force field for benzene, and the f basis functions are crucially important for reproducing the frequencies. Nevertheless, in recent years, several MP2 calculations have been reported in which the authors neglected to carefully investigate the forms of the normal modes.^{33,34} This may cause an erroneous assignment of the MP2-calculated frequencies of phenol and its hydrogen-bonded complexes.

In Table 1 are compared the theoretical results calculated for phenol by the B3LYP/6-311++G(df,pd) and the MP2/6-31G(df,p) methods. Several inconsistencies between the B3LYP and

TABLE 3: Comparison of the Experimental and Theoretical Frequencies of the “Troublesome” Vibrational Modes in Benzene and Phenol, Calculated with the MP2 and B3LYP Methods and Different Basis Sets

modes	exp ^a	MP2 ^b			TZ2P+f	B3LYP ^c		
		6-31G (d,p)	6-31G (df,p)	6-311G (2d,2p)		6-31G (df,p)	6-311G (2d,2p)	6-311++G (df,pd)
mode 4 (benzene)	707	490	507	641	684 ^d	707	709	723
Q8 (phenol)	686	456	453	644		687	690	660
mode 5 (benzene)	990	902	889	920	996 ^d	1001	996	1021
Q14 (phenol)	972	895	875	910		969	972	962
mode 14 (benzene)	1309	1438	1437	1410	1461 ^d	1318	1301	1335
Q22 (phenol)	1330	1448	1446	1423		1326	1318	1324

^a The experimental results for benzene are from ref 29, for phenol, the results are our data. ^b MP2 frequencies were scaled by 0.98, except as indicated. ^c B3LYP frequencies were scaled by 0.98. ^d Unscaled frequencies are from ref 30.

MP2 results are evident. The MP2 frequencies of the out-of-plane vibrations corresponding to the normal modes Q9, Q12, Q13, and Q14 are underestimated by about 40, 68, 96, and 100 cm^{-1} , respectively. However, the most striking fact is that the MP2 frequency of the ring puckering mode (Q8) is lower than the experimental one, by as much as 230 cm^{-1} , despite the use of the *f* polarization functions in the basis set. Furthermore, the MP2-predicted frequency of the mode Q22 is too high by about 112 cm^{-1} when compared to the experimental data. As follows from Table 2, similar inconsistencies are observed for the deuterated phenol. The MP2/6-31G(df,p) method does not reproduce the frequencies of the following modes: Q8, Q9, Q11, Q12, Q14, Q15, and Q22 in Ph-OD.

For comparison, similar calculations have been performed for benzene. From the detailed examination of the calculated potential energy distribution (PED) for benzene, it is clear that the MP2 method fails in predicting the frequencies of the analogous normal modes. In Figure 2 are illustrated the three troublesome normal modes in benzene and the corresponding modes in phenol, for which the MP2-predicted frequencies show the largest error with experiment. In this figure, comparison is made between the experimental frequencies and those computed by the B3LYP and MP2 methods with the same basis set, 6-31G(df,p). The atom displacements and PEDs are taken from the B3LYP calculations.

In benzene, mode 4 (B_{2g}) is observed at 707 cm^{-1} .²⁹ This mode is called the ring-puckering vibration (and is designated by the symmetry coordinate τ_1 in ref 21). The B3LYP-calculated frequency of this mode is in perfect agreement with experiment, whereas the MP2 frequency is dramatically too low, by about 200 cm^{-1} . Analogous results have been obtained for the corresponding mode Q8 in phenol, as is shown in Figure 2.

In mode 5 (B_{2g}), the amplitudes of the motion of the hydrogen atoms are larger than those in mode 4. Therefore, mode 5 in benzene, and the corresponding mode Q14 in phenol, are interpreted as arising from the out-of-plane CH vibrations. The MP2-calculated frequencies of these modes are underestimated by about 100 cm^{-1} when compared to the experimental data.

The third troublesome mode 14 (B_{2u}) in benzene, and the corresponding mode Q22 in phenol, have predominant contributions from the CC stretching vibrations (84% and 75%, respectively). As shown in Figure 2, the MP2 computations yield much too high frequencies: the experimental values are overestimated by 128 cm^{-1} for benzene and by 112 cm^{-1} for phenol. In contrast, the B3LYP/6-31G(df,p) calculated frequencies of these modes are in very good agreement with experiment.

To examine the basis set dependence of these modes, we have performed the MP2 and B3LYP calculations on benzene and phenol using different basis sets. The results for the problematical normal modes are compared in Table 3. It is seen for modes 4 and 5 in benzene (and modes Q8 and Q14 in phenol) that the

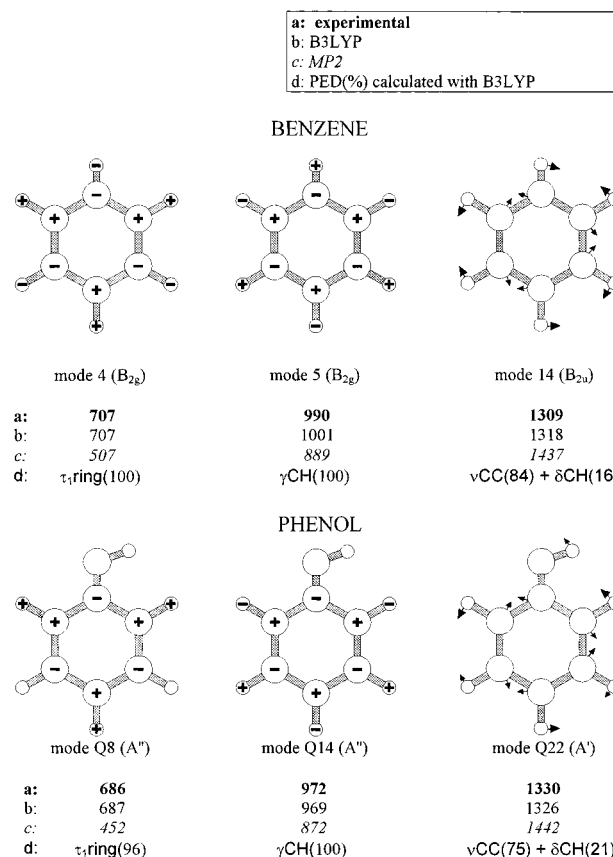


Figure 2. The three “troublesome” normal modes in benzene and phenol: theoretical frequencies, calculated by the B3LYP and MP2 methods with the 6-31G(df,p) basis set, versus experimental data.

use of the 6-311G(2d,2p) basis set improves the MP2 results when compared to those predicted at the MP2/6-31G(df,p) level. However, the frequency of mode 14 in benzene, and that of mode Q22 in phenol, shows still a large departure from the experimental ones. In Table 3, we have also shown the results reported for benzene by Handy et al.³⁰ Their calculations at the MP2/TZ2P+f level yielded the frequencies of modes 4 and 5 in satisfactory agreement with experiment; however, the frequency of mode 14 in benzene is the most overestimated (by 152 cm^{-1}). In contrast to the MP2 results, all B3LYP-calculated frequencies are in excellent agreement with experiment, as shown in Table 3. In particular, the frequencies computed at the B3LYP/6-31G(df,p) level reproduce very well the experimental data for phenol. A further increase in the basis set in the B3LYP calculations does not seem to improve the results obtained for both the molecules.

A similar failure of the MP2 method in calculating vibrational spectra has been encountered in our earlier studies on bicy-

clobutene (C₄H₄),³⁵ which is a nonplanar, highly strained molecule with an unsaturated CC bond. Simandiras et al.³⁶ have also reported anomalous frequency lowering in the MP2 calculations of acetylene and ethylene.

The question arises why the MP2 method fails in predicting the frequencies of some modes in aromatic and unsaturated molecules? The examination of the out-of-plane displacements of the carbon atoms, in mode 4 (and mode Q8 in phenol), reveals that distortion of the molecule along these normal coordinates will elongate all C—C bonds, as displayed in Figure 2. Further distortion may, eventually, lead to a hypothetical puckered structure of the ring, which consists of the radical carbon atoms. Thus, the MP2 method, with the inherent single-reference wave function, is inadequate for a proper description of different electron configurations that should be considered in this normal mode. The use of the very large basis set may somewhat “cure” this MP2 deficiency, by adding orbitals with angular momentum beyond that of the ground electronic state. Interestingly, these modes do not show significant basis-set dependence in the B3LYP calculations.

In the case of normal mode 14 in benzene (and mode Q22 in phenol), distortion of the molecule along the normal coordinates will lead to one of the Kekule structures of the benzene ring, as noted by Handy et al.³⁰ During this in-plane distortion, the electron density between two carbon atoms markedly increases in each “shorter” C—C bond. The MP2 method overestimates dynamical electron correlation effects during this normal mode. The predicted force constant is too high, which means that the MP2 potential surface for this normal mode is too steep. This, in turn, yields a too-large value of the vibrational frequency of this mode. According to the results collected in Table 3, a further enlargement of the basis set does not improve the MP2 results for these modes. It is interesting that calculations at the HF/6-311++G(df,pd) level (Table 1S) underestimate the frequency of mode Q22 in phenol, by almost 240 cm⁻¹. This is consistent with the fact that the frequency of this mode depends on the electron correlation effects (being neglected in the HF method). These results clearly show that both the MP2 and HF methods are inadequate for calculation of the frequencies of modes 14 in benzene and Q22 in phenol. Therefore, it is really outstanding that the hybrid density functional method (B3LYP), even with the use of the medium-size basis set 6-31G(df,p), overcomes this problem and excellently reproduces the frequencies of all troublesome normal modes in aromatic molecules.

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Supporting Information Available: Two tables containing the results from the B3LYP/6-31G(df,p) and HF/6-311++G(df,pd) calculations for phenol-OH and phenol-OD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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