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THEORETICAL INTERPRETATION OF THE FLUORESCENCE SPECTRA OF TOLUENE AND P-CRESOL

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The fluorescence spectra of toluene and p-cresol from ab initio calculations were interpreted on the ground states and the lowest excited singlet states of the two molecules. Determination was made on the energy minima and the optimized geometries of the ground states and the lowest excited singlet states from 4 in 4 CASSCF computations using 6-31G basis set. Also computed was the vibrational frequencies of both molecules in the two states. It is believed that this work constitutes the first complete calculation of the vibrational spectra of both ground and excited states of aromatic molecules.

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PREFACE

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THEORETICAL INTERPRETATION OF THE FLUORESCENCE SPECTRA OF TOLUENE AND P-CRESOL.

1. Introduction

In a recent paper[1] we presented some theoretical results on the ground states and the lowest excited singlet states of phenylalanine and tyrosine in order to interpret the fluorescence of the two molecules. In the present paper we present similar calculations on toluene and on p-cresol. Because of recent improvements in the Gaussian 92 Program Package[2] it is now possible to calculate the vibrational frequencies of both ground and excited states. Also, since toluene and p-cresol are smaller than tyrosine we are able to use the more accurate 4 in 4 complete active space MCSCF method for our computations[3,4]. We feel that it is instructive to perform more precise calculations on somewhat smaller systems in order to evaluate the accuracy of theoretical predictions. We also hope that the improved accuracy of our present theoretical results makes them of practical use for predictive purposes.

The fluorescence and phosphorescence spectra of aromatic molecules were studied extensively in the early fifties and sixties, a useful review together with a compilation of experimental data is presented in the book by Berlman[5]. Both processes involve the absorption of a photon by the molecule in its ground state and the subsequent reemission of a different photon with smaller energy while the molecule returns to its ground state. Under normal conditions the molecule is in its electronic ground state and in the corresponding lowest vibrational state. During the first step of the process, the absorption of a photon, the molecular geometry does not change. This means that the molecule is excited to a superposition of higher vibrational levels corresponding to the lowest excited electronic singlet state. The second step of the fluorescence process is an internal rearrangement of the molecular geometry to the energy minimum of the excited electronic state or to the lowest vibrational level of the excited state. The fluorescence corresponds to a transition from the energy minimum of the excited singlet state to the ground state while the molecular geometry remains unchanged, followed by an internal rearrangement of the molecular geometry to the lowest vibrational level of the ground state. Phosphorescence usually involves the lowest triplet level of the molecule[6]. In the present paper we limit ourselves to a consideration of fluorescence only.

In our previous work on the fluorescence of phenylalanine and tyrosine we tried to interpret the mechanism from three different theoretical sources of information: (1) the change in geometry due to excitation, (2) the changes in the Mulliken atomic charge densities due to excitation and due to the change in geometry and (3) an analysis of the molecular orbitals involved in the excitation. In our present study of toluene and p-cresol we have a fourth theoretical source of information since we are now able to compute the vibrational frequencies of both the ground and excited states. We mentioned that vibrational relaxation plays an essential role in the fluorescence mechanism. Our theoretical results on both sets of vibrational frequencies are therefore very useful both for the quantitative interpretation of the

mechanism and for making qualitative theoretical predictions.

We present the results of our computations in three different sections. The vibrational frequencies, their assignments and comparisons with experiment are presented in sections 3 and 4, all other theoretical results are presented in section 2.

2. General computations

We performed 4 in 4 CASSCF computations on toluene and p-cresol for the ground state and the first excited singlet state of both molecules using a 6-31G basis set. We determined the optimized geometries and the corresponding energy minima of the states. We therefore computed four energies for each molecule, namely the ground state and the excited state energies at both the ground and excited state optimized geometries.

We show our numbering scheme for the atoms in Fig. 1. The optimized geometries belonging to the energy minima of the ground and excited states are presented in Tables 1 (bond distances) and Table 2 (bond angles). The experimental crystal structure of p-cresol was reported by Bois[7,8]. We also list the experimental cresol data in Tables 1 and 2. We were unable to find corresponding experimental data for toluene in spite of an extensive literature search, but we suspect that the bond distances and bond angles in the phenyl rings of the two molecules are fairly similar. It may be seen from Table 1 that there is good agreement between the computed and the experimental bond distances in cresol. The possible error in the C-H bond distances is 0.1 angstroms and the errors in the C-C and C-O bond distances are .01 angstrom. The differences between the computed and experimental bond distances are within the experimental errors. The computed and experimental bond angles are presented in Table 2. Here, the experimental errors are larger (1 degree or a little more) and the differences between the computed and experimental values are larger also.

Our main purpose for computing the molecular geometries is a comparison of the bond distances and bond angles between the ground state and the first excited singlet state. We present therefore more decimal places in the computed data of Tables 1 and 2 than is actually justified. However, we believe that the changes in bond distances and bond angles are meaningful. An inspection of the data of Table 1 shows that the changes in bond distances are quite obvious, most C-C bond distances increase by a significant amount except the C-CH_3 bond distance and the C6-C12 bond distance. This same pattern occurs in both molecules, toluene and p-cresol.

It may be seen in Table 2 that the changes in bond angles are relatively insignificant. The changes in Mulliken atomic charge densities are also small, as may be seen in Table 3. We analyzed the nature of the molecular orbitals involved in the excitation and found that they are all π orbitals. The singlet state is obtained as a superposition of excitations from the highest pair of occupied π orbitals to the lowest pair of unoccupied π orbitals. It follows therefore that the excitation is localized in the benzene ring and that the substituents have little impact on the excitation.

We list the energies of all our computations in Table 4. The first energy is the optimized ground state energy, this means that we minimized the ground state energy by varying all geometry parameters. We then computed the energy of the first excited singlet state at this same geometry, the values for both molecules are listed on the third line of Table 4. The difference of these two energies is the excitation or absorption energy, which we list on the fourth line. The excitation energy is expressed in terms of cm^{-1}, the other energies in terms of hartrees. We also minimized the excited state energy relative to the geometry parameters, the corresponding energy is listed on the fifth line, the corresponding ground state energy at the same geometry is listed on the second line. The difference of these latter two energies is our predicted fluorescence energy, which is listed on the last and sixth line of the Table.

The interpretation of the excitation seems straightforward since our three sources of information are consistent. The excitation from a bonding to an anti-bonding π orbital reduces the bond order in the majority of the C-C bonds and this leads to slight increases in bond distances. The exception is the C6-C12 bond where the distance becomes smaller and where the bond order increases. This indicates the formation of a localized double C=C bond between C6 and C12 while the conjugation in the rest of the molecule decreases. The single C1-C4 bond does not seem to be affected by the excitation.

The geometry optimizations show an interesting feature, we found that in both molecules the methyl group rotates by 30 degrees upon excitation. This is a surprising conclusion and we checked it carefully, making sure that we are dealing with energy minima and not saddle points. In the ground state of toluene one of the hydrogens, H9, is in the molecular plane pointing towards C2, in the excited state the C1-C4-H11 plane is perpendicular to the benzene ring. In the ground state of p-cresol H10 is in the molecular plane pointing towards C3 and in the excited state the C1-C4-H11 plane is perpendicular to the benzene ring. All our computed vibrational frequencies are positive in the four different cases and this means that we obtained energy minima and not saddle points. Our conclusion is therefore that the electronic excitation is accompanied by a 30 degree rotation of the methyl group around its C1-C4 axis.

3. Vibrational frequencies of the electronic ground states

We mentioned in section 1 that it is now possible to calculate the vibrational frequencies of both ground and excited states. In the present section we report our results for the electronic ground states of toluene and p-cresol. We identify and we assign all vibrational modes and compare the computed frequencies with the available experimental data.

The infrared spectrum of toluene was reported by Fuson, Garrigou-Lagrange and Josien[9] as early as 1960, but we feel that the more recent experimental results of La Lau and Snyder[10] are more precise. Therefore we use the latter data for our analysis of the computed vibrational spectrum of toluene.

The toluene molecule is essentially planar and it is helpful to differentiate between the in-plane and the out-of plane vibrational modes in order to decide about the vibrational assignments. The detailed nuclear motions of each vibrational mode are obtained from the Gaussian 92 Program Package[2] and we derived all vibrational assignments of toluene from a visual inspection of these nuclear displacements. We identify 28 in-plane and 11 out-of-plane vibrational modes if we count the vibrational modes within the methyl group as in-plane. The frequency assignments seem to be straightforward (as opposed to some of the assignments for p-cresol that we discuss later). We present the results in Table 5. We also match each computed frequency with the corresponding experimental frequency[10] and list the ratios between the experimental and the computed frequencies.

The difference between toluene and p-cresol is minor. One of the hydrogens in toluene is replaced by a hydroxyl group. There are now 30 in-plane vibrations. One C-H stretch mode is replaced by a C-O and by a O-H stretch mode and one C-H bend mode is replaced a C-O and a O-H bend mode. There are 12 out-of-plane modes since a C-H bend mode is replaced by a C-O and a O-H bend mode. We expect therefore that the vibrational spectrum of p-cresol would be similar to the spectrum of toluene except for a few minor differences. This is true for most vibrational modes but there is one complication. The in-plane O-H bend mode and C-CH_3 stretch mode interact with some of the C-H bend modes. The result is a shift in the corresponding frequencies and a mixing if the nuclear motions which presents some difficulties in identifying the original vibrational modes. However, we did assign each vibrational mode of p-cresol and present the results in Table 6.

The infrared spectrum of p-cresol was reported by Garrigou-Lagrange, Lebas and Josien[11] as early as 1958 and by Wyss, Werder and Guenthard[12] and Green, Harrison and Kynaston[13] at a later time. It seems to us that the experimental results on the IR and Raman spectra that are reported by Jakobsen[14] are the most detailed and complete and we use Jakobsen's work therefore as the experimental data that we list in Table 6. It should be noted that Jakobsen's data are consistent with the other experimental results[11,12,13].

We processed our theoretical results according to a procedure that we introduced and used previously[15,16] and that we described in detail in a recent review article[17]. In this procedure we multiply each computed frequency by an empirical correction factor in order to improve the accuracy of the theoretical predictions. The empirical correction factors are obtained by averaging the ratios between experimental and computed frequencies for each type of vibrational mode. We derived the correction factors for toluene an p-cresol by averaging the ratios that we present in Tables 5 and 6. The results are listed in Table 7. It should be noted that we differentiate between in-plane and out-of-plane vibrations in deriving the correction factors. The corresponding values are slightly different as may be seen from the Table. We also present the corrected frequency predictions in Tables 5 and 6 in order to show the accuracy of the predictions. We use the correction factors of Table 7 for improving the accuracy of the frequency predictions of the first excited singlet state which we present in the next section.

4. Vibrational frequencies of the lowest excited singlet states.

We identified and assigned all vibrational modes corresponding to the lowest excited singlet states of toluene and p-cresol. The results are reported in Table 8 for toluene and in Table 9 for p-cresol. We are guided by our previous assignments of the vibrational modes in the ground states of the two molecules but there are some minor differences between the two electronic states. In the case of p-cresol there is a strong interaction and a mixing of the out-of-plane O-H and C-H bend modes and little interaction for the corresponding in-plane vibrations. It may be recalled that in the ground state of p-cresol we found mixing of the in-plane O-H and C-H bend modes but not of the corresponding out-of-plane vibrational modes.

We list the computed vibrational frequencies belonging to the lowest excited singlet state of toluene in Table 8 and the corresponding data for p-cresol in Table 9. We multiply each computed frequency by the corresponding correction factor of Table 7, the corrected excited state frequencies are presented in the third columns of Tables 8 and 9. We have matched the vibrational modes of the ground and excited states of each molecule and we list the corresponding frequencies in the last two columns of Tables 8 and 9. The column designated as corr contains the excited state frequencies and the column designated gr. st. contains the corresponding corrected ground state frequencies, copied from Tables 5 and 6. In this way we can compare the vibrational spectra of the ground and excited states of toluene and p-cresol.

It may be seen from Table 8 that there is a close match between the in-plane vibrational modes of ground and excited states of the toluene molecule. In general we expect the excited state frequencies to be somewhat smaller than the ground state frequencies. This is true for most frequencies but there are some exceptions, especially among the C-H bend modes. The C-H stretch modes for ground and excited states are very similar. The out-of-plane frequencies of the ground and excited states differ much more, especially the out-of-plane C-C bend modes which differ by roughly a factor two.

The variations in frequencies are consistent with our analysis of section 2, where we concluded that the excited singlet state is due to the excitation of an electron from a bonding to an antibonding π orbital. The result is a loss of rigidity in the benzene ring especially with respect to out-of-plane motions. We expect therefore significant changes in the out-of-plane C-C bend frequencies and some of the C-H bend frequencies and only small changes in the in-plane frequencies. This seems to be consistent with out computed vibrational spectra.

The vibrational frequencies of p-cresol are presented in Table 9, the first column describes the type of vibrational mode, the second column contains the computed frequencies of the excited singlet state, the third column lists the corrected frequencies and the fourth column the corresponding frequencies belonging to the ground state. In this way it is easy to see the changes in vibrational frequencies due to excitation of the molecule. We note again that the in-plane frequencies match fairly closely for p-cresol just as they did in the case of toluene. However, there are sizable differences for the out-of-plane frequencies (the bottom 12 modes of Table

9). There is a very large difference for the lowest C-H bend mode, 805 for the ground state and 116 for the excited state. At first we thought that we had made an error in the assignment but a closer inspection confirmed that we were indeed dealing with the identical C-H bend mode in both cases. We are unable to offer an explanation for this large discrepancy but the assignment and the two frequency values seem to be correct. We again believe that the electronic excitation causes a decrease in rigidity of the benzene ring, which affects the out-of plane C-C and C-H bend modes much more than the other modes. It is interesting to note that the C-CH_3 bend mode frequency does not change very much due to the excitation.

It is of interest to report the sum of all frequencies in both the ground state and excited state since these sums are relevant to the interpretation of the fluorescence spectra. In the case of toluene the sum of all frequencies is 54678 wave numbers for the ground state and 51770 wave numbers for the excited state. the sum of the in-plane frequencies is 47331 wave numbers for the ground state and 46693 wave numbers for the excited state, the corresponding sums for the out-of-plane vibrations are 7347 for the ground state and 5077 for the excited state. The change in out-of-plane frequencies is significantly larger than the change in in-plane frequencies. The situation is similar for p-cresol. Here the sums of in-plane, out-f-plane and all frequencies are 49429, 7002 and 56431 wave numbers for the ground state and 48813, 4675 and 53488 wave numbers for the excited state, respectively. It should be noted that the C-H and O-H stretch frequencies are practically the same for the ground and excited states. Our general conclusion is that the excitation primarily affects the rigidity of the benzene ring and the frequencies of the out-of-plane ring distortions.

5. Conclusions.

We announced in section 1 that we planned to explain the fluorescence mechanism of toluene and p-cresol from four different sources of theoretical information: (1) the changes in geometry due to excitation, (2) the changes in Mulliken charge densities due to excitation and due to the changes in geometry, (3) an analysis of the molecular orbitals involved in the excitation and (4) a comparison of the vibrational spectra of the ground and excited states.

We believe that the fourth point constitutes the most important aspect of the present study. We believe that our present work is one of the first computations of the vibrational spectra of both ground and excited state of some intermediate-size molecules. Our work is of course based on recent improvements in the Gaussian Program Package[2] but we believe that we are one of the first to take advantage of these recent developments[2]. The accuracy of the corrected theoretical frequencies may be judged from the data in Tables 5 and 6 and from previous work, we believe that the errors in the corrected frequencies are of the order of 10 wave numbers. These vibrational frequency results add a new dimension to the theoretical interpretation of fluorescence spectrum and we hope that it may stimulate novel experimental work on the fluorescence of aromatic compounds.

The general interpretation of the fluorescence of toluene and p-cresol is straightforward since all four sources of theoretical information are consistent and

point in the same direction. The excitation involves the excitation of an electron from a bonding to an anti-bonding π orbital, which leads to a decrease in the rigidity of the benzene ring. The excitation affects the out-of plane C-C bend modes and some of the out-of-plane C-H bend modes the most.

Our conclusions show that the computations permit a reasonably accurate qualitative interpretation of the fluorescence spectra of toluene and p-cresol. Unfortunately they are inadequate for an accurate quantitative predictions. It follows from the experimental data of Berman [5] that the fluorescence spectra of toluene and p-cresol have peaks at 35,000 and 33,000 cm^{-1}, respectively; our computed values are 41,500 in both cases. The absorption bands extend from 37,000 to 42,000 cm^{-1} in the case of toluene and from 34,000 to 40,000 cm^{-1} in the case of p-cresol, our computed excitation energies are 54,800 cm^{-1} in both cases. Even though we have computed all vibrational frequencies for both ground and excited states, we cannot predict how the vibrations affect our numerical predictions since we do not know the detailed form of the potential surfaces. Also, the calculation of the zer-point energy at a non-stationary point on the potential energy surface is somewhat ill-defined and difficult to calculate. It is of course possible to correct the various excitation energies for the zero-point vibrational energies but we doubt very much that this leads to accurate quantitative predictions. It seems therefore safer not to commit ourselves to any quantitative predictions about the effect of vibrations on the excitation energies.

In summary, we feel that our computations lead to reliable qualitative explanations of the fluorescence spectra of toluene and p-cresol but that our theoretical results are inadequate for making precise quantitative predictions.

Figure 1. Definition of atomic numbering in toluene and p-cresol.

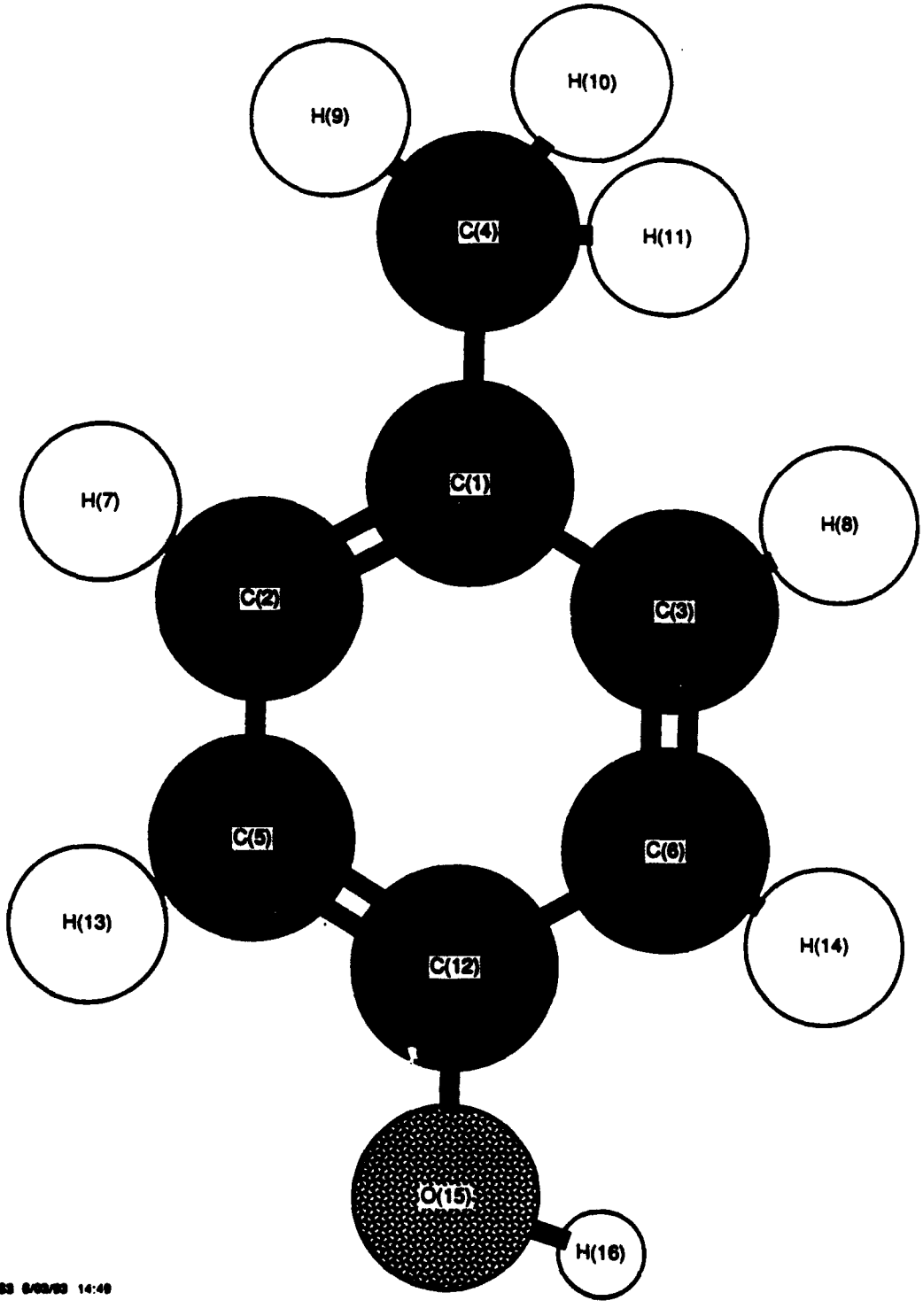

TABLE 1. Bond lengths of the ground and excited states of toluene and p-cresol.

Bond	Toluene		p-Cresol		
	Gr. st.	Exc. st.	Gr. State	Exc. St.	Exp [8]
C1-C2	1.3957	1.4719	1.4082	1.4699	1.406
C1-C3	1.4045	1.4779	1.3916	1.4760	1.391
C1-C4	1.5114	1.4973	1.5110	1.4968	1.520
C2-C5	1.3975	1.4743	1.3865	1.4732	1.397
C2-H7	1.0741	1.0716	1.0743	1.0707	1.0
C3-C6	1.3914	1.4300	1.4018	1.4256	1.401
C3-H8	1.0749	1.0719	1.0737	1.0710	0.9
C4-H9	1.0828	1.0844	1.0850	1.0843	0.9
C4-H10	1.0849	1.0850	1.0829	1.0847	1.0
C4-H11	1.0849	1.0900	1.0849	1.0897	1.1
C5-C12	1.3779	1.4278	1.3983	1.4266	1.388
C5-H13	1.0736	1.0709	1.0712	1.0688	1.0
C6-C12	1.3977	1.3593	1.3713	1.3581	1.397
C6-H14	1.0734	1.0737	1.0748	1.0750	1.0
C12-Y15	1.0733	1.0737	1.3797	1.3768	1.387
O15-H16	-	-	0.9497	0.9501	0.9

TABLE 2. Bond angles of the ground and excited states of toluene and p-cresol.

Bond Angle	Toluene		Cresol		
	Gr. st.	Exc. st.	Gr. St.	Exc. St.	Exp [8]
C2-C1-C3	118.24	117.44	117.85	117.94	118
C2-C1-C4	121.39	120.91	120.48	120.81	120
C3-C1-C4	120.37	120.59	121.68	120.57	122
C1-C2-C5	120.84	119.28	121.22	119.14	121
C1-C2-H7	119.63	120.15	119.52	120.46	-
C5-C2-H7	119.53	120.56	119.26	120.37	-
C1-C3-C6	120.80	119.99	121.17	119.84	122
C1-C3-H8	119.49	119.40	119.86	119.66	-
C6-C3-H8	119.70	120.61	118.97	120.50	-
C1-C4-H9	111.31	111.31	111.27	111.33	-
C1-C4-H10	111.20	111.25	111.26	111.24	-
C1-C4-H11	111.20	111.67	111.28	111.56	-
H9-C4-H10	107.72	107.89	107.66	107.93	-
H9-C4-H11	107.72	107.31	107.51	107.33	-
H10-C4-H11	107.51	107.20	107.67	107.24	-
C2-C5-C12	120.37	119.28	119.49	118.62	120
C2-C5-H13	119.53	119.91	121.78	122.02	-
C12-C5-H13	120.10	120.81	118.73	119.36	-
C3-C6-C12	120.01	122.03	119.85	121.51	118.3
C3-C6-H14	119.98	118.37	119.69	118.77	-
C12-C6-H14	120.01	119.60	120.46	119.72	-
C5-C12-C6	119.73	121.98	120.42	122.94	120.7
C5-C12-Y15	120.29	118.43	116.34	114.03	118.7
C6-C12-Y15	119.98	119.59	123.24	123.03	120.5
C12-O15-H16	-	-	114.64	114.68	120

TABLE 3. Atomic charges of toluene and p-cresol in the ground and excited states.

	Toluene		Cresol	
Atom	Gr. St.	Exc. St.	Gr. St.	Exc.St.
C1	0.000162	0.008561	-0.003352	0.010007
C2	-0.210016	-0.186206	-0.194621	-0.186614
C3	-0.197942	-0.190841	-0.207039	-0.192371
C4	-0.473570	-0.489654	-0.470702	-0.491082
C5	-0.194816	-0.193762	-0.179432	-0.179042
C6	-0.191013	-0.202227	-0.222779	-0.248248
H7	0.193477	0.189420	0.197708	0.194927
H8	0.191946	0.191036	0.197940	0.193538
H9	0.163342	0.163338	0.168755	0.165210
H10	0.168794	0.163185	0.162878	0.164923
H11	0.168794	0.167812	0.168180	0.171102
C12	-0.204921	-0.200493	0.349012	0.362907
H13	0.195750	0.191892	0.222544	0.221397
H14	0.194193	0.193816	0.193597	0.188080
Y15	0.195818	0.194125	-0.794874	-0.789190
H16	-	-	0.412634	0.414455

TABLE 4. Computed energies and excitation energies.

	Toluene	Cresol
Ground St. En.(Gr. St. Geom.)	-269.688 1465	-344.509 9818
Ground St En.(Exc. St. Geom.)	-269.663 3836	-344.485 6218
Excited St En.(Gr. St. Geom.)	-269.438 4307	-344.260 3460
Excitation En	54,806 cm^{-1}	54,789 cm^{-1}
Excited St. En.(Exc. St. Geom.)	-269.473 4651	-344.296 7082
Fluorescence En.	41,682 cm^{-1}	41,462 cm^{-1}

TABLE 5. Computed and exp[10] ground state frequencies of toluene.

Assignment	comp	exp [10]	ratio	corr
C-CH_3 wag	370.7	348	0.93867	354
C-C bend	572.2	522	0.91222	522
C-CH_3 bend	697.7	622	0.89150	637
C-C bend	853.4	788	0.92339	779
C-C bend	1079.4	967	0.89584	985
C-C bend	1107.1	991	0.89513	1011
C-C bend	1128.6	1005	0.89045	1030
C-H bend	1187.9	1084	0.91256	1090
C-H bend	1256.7	1157	0.92065	1153
C-H bend	1304.3	1182	0.90622	1197
C-CH_3 stretch	1330.9	1211	0.90988	1214
C-H bend	1370.6	1286	0.93825	1258
C-H bend	1498.8	1380	0.92075	1376
C-H_3 bend	1585.2	1445	0.91157	1455
C-C stretch	1605.2	1468	0.91454	1465
C-H_3 bend	1648.2	1497	0.90825	1513
C-C stretch	1651.0	1497	0.90672	1506
C-H_3 bend	1663.5	-	-	1527
C-C stretch	1739.4	1587	0.91239	1587
C-C stretch	1754.3	1606	0.91548	1601
C-H_3 sym str	3187.1	2920	0.91620	2901
C-H_3 asym str	3245.0	2963	0.91310	2954
C-H_3 asym str	3267.0	2985	0.91369	2974
C-H stretch	3337.6	3032	0.90843	3038
C-H stretch	3344.4	3040	0.90899	3044
C-H stretch	3356.4	3065	0.91329	3055
C-H stretch	3368.1	3072	0.91210	3066
C-H stretch	3383.6	3079	0.90999	3080
C-CH_3 rot	28.9	-	-	-
C-CH_3 wag	228.3	220	0.96371	225
C-C bend	452.9	407	0.89858	409
C-C bend	516.7	467	0.90386	466
C-C bend	772.7	698	0.90329	698
C-H bend	825.0	732	0.88726	733
C-H bend	940.8	841	0.89392	836
C-H bend	1016.6	898	0.88333	904
C-H bend	1087.0	967	0.88964	966
C-H bend	1160.4	1030	0.88764	1032
C-CH_3 bend	1184.1	1041	0.87912	1078

TABLE 6. Computed and exp[14] ground state frequencies of p-cresol.

Assignment	comp	exp [14]	ratio	corr
C-CH_3 wag	328.0	319	0.97256	313
C-O bend	456.4	430	0.94217	430
C-C bend	503.0	468	0.93041	459
C-C bend	719.2	642	0.89271	657
C-CH_3 bend	795.9	738	0.92722	727
C-C bend	901.2	841	0.93324	823
C-H bend	1098.5	1016	0.92395	1008
C-C bend	1124.7	1042	0.92290	1027
C-C bend	1175.5	1105	0.93999	1073
O-H, C-H bend	1229.1	1170	0.95191*	1128
C-H bend	1300.7	1178	0.90102	1194
O-H, C-H bend	1322.9	1212	0.91617	1214
C-CH_3 stretch	1365.0	1251	0.91647	1245
C-O stretch	1386.7	1294	0.93313	1294
C-H bend	1487.8	1380	0.92754	1366
C-C stretch	1574.4	-	-	1436
C-H_3 bend	1586.8	1464	0.92259	1456
C-H_3 bend	1648.0	-	-	1513
C-H_3 bend	1655.4	1520	0.91820	1519
C-C stretch	1684.1	-	-	1537
C-C stretch	1752.0	1600	0.91324	1599
C-C stretch	1780.3	1621	0.91052	1624
C-H_3 sym str	3186.2	2922	0.91709	2900
C-H_3 asym str	3243.6	2945	0.90795	2953
C-H_3 asym str	3265.8	2970	0.90943	2973
C-H stretch	3341.5	3032	0.90738	3042
C-H stretch	3349.0	3037	0.90683	3049
C-H stretch	3365.9	3058	0.90824	3064
C-H stretch	3399.6	3070	0.90216	3095
O-H stretch	4047.0	3711	0.91845	3711
C-CH_3 rot	54.9	-	-	-
C-CH_3 wag	159.7	161	1.00814	157
O-H bend	320.2	294	0.91822	294
C-C-O bend	363.6	333	0.91588	333
C-C bend	460.5	416	0.90337	416
C-C bend	564.8	508	0.89941	510
C-C bend	772.8	702	0.90839	698
C-H bend	905.7	816	0.90099	805
C-H bend	927.2	823	0.88765	824
C-H bend	1052.9	926	0.87947	936
C-H bend	1070.5	952	0.88929	952
C-CH_3 bend	1183.0	1114	0.94170	1077

TABLE 7. Correction factors for computed ground state vibrational frequencies.

Assignment	Corr. fact.
C-H stretch	0.91032
O-H stretch	0.91845
C-C stretch	0.91240
C-O stretch	0.93313
C-C bend (in)	0.91292
O-H, C-H bend (in)	0.91790
C-O bend (in)	0.94217
C-CH_3 wag (in)	0.95561
C-C bend (out)	0.90282
C-O bend (out)	0.91588
C-CH_3 wag (out)	0.98592
C-CH_3 bend (out)	0.91041
C-H bend (out)	0.88902
O-H bend (out)	0.91822

TABLE 8. Computed and corrected excited state frequencies of toluene.

Assignment	comp	corr	gr. st.
C-CH_3 wag	309.3	296	354
C-C bend	503.0	459	522
C-C bend	607.6	555	779
C-CH_3 bend	789.3	721	637
C-C bend	907.6	829	985
C-C bend	1032.5	943	1011
C-C bend	1070.4	977	1030
C-H bend	1152.5	1058	1090
C-H bend	1226.6	1126	1153
C-CH_3 stretch	1291.3	1178	1214
C-H bend	1310.4	1203	1197
C-H bend	1429.5	1312	1258
C-H bend	1540.0	1414	1376
C-C stretch	1559.8	1423	1465
C-H_3 bend	1580.5	1451	1455
C-C stretch	1604.7	1464	1465
C-H_3 bend	1638.6	1504	1513
C-H_3 bend	1640.8	1506	1527
C-C stretch	1666.1	1520	1587
C-C stretch	1793.3	1636	1601
C-H_3 sym str	3145.3	2863	2901
C-H_3 asym str	3214.4	2926	2954
C-H_3 asym str	3251.9	2960	2974
C-H stretch	3348.1	3048	3038
C-H stretch	3367.3	3065	3044
C-H stretch	3381.2	3078	3055
C-H stretch	3384.7	3081	3066
C-H stretch	3402.1	3097	3080
C-CH_3 bend	86.2	85	225
C-CH_3 rot	108.7	-	-
C-C bend	178.4	161	409
C-C bend	291.9	264	466
C-C bend	345.9	312	698
C-H bend	515.7	458	733
C-H bend	529.8	471	836
C-H bend	584.3	519	904
C-H bend	889.1	790	966
C-H bend	1111.3	1012	1078
C-H bend	1130.1	1005	1032

TABLE 9. Computed and corrected excited state frequencies of p-cresol.

Assignment	comp	corr	gr. st.
C-CH_3 wag	316.9	303	313
C-O bend	439.8	414	430
C-C bend	446.0	407	459
C-CH_3 bend	630.8	576	727
C-C bend	762.7	696	657
C-C bend	842.2	769	823
C-C bend	977.6	892	1027
C-C bend	1068.3	975	1073
C-H bend	1164.4	1069	1008
C-H bend	1204.0	1105	1128
O-H bend	1255.8	1153	1194
C-CH_3 stretch	1295.5	1182	1245
C-O stretch	1361.0	1270	1294
C-H bend	1426.9	1310	1214
C-H bend	1491.8	1369	1366
C-C stretch	1567.3	1430	1436
C-H_3 bend	1580.1	1450	1456
C-C stretch	1606.7	1466	1537
C-H_3 bend	1641.1	1505	1513
C-H_3 bend	1645.0	1510	1519
C-C stretch	1671.2	1430	1599
C-C stretch	1807.7	1649	1624
C-H_3 sym str	3149.3	2867	2900
C-H_3 asym str	3217.3	2929	2953
C-H_3 asym str	3254.3	2962	2973
C-H stretch	3342.4	3043	3042
C-H stretch	3391.8	3088	3049
C-H stretch	3396.4	3092	3064
C-H stretch	3428.1	3096	3095
O-H stretch	4042.1	3712	3711
C-CH_3 bend	75.0	74	157
C-CH_3 rot	96.6	-	-
C-H bend	130.3	116	805
C-C bend	249.3	225	416
C-C bend	270.3	244	510
O-H bend	365.3	335	294
C-O bend	383.9	353	333
C-H bend	483.7	430	824
C-H bend	511.2	454	936
C-C bend	637.7	576	698
C-H bend	964.5	857	952
C-CH_3 bend	1110.0	1011	1077

Blank

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