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Molecular Geometries and Vibrational Spectra of Phenol, Benzaldehyde, and Salicylaldehyde: Experimental versus Quantum Chemical Data

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Geometric and vibrational spectroscopic data (rotational constants, bond distances and angles, vibrational frequencies, IR intensities, and OH/OD isotope effects) of phenol, benzaldehyde, and salicylaldehyde as calculated at various levels of theory (HF/6-31G(d,p), HF/6-311++G(d,p), MP2/6-31G(d,p), B3P86/6-31G(d,p), BLYP/6-31G(d,p), B3LYP/6-31G(d,p), and B3LYP/6-311++G(d,p)) are reported. The theoretical results are discussed mainly in terms of comparisons with available experimental data. For geometric data (rotational constants and bond distances) the best agreement between theory and experiment is obtained at the MP2 and B3LYP levels. B3P86 calculated data are slightly worse, while HF and BLYP calculations yield distinctly too small and too large bond distances, respectively. B3LYP calculated vibrational spectroscopic data excellently agree with experimental IR spectra for phenol, phenol-OD, and benzaldehyde, and with minor restrictions, also for salicylaldehyde and salicylaldehyde-OD. Considering frequency sequences, IR intensities, and OH/OD isotope effects, reliable and consistent assignments are given. BLYP and B3P86 calculated vibrational spectroscopic data are slightly worse, whereas MP2 and HF calculations suffer from several shortcomings that are already known from calculations of smaller molecules, such as benzene.

Introduction

Recently, we have reported spectroscopic and theoretical data relevant to the characterization of intramolecular hydrogen bonding in a series of 2-hydroxybenzoyl compounds.^{1,2} These studies have shown that the experimentally observed sequence of $\nu(\text{OH})$ stretching frequencies, which can be directly related to the sequence of hydrogen bond strengths, is reasonably well reproduced by quantum chemical calculations at moderate computational levels, such as HF/6-31(d,p) or B3LYP/6-31(d,p). On the basis of hydrogen bond distances and partial charges, the calculations provided a consistent interpretation of this sequence. Within the course of these investigations, we have performed some more extensive calculations on salicylaldehyde, which is the smallest member of the family, and additionally, also on the two parent compounds, phenol and benzaldehyde. The main purpose of these studies was to gain more detailed insight into methodological effects, i.e., into systematic differences between data obtained at different computational levels, with specific regard to the correspondence between calculation and experiment.

Molecular geometries of the three title compounds have been determined experimentally by microwave spectroscopy,^{3–5} rotationally resolved fluorescence spectroscopy,⁶ and electron diffraction.^{7,8} Optimized geometries have been calculated at various computational levels for phenol,^{9–14} benzaldehyde,^{8,15,16} and salicylaldehyde.^{8,17,18} IR and Raman spectra of phenol have been experimentally studied to some detail in earlier works. Based on symmetry considerations, Evans¹⁹ has made extensive assignments for fundamentals and also for overtones and combinational bands. Following earlier considerations about the normal coordinates of monosubstituted benzenes,²⁰ Bist et

al.²¹ have given assignments in terms of “benzene-like” vibrations. From a closer inspection, some obvious differences between Evans’ and Bist’s work become apparent, and both assignments seem to be partly arbitrary. Concerning quantum chemical vibrational data of phenol, to our knowledge the most relevant calculations seem to be those of Schütz et al.⁹ performed at the HF/6-31G** level and, most recently, those of Michalska et al.¹⁴ performed at the MP2/6-31G** and BLYP/6-31G** levels. In both instances, the authors have made assignments based on a comparison between Bist’s benzene-like vibrations²¹ and the calculated normal coordinates. As to benzaldehyde and salicylaldehyde, basic IR and Raman spectra are well-known and covered in several spectral compilations,²² and more detailed experimental or theoretical studies on the vibrational spectra of these two compounds are, however, not available in the literature.^{23–25}

In the present paper, we report calculated geometric and vibrational spectroscopic data of phenol, benzaldehyde, and salicylaldehyde, along with corresponding experimental data as far as available. The calculations include ab initio (HF and MP2) methods, as well as density functional theory methods (B3P86, BLYP, and B3LYP) using 6-31G(d,p) and 6-311++G(d,p) basis sets. The data are presented and inspected in terms of (i) comparisons between experimental and calculated data, (ii) comparisons between theoretical data calculated at different approximation levels, and (iii) comparisons between corresponding data of the three title compounds. In some instances, reference is also made to corresponding data of benzene, which might be termed the “parent–parent” compound. First, we briefly consider rotational constants, which may serve as a first check for the relevance of calculated equilibrium geometries. Second, bond distances are inspected with respect to systematic differences between different approximation levels and with respect to obvious differences between the three title compounds. Third, and above all, we deal with vibrational spectroscopic data. Based on vibrational frequency sequences, intensity patterns, and OH/OD isotope effects obtained from B3LYP

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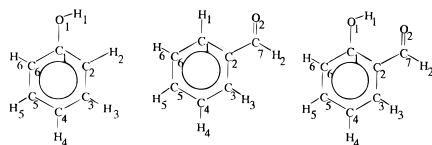
[‡] Institute of Theoretical Chemistry.

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

TABLE 1: Experimental and Calculated Rotational Constants (MHz)

		exptl ^a	B3LYP(II)	B3LYP(I)	BLYP(I)	B3P86(I)	MP2(I)	HF(I)	HF(II)
benzene	$A = B = 2C$	5689.3	5703.7	5691.0	5609.5	5715.0	5693.3	5777.7	5775.8
phenol	A	5650.5	5667.2	5650.4	5563.7	5676.9	5650.6	5750.0	5752.6
	B	2619.2	2618.0	2614.1	2573.7	2630.0	2614.6	2659.1	2660.0
	C	1789.9	1790.8	1787.3	1759.7	1797.3	1787.5	1818.3	1818.9
benzaldehyde	A	5234.3	5253.9	5231.1	5134.3	5251.1	5228.3	5323.9	5330.5
	B	1564.2	1560.6	1561.3	1537.6	1571.8	1563.8	1581.9	1579.7
	C	1204.7	1203.2	1202.4	1184.3	1209.7	1203.8	1219.5	1218.6
salicylaldehyde	A	3216.0	3221.0	3229.0	3192.0	3263.0	3202.0	3229.0	3223.0
	B	1494.0	1494.0	1491.0	1470.0	1501.0	1489.0	1508.0	1510.0
	C	1020.0	1021.0	1020.0	1006.0	1028.0	1016.0	1028.0	1028.0

^a From rotationally resolved IR spectra (benzene³⁴) and from microwave spectra (phenol,³ benzaldehyde,⁴ and salicylaldehyde⁵).

SCHEME 1

calculations, reliable and consistent assignments are given for the IR spectra of the three title compounds.

Computational and Experimental Section

The quantum chemical calculations performed in this work were done with the Gaussian94²⁶ and Gaussian92²⁷ programs. Geometry optimizations and vibrational spectroscopic data were computed at HF, MP2, B3LYP,^{27,28} BLYP,^{29,30} and B3P86³¹ levels using the 6-31G(d,p)³² basis set. Additionally, HF and B3LYP calculations were also performed with the enlarged 6-311++G(d,p)³³ basis set (short-cut notations (I) and (II) are subsequently used to distinguish between (I) 6-31G(d,p) and (II) 6-311++G(d,p) basis sets). In order to improve the visual comparison between experimental and calculated IR spectra in the figures shown below, the calculated absorption lines have been replaced by Gaussian functions with a half-width of 2 cm^{-1} .

Solution and vapor phase IR spectra were measured with Perkin-Elmer 1740 (4000–500 cm^{-1}) and 580B (500–200 cm^{-1}) spectrometers. Because our high-temperature vapor phase spectra (150–200 °C) are only poorly resolved, we exclusively refer to spectra and spectroscopic data of dilute CCl_4 solutions (CS_2 solutions for the 800–700 cm^{-1} range) in the subsequent discussion. As should be noted, the differences between vapor phase and solution frequencies amount to a few wavenumbers only, with the exception of $\nu(\text{O-H})$ and $\nu(\text{C=O})$ stretching vibrations, where the shifts measure about 50 (phenol)–30 (salicylaldehyde) cm^{-1} and about 15 (benzaldehyde and salicylaldehyde) cm^{-1} , respectively. The experimental IR intensities quoted in the tables correspond to absorbance values at band maxima and were taken from spectra normalized to $A = 100$ for the strongest band. The IR spectra shown in the figures are transmission spectra normalized to $T = 98\%$ ($A = 1.5$) for the strongest bands.

The atom numbering of the three compounds is shown in Scheme 1. In order to distinguish between the different types of bonds, we use the following short-cut notation: CH and CC for bonds of the phenyl ring; OH and C–O for bonds involving the phenolic group; C–H, C=O, and C–C for bonds involving the aldehyde group. The internal coordinates are designated $\nu()$ for stretching, $\delta()$ for in-plane deformational, and $\gamma()$ for out-of-plane deformational coordinates, respectively.

Results

A. Rotational Constants. Experimental and calculated rotational constants of the three title compounds and of benzene

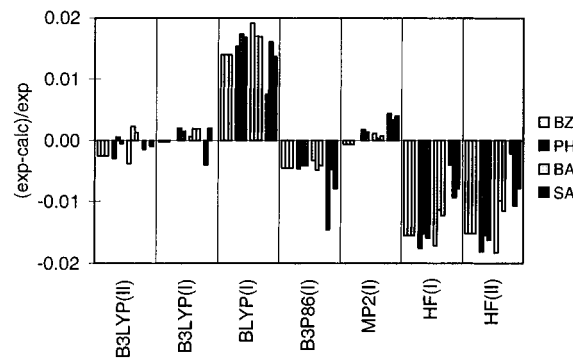


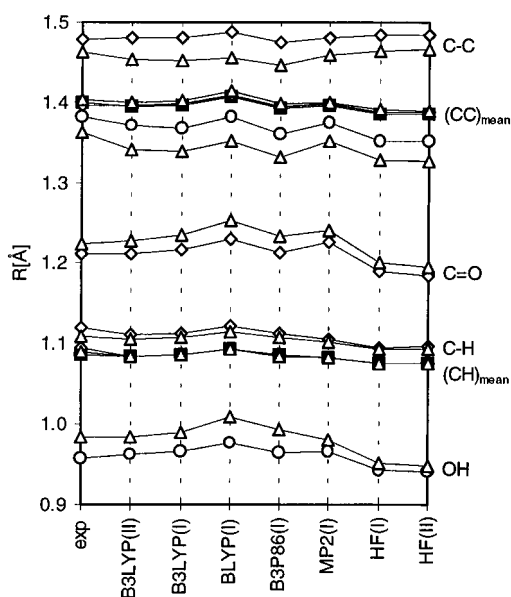
Figure 1. Relative differences between experimental^{13–5,34} and calculated rotational constants, $(\text{exptl} - \text{calcd})/\text{exptl}$, of benzene (BZ), phenol (PH), benzaldehyde (BA), and salicylaldehyde (SA).

are summarized in Table 1. Additionally, Figure 1 shows the relative differences between the experimental and the calculated rotational constants, $(\text{exptl} - \text{calcd})/\text{exptl}$, as obtained at the seven computational levels, which may serve as a first check for the relevance of the calculated geometric data. The best correspondence between experiment and theory is obtained at MP2 and B3LYP levels (the mean absolute deviations are less than 0.2%) and at the B3P86 level ($<0.6\%$), whereas the calculated rotational constants are throughout too large at the HF level ($\approx 1.3\%$) and are throughout too small at the BLYP level ($\approx 1.5\%$). These findings directly correspond to the well-known shortcomings of HF calculations (too small bond distances) and of BLYP calculations (too large bond distances). As to the two different basis sets 6-31G(d,p) and 6-311++G(d,p) the differences between the calculated rotational constants are almost negligible for both of the B3LYP and the HF levels.

B. Distances and Angles. Experimental and calculated bond distances of the three title compounds and of benzene³⁵ are depicted in Figure 2 (for aromatic CC and CH bonds, only mean values are displayed). Additionally, selected experimental and calculated geometric data of phenol, benzaldehyde, and salicylaldehyde are compiled in Table 2 (B3LYP and BLYP calculations) and Table 2S (B3P86, MP2, and HF calculations). The three title compounds can be considered as being essentially planar from experiment (the deviations from planarity are within experimental errors) and are predicted to be planar at all seven computational levels. Concerning methodological effects, in agreement with the above-discussed rotational constants, the HF calculated distances are the smallest (except those of the aldehyde C–C bonds), the BLYP calculated distances are the largest, while the remaining methods yield very similar results in between. The bond distances (and also the angles) as obtained with the two basis sets 6-31G(d,p) and 6-311++G(d,p) show only minor differences for both of the HF and B3LYP calculations. As to the aldehyde C–C bonds, the rather large HF calculated distances, which are accompanied by a corresponding shortening of the C=O distances, result from the

TABLE 2: Selected Experimental and Calculated Bond Distances (Å) and Angles (deg)

	phenol				benzaldehyde				salicylaldehyde			
	exptl ^a	B3LYP(II)	B3LYP(I)	BLYP(I)	exptl ^a	B3LYP(II)	B3LYP(I)	BLYP(I)	exptl ^a	B3LYP(II)	B3LYP(I)	BLYP(I)
(CH) _{mean}	1.086	1.084	1.086	1.093	1.095	1.084	1.084	1.093	1.090	1.084	1.086	1.093
(CC) _{mean}	1.399	1.394	1.397	1.407	1.397	1.396	1.396	1.408	1.404	1.400	1.402	1.413
C1–C2		1.396	1.399	1.410	1.400	1.401	1.403	1.414	1.418	1.419	1.422	1.437
C1–O1	1.381	1.370	1.368	1.383					1.362	1.341	1.339	1.351
O1–H1	0.958	0.963	0.966	0.977					0.985	0.984	0.990	1.009
C2–C1–O1	121.2	122.5	122.6	122.7					120.9	121.9	121.7	121.4
C1–O1–H1	106.4	109.7	109.0	108.1					104.8	107.8	107.0	105.8
C2–C7					1.479	1.481	1.480	1.488	1.462	1.454	1.452	1.456
C7–O2					1.212	1.211	1.216	1.230	1.225	1.228	1.235	1.253
C7–H2					1.120	1.111	1.113	1.123	1.110	1.106	1.108	1.115
C1–C2–C7					120.9	120.6	120.2	120.3	121.4	120.4	119.9	119.6
C2–C7–O2					123.6	125.0	124.7	124.8	123.8	124.4	124.3	124.2
O1...O2									2.650	2.640	2.619	2.617
H1...O2									1.740	1.767	1.729	1.695

^a Electron diffraction data.^{7,8}**Figure 2.** Experimental^{7,8} and calculated bond distances [Å] of benzene, phenol (○), benzaldehyde (◇), and salicylaldehyde (△).

systematic underestimation of conjugation effects associated with HF calculations.

Comparison between the bond distances of the four compounds reveals common trends at all computational levels (Figure 2). (i) The average CH distances are almost identical for all four compounds, whereas the mean CC distances are slightly larger for salicylaldehyde than for the other three compounds. (ii) In more detail, the increase of (CC)_{mean} of salicylaldehyde arises from a lengthening of the C1–C2, C2–C3, C4–C5, and C1–C6 bonds, while the C3–C4 and C5–C6 bond distances are shortened with respect to the other three compounds. As noted previously,⁸ this bond length alternation points to some resonance stabilization of the hydrogen-bonded chelate ring and a corresponding destabilization of the phenyl ring. Quite noticeably, the overall lengthening of the aromatic CC bonds is almost exactly balanced by a corresponding decrease of the C–O, C=O, and C–C bonds within the chelate ring, when compared with phenol and benzaldehyde. (iii) Expectedly and characteristic for hydrogen bonding, we find the OH distance to be distinctly larger in salicylaldehyde than that in phenol, while for the C–O bond the opposite is true. (iv) The C=O distance is distinctly larger in salicylaldehyde than that in benzaldehyde, while the C–H and C–C distances are smaller in salicylaldehyde than those in benzaldehyde.

C. Vibrational Spectra of Benzene. A statistical summary about the correspondence between experimental anharmonic and calculated harmonic frequencies of the three title compounds and of benzene is given in Table 3 (correlation coefficients and mean absolute deviations). Because reliable experimental ν -(CH) stretching frequencies are not available for the title compounds, the ν (XH) (including ν (OH)) stretching frequencies have been excluded from the statistics. Vibrational spectra of benzene have been extensively studied by experiment and theory^{34,36–49} and we have nothing essential to add on these investigations. Nevertheless, since benzene is our parent–parent compound it might be useful to notice some points that may be relevant for the subsequent treatment of the title compounds. (i) The ν (CH) stretching frequency range of the experimental benzene vibrational spectra is largely perturbed by combination bands. This becomes immediately apparent from the IR spectrum, which displays three bands in the frequency range $\nu > 3000 \text{ cm}^{-1}$, while only one ν (CH) stretching mode should be IR active. (ii) With large basis sets, HF calculations not only yield the commonly much too high frequencies throughout, there also remain some interchanges, e.g., the ν_5 mode, when compared with the experimental frequency sequence. For instance, the mean absolute deviation from the experimental harmonic frequencies amounts to 105 cm^{-1} for unscaled HF/TZ2Pf frequencies³⁶ (the correlation coefficient is 0.99932). (iii) At the MP2 level, well-known problems mainly concern the ν_4 and the ν_{14} frequencies. Whereas the ν_{14} frequency seems to converge with higher basis sets (413 cm^{-1} with 6-311++(d,p) basis and 684 cm^{-1} with TZ2Pf basis,⁴¹ the experimental harmonic frequency is 707 cm^{-1} ⁴³), the failure with a correct description of the Kekule-type multireference ν_4 mode has more basic reasons. Besides, even with large basis sets, the overall correspondence with the experimental data remains rather poor. Without scaling, the mean absolute deviations from the experimental harmonic frequencies amount to 46 and 31 cm^{-1} for the MP2 frequencies calculated with 6-311++(d,p) and TZ2Pf basis sets,⁴¹ respectively (the correlation coefficients are 0.99687 and 0.99944). (iv) It has already pointed out in the early 1990s the problems associated with HF and MP2 calculations are largely overcome with DFT calculations.⁴¹ Very recently, it has been shown that, in particular, B3LYP calculations with larger basis sets provide frequencies that without any scaling are very close to the experimental data, e.g., the mean absolute deviation from the experimental harmonic frequencies amounts 17 cm^{-1} for unscaled B3LYP/ TZ2Pf³⁶ frequencies (the correlation coefficient is 0.99996). (v) From Table 3, when both, mean absolute differences and correlation coefficients are

TABLE 3: Experimental Anharmonic versus Calculated Harmonic Frequencies (XH Stretching Frequencies Are Excluded, See Text): Mean Absolute Differences (cm⁻¹) (First Line) and Correlation Coefficients (Second Line)

	B3LYP(II)	B3LYP(I)	BLYP(I)	B3P86(I)	MP2(I)	HF(I)	HF(II)
benzene	17 0.99992	22 0.99967	11 0.99931	24 0.99936	54 0.98429	92 0.99469	83 0.99474
phenol	17 0.99963	24 0.99950	14 0.99904	28 0.99922	49 0.99162	97 0.99778	87 0.99777
benzaldehyde	23 0.99972	29 0.99966	8 0.99978	32 0.99950	44 0.99458	107 0.99726	98 0.99740
salicylaldehyde	22 0.99933	33 0.99894	17 0.99758	39 0.99791	54 0.99353	112 0.99757	100 0.99741

TABLE 4: Vibrational Frequencies, IR Intensities, and Assignments of Phenol

exptl ^a		B3LYP(II)		B3LYP(I)		BLYP(I)		assignments ^b
ν^c	A^d	ν^c	A^e	ν^c	A^e	ν^c	A^e	
3611	78	3839	61	3827	41	3661	25	$\nu(\text{OH})$
(3092)	sh ^f	3198	4	3214	6	3131	7	$\nu(\text{CH})$
(3076)	5	3192	16	3207	22	3124	27	$\nu(\text{CH})$
(3044)	12	3178	17	3191	22	3108	27	$\nu(\text{CH})$
(3019)	6	3169	0	3183	0	3100	0	$\nu(\text{CH})$
		3152	14	3163	16	3080	19	$\nu(\text{CH})$
1605	50	1646	38	1668	46	1602	33	$\nu(\text{CC}) + [\delta(\text{CH})]$
1598	69	1636	51	1654	35	1589	36	$\nu(\text{CC}) + [\delta(\text{CH})]$
1499	88	1528	58	1547	50	1496	33	$\delta(\text{CH}) + \nu(\text{CC})$
1470	45	1500	24	1514	28	1468	28	$\delta(\text{CH}) + \nu(\text{CC})$
1342	35	1369	28	1378	36	1348	28	$\delta(\text{CH}) + \delta(\text{OH}) + [\delta(\text{CC})]$
1330	10	1349	5	1365	3	1330	8	$\nu(\text{CC}) + \delta(\text{CH})^g$
1257	67	1275	90	1305	81	1254	64	$\nu(\text{C-O}) + [\delta(\text{CH}) + \delta(\text{CC})]$
1179	96	1192	119	1200	138	1168	139	$\delta(\text{CH}) + \delta(\text{OH}) + \nu(\text{CC})$
1167	sh ^f	1191	5	1197	1	1166	7	$\delta(\text{CH}) + \nu(\text{CC}) + [\delta(\text{OH})]$
1151	40	1177	32	1183	18	1156	14	$\delta(\text{CH}) + \nu(\text{CC})$
1069	16	1094	14	1102	11	1070	11	$\nu(\text{CC}) + \delta(\text{CH})$
1024	7	1043	6	1051	4	1017	3	$\nu(\text{CC}) + \delta(\text{CH})$
1000	7	1012	2	1013	2	983	2	$\delta(\text{CC}) + \nu(\text{CC})$
977	2	969	0	981	0	940	0	$\gamma(\text{CH})$
		948	0	955	0	911	0	$\gamma(\text{CH})$
883	10	874	5	884	5	846	4	$\gamma(\text{CH})$
826	9	816	0	822	0	789	0	$\gamma(\text{CH})$
811	22	828	23	834	18	805	18	$\nu(\text{CC}) + \delta(\text{CC}) + \nu(\text{C-O})$
750	100	745	83	761	52	732	44	$\gamma(\text{CH}) + \gamma(\text{C-O})$
689	53	667	11	699	11	675	8	$\gamma(\text{CC})$
620	2	633	0	633	0	616	0	$\delta(\text{CC})$
529	2	537	2	536	1	521	1	$\delta(\text{CC}) + [\nu(\text{C-O})]$
506	27	508	14	518	6	499	6	$\gamma(\text{CC}) + \gamma(\text{C-O})^h$
420	sh ^f	414	2	421	0	407	0	$\gamma(\text{CC})$
405	10	403	11	405	10	392	9	$\delta(\text{C-O})$
322	15	338	111	365	119	376	109	$\gamma(\text{OH})$
235	sh ^f	227	1	234	1	225	0	$\gamma(\text{CC}) + [\gamma(\text{CH})]$

^a From IR spectra of CCl₄ and CS₂ solutions (see text). ^b From B3LYP(II) calculations (contributions between 10% and 20% are given in brackets). ^c Frequencies (cm⁻¹). ^d IR absorbance maxima, normalized to $A = 100$ for the strongest band. ^e IR intensities (km/mol). ^f Shoulder. ^g $+\delta(\text{OH})$ at B3P86 and HF levels. ^h Almost pure $\gamma(\text{C-O})$ at MP2 level.

considered, the advantages of DFT calculations are obvious. The experimental frequency sequence is almost perfectly reproduced with all the three functionals included in this study; there remain only two minor interchanges that concern ν_{12} and ν_1 at the B3LYP/6-31G(d,p) and at B3P86/6-31G(d,p) levels.

D. Vibrational Spectra of Phenol. Experimental and calculated frequencies and IR intensities of phenol are summarized in Table 4 (B3LYP and BLYP calculations) and Table 4S (B3P86, MP2, and HF calculations). The last column of Table 4 contains qualitative mode decompositions (contributions down to 10% are given) as obtained from B3LYP/6-311++G-(d,p) calculations. For the other calculational levels, the mode decompositions are qualitatively rather similar and the assignments of Table 4 apply quite well (the most apparent differences are indicated in Table 4).

As noted in the introduction, Schütz et al.,⁹ as well as Michalska et al.,¹⁴ have given assignments based on comparisons between calculated normal coordinates and Bist's benzene-like vibrations.²¹ Despite some effort, we were not able to conse-

quently reproduce these assignments, because in several instances the correspondence between benzene and phenol vibrational modes is by far not unequivocal. We have therefore chosen an other, most obvious approach, i.e., a direct comparison between experimental and calculated spectra by considering both the frequency sequence and the intensity pattern. Let us first omit the high-frequency $\nu(\text{CH})$ stretching frequencies (and also the $\nu(\text{OH})$ stretching frequency), which provide some special problems (see below). As shown in Figure 3, the B3LYP/6-311++G-(d,p)-calculated IR spectrum agrees almost perfectly with the experimental one. For 18 out of the 28 non- $\nu(\text{XH})$ vibrations, we calculate IR intensities $A_{\text{calcd}} \geq 5$ km/mol and each of these vibrations has a directly corresponding experimental IR band with an absorbance maximum of $A_{\text{exptl}} \geq 10$ (relative to $A_{\text{exptl}} = 100$ for the most prominent band) (Table 4). Moreover, the majority of the remaining 10 vibrations, for which IR intensities of $A_{\text{calcd}} < 5$ km/mol are calculated, can consistently be assigned to corresponding weak experimental features (Table 4). In some instances, the Raman spectrum and

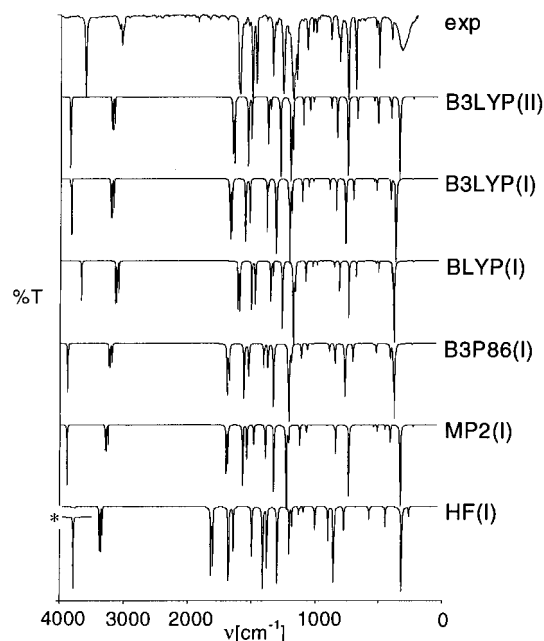


Figure 3. Experimental and calculated IR spectra of phenol (* denotes an offset of 420 cm^{-1}).

the spectra of deuterated phenol (see below) provide additional evidence. Only for one of these vibrations, $\nu_{\text{calcd}} = 816 \text{ cm}^{-1}$, we observe a somewhat larger difference between calculated ($A_{\text{calcd}} \approx 0 \text{ km/mol}$) and experimental ($A_{\text{exptl}} = 9$) intensities. Only for one vibration, $\nu_{\text{calcd}} = 948 \text{ cm}^{-1}$, with calculated zero IR and Raman intensities, we were not able to determine a

reliable experimental frequency (the corresponding frequencies reported by Evans¹⁷ and Bist⁹ for the $\nu = 900\text{--}1000 \text{ cm}^{-1}$ range are largely different and seem partly to be arbitrary). On the other hand, besides the assigned IR absorption bands, there remain only few, very weak ($A_{\text{exptl}} < 4$) experimental IR features below 1600 cm^{-1} that cannot be attributed to fundamentals; they should be due to overtones or to combination transitions (in some instances this complies with Evans' assignments¹⁷).

The assignments just given are highly supported by the experimental and calculated vibrational spectra of phenol-OD, i.e., phenol deuterated at the OH group. Once more, we obtain excellent agreement between experiment and B3LYP/6-311++G-(d,p) calculation (Table 5), and in particular, the isotope shifts $\nu(\text{phenol}) - \nu(\text{phenol-OD})$ are excellently reproduced. The latter not only applies to the significant isotope shifts of three fundamentals with dominating $\nu(\text{OH/OD})$, $\delta(\text{OH/OD})$, and $\gamma(\text{OH/OD})$ character, but also to almost all the finer details of isotope shifts (Table 5).

Whereas the B3LYP/6-311++G(d,p) calculations are obviously capable of almost perfectly reproducing the experimental IR spectra in the lower frequency range, the correspondence is distinctly worse in the range of $\nu(\text{CH})$ stretching frequencies. Experimental and calculated IR spectra show significant differences in this range for both phenol and phenol-OD, and reasonable assignments are hardly possible. As noted above, similar problems are known from benzene. They arise from Fermi resonance effects, which largely disturb the pattern of $\nu(\text{CH})$ fundamentals. The same seems to be true for phenol, and it is not even clear which of the experimentally determined IR frequencies actually correspond to $\nu(\text{CH})$ fundamentals. In

TABLE 5: Vibrational Frequencies, Isotopic Shifts, and Assignments of Phenol-OD

exptl ^a		B3LYP(II)		B3LYP(I)		BLYP(I)		assignments ^b
ν^c	$\Delta\nu^d$	ν^c	$\Delta\nu^d$	ν^c	$\Delta\nu^d$	ν^c	$\Delta\nu^d$	
(3094)	(-2)	3198	0	3214	0	3131	0	$\nu(\text{CH})$
(3072)	(4)	3192	0	3207	0	3124	0	$\nu(\text{CH})$
(3038)	(6)	3178	0	3191	0	3108	0	$\nu(\text{CH})$
(3016)	(3)	3169	0	3183	0	3100	0	$\nu(\text{CH})$
		3152	0	3163	0	3080	0	$\nu(\text{CH})$
2667	944	2795	1044	2786	1041	2665	994	$\nu(\text{OD})$
1602	3	1643	3	1665	3	1599	3	$\nu(\text{CC}) + \delta(\text{CH})$
		1632	4	1649	5	1584	5	$\nu(\text{CC}) + [\delta(\text{CH})]$
1497	2	1525	3	1543	4	1492	4	$\delta(\text{CH}) + \nu(\text{CC})$
1462	8	1491	9	1505	9	1459	9	$\delta(\text{CH}) + \nu(\text{CC})$
1332	10	1354	15	1365	0	1335	13	$\delta(\text{CH}) + \nu(\text{CC})$
1302	28	1335	14	1348	30	1313	17	$\nu(\text{CC}) + \delta(\text{CH})$
1246	11	1269	6	1299	6	1246	8	$\nu(\text{C-O}) + [\nu(\text{CC}) + \delta(\text{CH}) + \delta(\text{CC})]$
1167	0	1191	0	1197	0	1166	0	$\delta(\text{CH}) + \nu(\text{CC})$
1152	-1	1179	-2	1185	-2	1157	-1	$\delta(\text{CH}) + [\nu(\text{CC})]$
1075	-6	1102	-8	1109	-7	1078	-8	$\nu(\text{CC}) + \delta(\text{CH})$
1024	0	1043	0	1051	0	1018	-1	$\nu(\text{CC}) + \delta(\text{CH})$
999	1	1013	-1	1014	-1	983	0	$\delta(\text{CC}) + \nu(\text{CC})$
		969	0	981	0	940	0	$\gamma(\text{CH})$
		948	0	955	0	911	-1	$\gamma(\text{CH})$
918	261	928	264	936	264	912	256	$\delta(\text{OD}) + [\nu(\text{CC})]$
880	3	874	0	884	0	846	0	$\gamma(\text{CH})$
825	1	816	0	822	0	789	0	$\gamma(\text{CH})$
806	5	820	8	826	8	799	-6	$\delta(\text{CC}) + \nu(\text{CC}) + \nu(\text{C-O})$
751	-1	745	0	761	0	732	0	$\gamma(\text{CH})$
688	1	667	0	699	0	675	0	$\gamma(\text{CC})$
618	2	633	0	633	0	616	0	$\delta(\text{CC})$
523	6	531	6	531	5	516	5	$\delta(\text{CC}) + [\nu(\text{C-O})]$
504	2	508	0	517	1	499	0	$\gamma(\text{CC}) + \gamma(\text{CH})$
		414	0	420	1	406	1	$\gamma(\text{CC})$
385	20	383	20	385	20	373	19	$\delta(\text{C-O})$
253	69	257	81	275	90	281	95	$\gamma(\text{OD}) + [\gamma(\text{CC})]$
215	20	217	10	226	8	220	5	$\gamma(\text{CC}) + \gamma(\text{OD})$

^a From IR spectra of CCl_4 and CS_2 solutions (see text). ^b From B3LYP(II) calculations (contributions between 10% and 20% are given in brackets). ^c Frequencies (cm^{-1}). ^d $\nu(\text{phenol}) - \nu(\text{phenol-OD})$ (cm^{-1}).

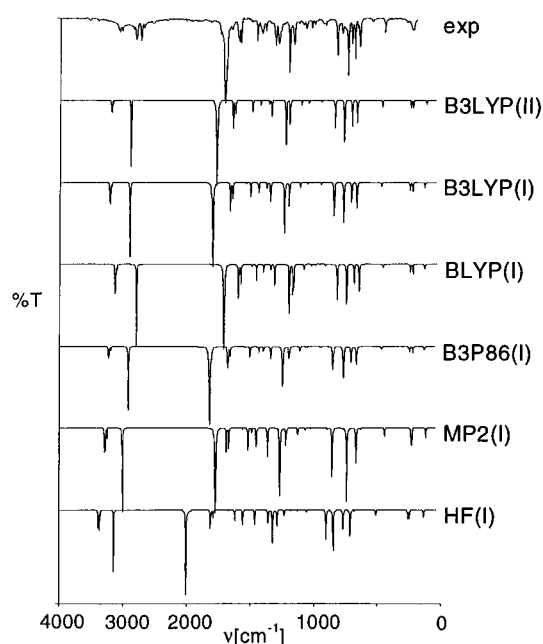
TABLE 6: Vibrational Frequencies, IR Intensities, and Assignments of Benzaldehyde

exptl ^a		B3LYP(II)		B3LYP(I)		BLYP(I)		assignments ^b
ν^c	A^d	ν^c	A^e	ν^c	A^e	ν^c	A^e	
(3104)	sh ^f	3198	8	3218	7	3135	10	$\nu(\text{CH})$
(3088)	2	3191	12	3208	16	3125	21	$\nu(\text{CH})$
(3067)	3	3181	13	3199	17	3116	21	$\nu(\text{CH})$
(3040)	sh ^f	3170	1	3187	3	3104	4	$\nu(\text{CH})$
(3031)	3	3162	3	3179	3	3096	3	$\nu(\text{CH})$
(2813)	7	2889	118	2900	132	2792	150	$\nu(\text{C}-\text{H})$
1709	100	1766	302	1796	226	1706	195	$\nu(\text{C}=\text{O})$
1598	9	1639	33	1657	27	1591	28	$\nu(\text{CC}) + \delta(\text{CH})$
1586	8	1622	14	1640	13	1574	15	$\nu(\text{CC}) + [\delta(\text{CH})]$
1495		1520	1	1534	1	1485	2	$\delta(\text{CH}) + \nu(\text{CC})$
1456	7	1484	12	1497	12	1450	12	$\delta(\text{CH}) + \nu(\text{CC})$
1388	4	1421	6	1436	9	1395	5	$\delta(\text{C}-\text{H}) + [\delta(\text{CH})]$
1337	1	1354	5	1370	5	1339	4	$\delta(\text{CH}) + \nu(\text{CC})$
1311	10	1336	17	1343	17	1306	16	$\delta(\text{CH}) + \nu(\text{CC})$
1203	29	1223	59	1233	58	1192	46	$\nu(\text{C}-\text{C}) + \nu(\text{CC}) + \delta(\text{CH}) + [\delta(\text{CC})]$
1167	10	1191	28	1196	22	1164	21	$\delta(\text{CH}) + \nu(\text{CC})$
1160	sh ^f	1184	2	1189	2	1160	15	$\delta(\text{CH}) + \nu(\text{CC})$
1072	2	1102	5	1108	4	1076	4	$\nu(\text{CC}) + \delta(\text{CH})$
1024	2	1044	3	1050	1	1017	1	$\nu(\text{CC}) + \delta(\text{CH}) + [\delta(\text{CC})]$
1010	sh ^f	1036	2	1038	0	998	0	$\gamma(\text{C}-\text{H}) + \gamma(\text{CH})$
1005	2	1017	1	1017	0	987	1	$\delta(\text{CC}) + \nu(\text{CC})$
980	1	1012	0	1011	0	972	0	$\gamma(\text{CH}) + [\gamma(\text{C}-\text{H})]^g$
960		997	0	990	0	951	0	$\gamma(\text{CH})$
920	1	943	2	943	2	909	1	$\gamma(\text{CH})$
855	1	868	0	871	0	843	0	$\gamma(\text{CH})$
827	16	837	33	842	31	816	28	$\nu(\text{CC}) + \nu(\text{C}-\text{C}) + [\delta(\text{C}=\text{O}) + \delta(\text{CC})]$
742	31	764	54	766	40	743	35	$\gamma(\text{CH}) + \gamma(\text{CC})^h$
688	19	702	31	705	17	683	14	$\gamma(\text{CC}) + [\gamma(\text{CH})]$
651	11	661	25	662	24	643	20	$\delta(\text{CC}) + \delta(\text{C}=\text{O})$
617	1	630	0	629	0	613	0	$\delta(\text{CC})$
449	10	464	7	468	4	455	3	$\gamma(\text{CC}) + \gamma(\text{C}-\text{C})$
404	1	443	0	444	0	431	0	$\delta(\text{CC}) + \nu(\text{C}-\text{C})$
385	1	416	0	421	0	407	0	$\gamma(\text{CC})$
236	8	237	8	243	6	238	5	$\gamma(\text{CC}) + \gamma(\text{C}-\text{C}) + \gamma(\text{C}=\text{O})$
223	8	221	8	222	8	217	7	$\delta(\text{C}-\text{C}) + \delta(\text{C}=\text{O})$
130		115	5	125	4	124	3	$\gamma(\text{C}=\text{O}) + \gamma(\text{CC}) + \gamma(\text{C}-\text{C})$

^a From IR spectra of CCl_4 and CS_2 solutions (see text). ^b From B3LYP(II) calculations (contributions between 10% and 20% are given in brackets). ^c Frequencies (cm^{-1}). ^d IR absorbance maxima, normalized to $A = 100$ for the strongest band. ^e IR intensities (km/mol). ^f Shoulder. ^g $-\gamma(\text{C}-\text{H})$ at MP2 level. ^h $-\gamma(\text{CC})$ at MP2 level.

Tables 4 and 5, the observed “ $\nu(\text{CH})$ ” frequencies are simply arranged in decreasing order and they have been excluded from statistical considerations (Table 3). As to the $\nu(\text{OH})$ stretching frequency, the difference between experiment and B3LYP/6-311++G(d,p) calculation, which amounts to about 180 cm^{-1} if the experimental gas phase value is used, can mainly be attributed to the large anharmonicity associated with OH vibrations, e.g., the mean anharmonic shift of the two $\nu(\text{OH})$ frequencies of gaseous water is also about 180 cm^{-1} .

Thus, as it turns out, with the exception of the $\nu(\text{CH})$ stretching vibrations, the correspondence between the experimental and the B3LYP/6-311++G(d,p) calculated IR spectra of phenol is almost perfect. Concerning vibrational spectroscopic data as obtained at other levels of theory (Tables 4 and 4S, and Figure 3), the differences and trends are essentially those that already become apparent with benzene and that are partially well-known from literature studies (see above). Moreover, they also agree well with related findings about the bond distances (Tables 2 and 2S). Without going too much into details, some points should be noticed. (i) When both, mean absolute deviations and correlation coefficients are considered, (Table 3), the B3LYP calculated results are only slightly better on the whole with the 6-311++G(d,p) than those with the 6-31G(d,p) basis. (ii) BLYP yields similarly good results, but most of the calculated frequencies are smaller than the experimental ones (20 out of 34, which compares with seven at B3LYP/6-311++G(d,p) and two at B3LYP/6-31G(d,p) levels). The systematic underestimation of force constants associated with

**Figure 4.** Experimental and calculated IR spectra of benzaldehyde.

BLYP calculations is also obvious from the $\nu(\text{OH})$ frequency, which is very close to the experimental (anharmonic) gas phase frequency. (iii) The B3P86 description is slightly poorer than the B3LYP description. (iv) MP2 calculated results are

TABLE 7: Vibrational Frequencies, IR Intensities, and Assignments of Salicylaldehyde

exptl ^a		B3LYP(II)		B3LYP(I)		BLYP(I)		assignments ^b
ν^c	A^d	ν^c	A^e	ν^c	A^e	ν^c	A^e	
3160		3413	240	3348	227	3058	218	$\nu(\text{OH})$
(3091)		3202	5	3220	6	3137	10	$\nu(\text{CH})$
(3071)		3196	10	3214	14	3130	18	$\nu(\text{CH})$
	sh ^f	3175	6	3193	8	3111	6	$\nu(\text{CH})$
(3037)		3163	4	3176	5	3094	10	$\nu(\text{CH})$
2840	8	2949	88	2965	100	2872	122	$\nu(\text{C-H})$
1668	100	1705	422	1733	331	1645	262	$\nu(\text{C=O})$
1622	21	1659	56	1677	43	1609	9	$\nu(\text{CC})+[\delta(\text{CH})]^g$
1582	17	1614	58	1634	71	1578	4	$\nu(\text{CC})+[\delta(\text{OH})+\delta(\text{CH})]$
1488	22	1517	56	1534	83	1488	85	$\delta(\text{CH})+\nu(\text{CC})+[\delta(\text{OH})]$
1462	24	1488	67	1506	59	1449	49	$\delta(\text{CH})+\nu(\text{CC})$
1413	5	1409	79	1442	81	1410	80	$\delta(\text{C-H})+\delta(\text{CH})+\delta(\text{OH})$
1385	14	1420	39	1423	49	1377	36	$\delta(\text{C-H})+\delta(\text{OH})+[\nu(\text{CC})]^h$
1322	6	1358	11	1378	14	1341	16	$\nu(\text{CC})+[\delta(\text{CH})]$
1284	41	1318	121	1343	90	1298	73	$\nu(\text{C-O})+\delta(\text{CH})+[\delta(\text{CC})]$
1229	14	1253	43	1264	42	1227	32	$\delta(\text{CH})+\nu(\text{CC})$
1202	21	1222	65	1233	64	1202	55	$\delta(\text{CH})+\nu(\text{CC})+[\nu(\text{C-C})]$
1150	20	1177	34	1182	26	1155	20	$\delta(\text{CH})+\nu(\text{CC})$
1114	4	1139	7	1146	6	1114	5	$\delta(\text{CH})+\nu(\text{CC})$
1029	6	1047	9	1053	6	1019	5	$\nu(\text{CC})+\delta(\text{CH})$
1010	1	1017	2	1022	1	978	3	$\gamma(\text{C-H})$
975		988	0	996	0	956	0	$\gamma(\text{CH})$
943	2	955	1	953	1	912	0	$\gamma(\text{CH})$
885	18	896	25	896	22	871	20	$\delta(\text{CC})$
857	2	865	0	875	0	840	13	$\gamma(\text{CH})$
767	15	778	18	785	16	757	12	$\nu(\text{CC})+\nu(\text{C-O})$
757	31	763	169	773	63	747	51	$\gamma(\text{CH})+\gamma(\text{OH})^i$
739	13	688	0	732	2	708	1	$\gamma(\text{CC})+\gamma(\text{C-O})$
714	21	781	13	838	96	869	71	$\gamma(\text{OH})+\gamma(\text{CH})^j$
667	11	675	29	677	28	658	24	$\delta(\text{CC})+\delta(\text{C=O})+[\nu(\text{CC})]$
563	2	572	4	572	3	555	3	$\delta(\text{CC})+\nu(\text{CC})$
539	3	542	4	549	3	530	3	$\gamma(\text{CC})+\gamma(\text{C-O})$
451	5	461	5	468	6	461	4	$\delta(\text{C-O})+\delta(\text{C=O})$
430	2	434	2	440	1	426	1	$\gamma(\text{CC})+\gamma(\text{C-C})$
409	4	418	4	419	3	408	3	$\delta(\text{CC})+[\delta(\text{C-O})+\nu(\text{C-C})]$
292	2	298	4	309	3	308	2	$\gamma(\text{C=O})+\gamma(\text{C-C})+\gamma(\text{C-O})+[\gamma(\text{CC})]$
261	3	269	9	278	8	278	8	$\delta(\text{C-C})+\delta(\text{C=O})$
214	1	211	2	216	2	212	2	$\gamma(\text{CC})+\gamma(\text{C=O})$
140		140	0	146	0	144	0	$\gamma(\text{C-C})+\gamma(\text{CC})+\gamma(\text{C=O})$

^a From IR spectra of CCl₄ and CS₂ solutions (see text). ^b From B3LYP(II) calculations (contributions between 10% and 20% are given in brackets). ^c Frequencies (cm⁻¹). ^d IR absorbance maxima, normalized to $A = 100$ for the strongest band. ^e IR intensities (km/mol). ^f Shoulder. ^g $+\delta(\text{C-O})$ at BLYP level. ^h $-\delta(\text{OH})$ at BLYP, B3P86, MP2, and HF levels. ⁱ $-\gamma(\text{OH})$ at B3LYP(I), BLYP, B3P86, MP2, and HF levels. ^j $-\gamma(\text{CH})$ at B3LYP(I), BLYP, B3P86, MP2, and HF levels.

distinctly worse, in particular with respect to the correlation coefficients (because of several interchanges). (v) HF calculations yield the well-known distinctly overestimated frequencies and also several interchanges, with only minor differences between 6-31G(d,p) and 6-311++G(d,p) basis sets.

E. Vibrational Spectra of Benzaldehyde. Experimental and calculated frequencies and IR intensities of benzaldehyde are summarized in Table 6 (B3LYP and BLYP calculations) and Table 6S (B3P86, MP2, and HF calculations), along with qualitative mode decompositions as obtained from B3LYP/6-311++G(d,p) calculations. The mode decompositions obtained for the other calculation levels are qualitatively rather similar and the assignments of Table 6 apply even better to the other calculations, than was the case with phenol (two minor deviations are indicated in the Table 6).

Comparing theory with experiment, almost everything we have learned from phenol also applies to benzaldehyde. As shown in Figure 4, the B3LYP/6-311++G(d,p) calculated IR spectrum excellently agrees with the experimental IR spectrum in the range below the $\nu(\text{CH})$ stretching frequencies. Almost all calculated vibrations can unambiguously be assigned to corresponding experimental spectral features and vice versa by considering both frequency sequence and intensity pattern. The assignments (Table 6) may possibly be somewhat tentative in

only three or four cases, and only some minor spectral features ($A_{\text{exptl}} < 4$) remain unassigned (the most obvious case is a band at 1654 cm⁻¹ with $A_{\text{exptl}} = 3$, see below). In the range of $\nu(\text{CH})$ stretching vibrations, the same problems arise with the determination of experimental fundamental frequencies, as it is the case with benzene and phenol. Additionally, with benzaldehyde a similar problem also concerns the aldehyde $\nu(\text{C-H})$ stretching vibration, which is well-known to be component of a strongly coupled Fermi doublet, and a comparison with calculated harmonic frequencies is hardly meaningful. As to the other computational levels, the differences and trends (Tables 3, 6, and 6S) are largely similar to those obtained for phenol. Compared to experiment, all the DFT calculations yield reasonably good results with respect to both mean absolute frequency differences and correlation coefficients, while MP2 and HF results are distinctly worse.

F. Vibrational Spectra of Salicylaldehyde. Experimental and calculated vibrational frequencies and IR intensities are compiled in Table 7 (B3LYP and BLYP calculations) and Table 7S (B3P86, MP2, and HF calculations), along with qualitative mode decompositions, as obtained from B3LYP/6-311++G(d,p) calculations. Although the mode decompositions as obtained at the other calculational levels are qualitatively largely similar for the great majority of vibrations, there are distinctly

TABLE 8: Vibrational Frequencies, Isotopic Shifts, and Assignments of Salicylaldehyde-OD

exptl ^a		B3LYP(II)		B3LYP(I)		BLYP(I)		assignments ^b
ν^c	$\Delta\nu^d$	ν^c	$\Delta\nu^d$	ν^c	$\Delta\nu^d$	ν^c	$\Delta\nu^d$	
(3086)	(5)	3202	0	3220	0	3137	0	$\nu(\text{CH})$
(3065)	(6)	3196	0	3214	0	3130	0	$\nu(\text{CH})$
(3051)		3175	0	3193	0	3111	0	$\nu(\text{CH})$
(3028)	(9)	3163	0	3176	0	3094	0	$\nu(\text{CH})$
(2837)	(3)	2949	0	2966	-1	2873	-1	$\nu(\text{C}-\text{H})$
2370	790	2488	925	2441	907	2232	826	$\nu(\text{OD})$
1665	3	1702	3	1727	6	1633	12	$\nu(\text{C}=\text{O})$
1615	7	1654	5	1672	5	1604	5	$\nu(\text{CC})+[\delta(\text{CH})]$
1569	13	1594	20	1610	24	1543	35	$\nu(\text{CC})+[\delta(\text{CH})]$
1475	13	1500	27	1515	19	1464	24	$\delta(\text{CH})+\nu(\text{CC})$
1461	1	1488	0	1506	0	1448	1	$\delta(\text{CH})+\nu(\text{CC})$
1387	-2	1414	6	1426	-3	1381	-4	$\delta(\text{C}-\text{H})$
1323	-1	1366	-8	1387	-9	1351	-10	$\nu(\text{CC})+[\delta(\text{CH})]$
1295	-11	1323	-5	1345	-2	1301	-3	$\nu(\text{C}-\text{O})+\delta(\text{CH})$
1263	-34	1288	-35	1296	-32	1257	-30	$\delta(\text{CH})+\nu(\text{CC})+[\nu(\text{C}-\text{O})]$
1214	-12	1236	-14	1249	-16	1215	-13	$\nu(\text{C}-\text{C})+\delta(\text{CH})+\nu(\text{CC})$
1151	-1	1177	0	1182	0	1155	0	$\delta(\text{CH})+\nu(\text{CC})$
1130	-16	1154	-15	1160	-14	1130	-16	$\delta(\text{CH})+\nu(\text{CC})$
1038	-9	1054	-7	1063	-10	1012	-7	$\nu(\text{CC})+\delta(\text{CH})+[\delta(\text{OD})]$
990	423	1020	389	1037	405	1040	370	$\delta(\text{OD})+\nu(\text{CC})+[\delta(\text{CC})]$
		1016	1	1022	0	976	2	$\gamma(\text{CH})$
		988	0	996	0	956	0	$\gamma(\text{CH})$
943	0	955	0	953	0	912	0	$\gamma(\text{CH})$
872	13	886	10	887	9	864	7	$\delta(\text{CC})$
857	0	864	1	874	1	841	-1	$\gamma(\text{CH})$
767	0	777	1	784	1	756	1	$\nu(\text{CC})+[\nu(\text{C}-\text{O})]$
756	1	769	-6	773	0	747	0	$\gamma(\text{CH})$
728	11	688	0	736	-4	713	-5	$\gamma(\text{CC})+\gamma(\text{C}-\text{O})$
666	1	674	1	675	2	656	2	$\delta(\text{CC})+\delta(\text{C}=\text{O})+[\nu(\text{CC})]$
		574	207	614	224	632	247	$\gamma(\text{OD})+\gamma(\text{CC})$
559	4	569	3	569	3	552	3	$\delta(\text{CC})+\nu(\text{CC})$
516	23	532	10	542	7	526	3	$\gamma(\text{CC})+\gamma(\text{OD})+\gamma(\text{C}-\text{O})$
438	13	449	12	456	12	450	11	$\delta(\text{C}-\text{O})+\delta(\text{C}=\text{O})+[\delta(\text{CC})]$
		434	0	440	0	426	0	$\gamma(\text{CC})+[\gamma(\text{C}-\text{C})]$
404	5	413	5	415	4	404	4	$\delta(\text{CC})+\delta(\text{C}-\text{O})+[\nu(\text{C}-\text{C})]$
292	0	298	0	309	0	308	0	$\gamma(\text{C}=\text{O})+\gamma(\text{C}-\text{C})+\gamma(\text{C}-\text{O})+[\gamma(\text{CC})]$
258	3	265	4	274	4	274	4	$\delta(\text{C}-\text{C})+[\delta(\text{C}=\text{O})]$
210	4	208	3	214	2	209	3	$\gamma(\text{CC})+\gamma(\text{C}=\text{O})$
		140	0	146	0	144	0	$\gamma(\text{C}-\text{C})+\gamma(\text{CC})+[\gamma(\text{C}=\text{O})]$

^a From IR spectra of CCl_4 and CS_2 solutions (see text). ^b From B3LYP(II) calculations (contributions between 10% and 20% are given in brackets). ^c Frequencies (cm^{-1}). ^d $\nu(\text{salicylaldehyde}) - \nu(\text{salicylaldehyde-OD})$ (cm^{-1}).

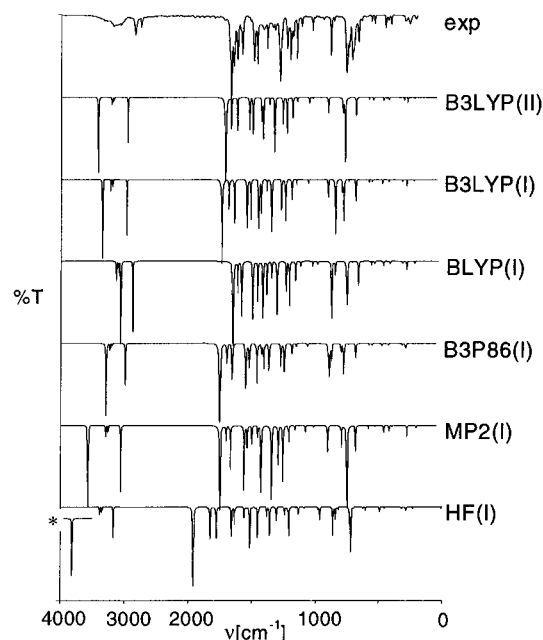


Figure 5. Experimental and calculated IR spectra of salicylaldehyde (* denotes an offset of 200 cm^{-1}).

more and also more prominent differences, than is the case with the two parent compounds (Table 7 and see also below).

The agreement between experimental and B3LYP/6-311++G-(d,p) calculated IR spectra is slightly worse for salicylaldehyde than for the two parent compounds (Figure 5), but nevertheless, reasonably justified assignments can be made in the lower frequency range (below $\nu(\text{XH})$ stretching frequencies) for about 80% of the modes of vibrations (Table 7). For some three to four vibrations the assignments could be questionable, and in the experimental spectrum there remain some more unassigned residuals (1649 , 1340 , and 1182 cm^{-1}) than is the case with that of the two parent compounds. Most prominently, this applies to the absorption band at 1649 cm^{-1} in the solution spectrum. Because the intensity of this band decreases significantly as the $\nu(\text{C}=\text{O})$ frequency increases by going from condensed (liquid) to solution and to vapor phase spectra (in the latter case the band is absent), it can reasonably well be interpreted in terms of Fermi resonance (most likely the same applies to the unassigned 1654 cm^{-1} band of benzaldehyde, see above).

The most apparent problem with the vibrational spectrum of salicylaldehyde concerns four frequencies in the range $\nu_{\text{exptl}} = 714\text{--}767\text{ cm}^{-1}$, where experimental and calculated spectral patterns exhibit significant differences, and where there are also distinct differences between the B3LYP results as obtained with 6-311++G(d,p) and with 6-31G(d,p) basis sets (Figure 5). The reasons for this become clearly apparent from an inspection of the corresponding normal coordinates. For two of the four

vibrations the 6-311++G(d,p) and the 6-31G(d,p) calculated normal coordinates are largely similar, $\nu(\text{CC})+\nu(\text{C-O})$ and $\gamma(\text{CC})+\gamma(\text{C-O})$, but for the other two modes 6-311++G(d,p) calculates two strongly mixed $\gamma(\text{OH})+\gamma(\text{CH})$ vibrations (781 and 763 cm^{-1}), whereas 6-31G(d,p) calculates an almost pure $\gamma(\text{OH})$ and an almost pure $\gamma(\text{CH})$ vibration (838 and 773 cm^{-1}), which indicates, that the poor description of the force field for these modes could be a problem of basis set convergence.

The interpretation of the IR spectra of deuterated salicylaldehyde (Table 8) provide more problems, than was the case with phenol. Considering the experimental spectra, the correspondence between salicylaldehyde and salicylaldehyde-OD bands is not obvious in all instances. The reasons for most of the problems in the 1400–1000 cm^{-1} frequency range become clear from the calculated spectra (Table 8). First, most of the bands become, partially significantly, shifted to higher frequencies on deuteration, which is rather exceptional than common. Second, for several vibrations the mode decompositions are significantly different for salicylaldehyde and salicylaldehyde-OD, which strongly affects not only the frequencies, but also the corresponding intensities. In particular, this applies to the contributions of the $\delta(\text{OH/D})$ internal coordinates: whereas in salicylaldehyde the $\delta(\text{OH})$ in-plane deformation contributes to a minor extent (less than 25%) to several normal coordinates, in salicylaldehyde-OD the $\delta(\text{OD})$ in-plane deformation contributes mainly (about 60%) to only one normal coordinate. As to the critical 800–700 cm^{-1} frequency range, where we observe larger differences between experimental and calculated spectra of salicylaldehyde, the agreement between experiment and theory is distinctly better and the isotopic shifts, experimental as well as calculated ones, provide valuable help for more reliable assignments.

Concerning $\nu(\text{CH})$ and $\nu(\text{C-H})$ stretching frequencies, expectedly, the problems are just the same as with the parent compounds. Reliable experimental $\nu(\text{CH})$ fundamentals have not been determined to date and the aldehyde $\nu(\text{C-H})$ stretching vibration is one component of a strongly coupled Fermi doublet.

Comparisons between the data obtained at different levels of theory reveal very similar differences as is the case with the parent compounds (Table 3). Only in the case of BLYP calculations the results are distinctly worse than with the parent compounds. The main reasons become immediately apparent from the frequency of the $\nu(\text{OH})$ stretching vibration that is significantly below the experimental one and even below the calculated $\nu(\text{CH})$ frequencies. On the other hand, while the $\nu(\text{OH/D})$ stretching force constants are calculated much too small at BLYP level, the corresponding $\delta(\text{OH/D})$ in-plane and $\gamma(\text{OH/D})$ out-of-plane deformational force constants are calculated much too high. Consequently, poor results are obtained for a number of vibrational modes with contributions from $\delta(\text{OH/D})$ and $\gamma(\text{OH/D})$.

Summary

Geometric and vibrational spectroscopic data (rotational constants, bond distances and angles, vibrational frequencies, IR intensities, and OH/OD isotope effects) of phenol, benzaldehyde, and salicylaldehyde have been calculated at various levels of theory (HF, MP2, B3P86, B3LYP, and BLYP) using the 6-31G(d,p) basis set throughout and additionally the 6-311++G(d,p) basis set in two instances. For geometric data, the best agreement between theory and experiment was obtained at MP2 and B3LYP levels, while B3P86 calculated geometric data are slightly worse, and HF and BLYP calculated geometric data are distinctly worse. The findings agree with common trends associated with the different computational levels, such

as the systematic underestimation of bond distances with HF calculations and the systematic overestimation of bond distances with BLYP calculations.

For vibrational spectroscopic data, DFT calculations have been proven to be superior over MP2 and HF calculations. In particular, it has been shown that, for phenol, phenol-OD, and benzaldehyde, the frequency sequences and intensities from B3LYP calculations excellently agree with experimental results (except of $\nu(\text{XH})$ stretching fundamentals, which have not been determined yet for both compounds). Reliable and almost complete assignments of the IR spectra have been given. For BLYP calculated vibrational spectroscopic data the agreement with experiment is similarly good or even better, although most frequencies are lower than the experimental fundamentals. B3P86 calculated data are slightly worse, whereas MP2 and HF calculations suffer from several obvious shortcomings, concerning both frequency sequences and intensities, that are already apparent from calculations of smaller molecules, such as benzene.

With salicylaldehyde and salicylaldehyde-OD, there remain some more inconsistencies between B3LYP calculated and experimental IR spectra, than is the case with phenol and benzaldehyde. In particular, this applies to some low-frequency vibrations, where the agreement between theory and experiment is rather poor. Since B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) calculations yield significantly different results in these instances, the failure with a correct description of the force field seems to be a problem of insufficient basis set convergence.

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Supporting Information Available: Tables 2S, 4S, 6S, and 7S that contain geometric and vibrational spectroscopic theoretical data as obtained at B3P86/6-31G(d,p), MP2/6-31G(d,p), HF/6-31G(d,p), and HF/6-311++G(d,p) levels of theory (4 pages). Ordering information is given on any current masthead page.

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