Density Functional Theory Calculation of Molecular Structure and Vibrational Spectra of Dibenzofuran in the Ground and the Lowest Triplet State

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The molecular geometries and harmonic vibrational frequencies of dibenzofuran in the ground and the lowest triplet state have been calculated using the Hartree-Fock and Becke-3-Lee-Yang-Parr (B3LYP) density functional methods with the 6-31G* basis set. Upon the excitation to the lowest triplet state, the molecular structure retains the planar form but distorts from a benzene-like to a quinone-like form in skeleton. Scaled vibrational frequencies for the ground and lowest triplet state obtained from the B3LYP calculation show excellent agreement with the available experimental data. A few vibrational fundamentals for both states are newly assigned based on the B3LYP results.

Keywords : Dibenzofuran, Molecular structure, Vibration, Lowest triplet state.

Introduction

Dibenzofuran (DBF) and its derivatives have been extensively studied experimentally[1-8] and theoretically[9-11] to investigate their molecular structure and the spectroscopic properties. The complete vibrational analysis for DBF in the ground state would be very useful for the interpretation of the vibronic structures in the absorption and fluorescence spectra. Although the determination of symmetry for observed vibrational frequencies of DBF in the ground state by Bree, Vilkos and Zwarich (BVZ)[7] on the basis of the polarized infrared and Raman spectra of a single crystal is very excellent, their selection of fundamental frequencies from the complicated infrared and Raman spectra is not complete, and has some ambiguities because the selection was done based on the assumption that the fundamental modes show the most intense bands in the spectra. Klots and Collier (KC) clarified most of the ambiguities in the assignment of fundamentals based on the newly recorded infrared and Raman spectra of DBF in the gas, liquid, and solid phases and the frequencies that have been calculated at the level of AM1 and scaled using factors derived from the vibrational analysis for monocyclic and bicyclic compounds.[1] However, there still remain some ambiguities in the assignment of fundamentals. Recently, Buntinx and Poizat (BP) recorded the transient resonance Raman spectra of DBF in the first-excited triplet state and then suggested on the basis of the tentative vibrational assignments of the observed peaks that DBF in the first-excited triplet state takes a quinone-like structure.[3] It is necessary to perform the complete vibrational analysis for DBF in the ground and the first triplet state in order to remove the remained ambiguities in the assignment of fundamentals of DBF in the ground state, assign the peaks observed in the resonance raman spectra of DBF in the lowest triplet state, and confirm BP's suggestion.

Density functional theory calculations[12-24] have been reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies, and for the anharmonicity. There are some results indicating that the vibrational frequencies and intensities from density functional calculations are better than those obtained from second order Möller-Plesset perturbation theory.[24] Rauhut and Pulay (RP)[18] calculated the vibrational spectra of thirty one molecules by using the Becke-Lee-Yang-Parr (BLYP)[25] and Becke-3-Lee-Yang-Parr (B3LYP)[26] functionals with the 6-31G* basis set. They reproduced the experimental vibrational frequencies and infrared intensities very well. In their work, they calculated vibrational frequencies of twenty smaller molecules (the training set) whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using the least square procedure. The scaling factors are successfully applied to other eleven larger molecules (the test set). Even when a single scaling factor of 0.995 (0.963) for the BLYP (B3LYP) method is employed, root-mean-square (RMS) deviations for the training and test sets are 26.2(18.5) and 26.9(19.7) cm^{-1}, respectively. Thus, vibrational frequencies calculated by using the B3LYP functional with the 6-31G* basis can be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra.

By using the B3LYP/6-31G* method, we have calculated the vibrational frequencies of DBF in the ground state to distinguish the fundamentals from the many experimental vibrational frequencies and to predict the spectral positions of the missing lines. Furthermore, the similar theoretical vibrational analysis is performed for the DBF in the lowest triplet state to confirm BP's suggestion - based on the analysis of the transient Raman spectra - that the DBF in the first-excited state takes a quinone-like structure.

Calculations

The molecular structures of DBF in the ground and the first-excited triplet state are optimized at the levels of Hartree-Fock and B3LYP with the 6-31G* basis set. The unrestricted Hartree-Fock and unrestricted B3LYP methods are employed in the geometry optimization for DBF in the triplet state. The expectation values of $< \hat{S}^2 >$ are 2.66 and 2.03 for the UHF and B3LYP results, respectively. Whereas the degree of spin contamination is high for the UHF result, it is very low for the B3LYP result. The harmonic vibrational frequencies for the DBF in the ground state are calculated with the B3LYP with the 6-31G* basis. All the calculations for geometry optimization and harmonic vibrational frequencies are performed by using the Gaussian 98 program.[27]

The calculated vibrational frequencies are scaled by employing multiple scaling factors. To get the vibrational frequencies scaled with multiple scaling factors, cartesian force constant matrix is transformed into the corresponding one in redundant internal coordinates and then scaled by the following equation:

$$F_{ij}^{scal} = \sqrt{s_i s_j} F_{ij}^{int} \tag{1}$$

where s_i and s_j are scaling factors for the internal coordinate *i* and *j*, respectively; then, the scaled-force constant-matrix is diagonalized to provide the vibrational frequencies. The scaling factors can be optimized by using a least square method, that is, by minimizing

$$\chi^2(s) = \sum_i \left(\frac{v_i^{\text{scaled}}(s) - v_i^{\text{exp}}}{v_i^{\text{exp}}} \right)^2 \omega_i \tag{2}$$

where ω_i is the weighting factor for the *i*th mode - one or zero. It should be noted that, in this work, redundant internal coordinates are employed in the transformation of force constant matrix, instead of nonredundant internal coordinates that are common in the scaled, quantum-mechanical, force-field calculations.

Two sets of scaling factors are employed here to get scaled vibrational frequencies of DBF in the ground state. The first set of scaling factors are derived from the vibrational analysis for benzene and furan and is directly applied to DBF without any modifications. The second set is obtained by optimizing the first set for DBF with a weighting factor of zero for some uncertain fundamental modes. Calculated vibrational frequencies for the lowest triplet state are directly scaled by using only a single scaling factor of 0.963, that is recommended by RP[18] since the use of multiple scaling factors is not appropriate for this case due to the lack of known transferable-scaling factors for the excited state and also the insufficient number of peaks observed in the transient Raman spectra of the excited state. For comparison with the scaled-vibrational frequencies for the triplet state on the equal basis, a new set of vibrational frequencies for the ground state is also calculated by using the same method as for the triplet state. The scalings are carried out by using a modified version of REDONG program.[28]

Table 1. Optimized and experimental geometries of Dibenzofuran in the ground and the lowest triplet state

Parameter[a]	Ground State			Triplet State	
	HF	B3LYP	Exp.[b]	HF	B3LYP
R(C_1-C_{10})	1.380	1.388	1.401	1.345	1.356
R(C_1-C_2)	1.384	1.396	1.383	1.439	1.444
R(C_2-C_3)	1.395	1.405	1.377	1.418	1.415
R(C_3-C_4)	1.383	1.394	1.386	1.380	1.379
R(C_4-C_{11})	1.389	1.400	1.387	1.465	1.455
R(O_9-C_{10})	1.357	1.377	1.418	1.367	1.381
R(C_{10}-C_{11})	1.390	1.408	1.382	1.470	1.455
R(C_{11}-C_{12})	1.458	1.452	1.480	1.334	1.375
R(C_1-H_{14})	1.074	1.085	0.95	1.075	1.084
R(C_2-H_{15})	1.075	1.086	0.91	1.074	1.085
R(C_3-H_{16})	1.075	1.086	1.07	1.076	1.087
R(C_4-H_{17})	1.075	1.087	0.98	1.074	1.085
∠ (C_1-C_{10}-C_{11})	123.1	123.3	123.9	123.8	123.9
∠ (C_1-C_{10}-O_9)	125.2	125.0	123.2	126.8	126.0
∠ (C_1-C_2-C_3)	121.4	121.3	122.1	121.2	121.3
∠ (C_2-C_1-C_{10})	116.8	116.7	115.3	117.4	116.7
∠ (C_2-C_3-C_4)	120.8	121.0	121.4	122.1	122.0
∠ (C_3-C_4-C_{11})	118.6	118.6	118.5	118.2	118.1
∠ (C_4-C_{11}-C_{10})	119.3	119.0	118.9	117.3	117.9
∠ (C_4-C_{11}-C_{12})	135.7	135.6	–	135.6	135.4
∠ (O_9-C_{10}-C_{11})	111.7	111.7	112.9	109.3	110.1
∠ (C_{10}-C_{11}-C_{12})	105.0	105.4	105.6	107.1	106.7
∠ (C_{10}-O_9-C_{13})	106.6	106.0	104.4	107.1	106.4
∠ (C_2-C_1-H_{14})	122.1	122.1	129.7	121.1	121.4
∠ (C_{10}-C_1-H_{14})	121.1	121.2	115.1	121.5	121.9
∠ (C_1-C_2-H_{15})	119.3	119.2	117.8	119.2	119.0
∠ (C_3-C_2-H_{15})	119.4	119.5	120.0	119.5	119.7
∠ (C_2-C_3-H_{16})	119.4	119.4	117.4	118.6	118.6
∠ (C_4-C_3-H_{16})	119.8	119.6	120.9	119.3	119.4
∠ (C_3-C_4-H_{17})	120.5	120.6	118.9	121.6	121.6
∠ (C_{11}-C_4-H_{17})	120.9	120.8	123.5	120.2	120.2

[a]Bond lengths in Angstrom and angles in degree. [b]Values from an X-ray diffraction experiment. Reference 8.

Results and Discussion

Molecular Geometries and Excitation Energies. DBF in the ground state has C_{2v} symmetry. The optimized geometries at the levels of HF and B3LYP with 6-31G* are listed in Table 1 with the experimental geometry obtained from an X-ray diffraction experiment.[8] The atomic numbering in DBF is shown in Figure 1.

The CC bond lengths obtained from the B3LYP calculation are longer than those from the HF one by about 0.01 Å, except for the C_{11}-C_{12} bond length. The B3LYP C_{11}-C_{12} bond is shorter than the corresponding one by only 0.004 Å. This pattern is also observed in the optimized geometries of carbazole, fluorene, 9-fluonenone and biphenyl at the HF and B3LYP levels.[19-22]

It is well known that the HF calculation with the 6-31G* basis set underestimates bond lengths and the inclusion of the electron correlation makes them longer. This elongation usually makes the agreement better between the optimized and the experimental geometric parameters. This pattern is also observed here. One exception to this pattern is C_{11}-C_{12},

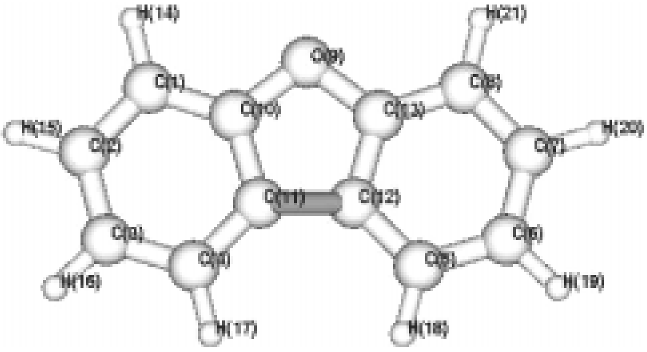

Figure 1. The atomic numbering in dibenzofuran.

the interring bond distance. Inclusion of the electron correlation makes this bond shorter because of the increased resonance in the correlated wavefunction. The optimized bond lengths at both levels are in good agreement with the corresponding bond lengths obtained from the X-ray diffraction. The bond angles from the HF and B3LYP calculations are in good accord with each other and with the experiment.

The molecular structure optimized at the HF and B3LYP levels for the first-excited triplet state is also included in Table 1. The calculated geometry of the triplet state retains a planar C_{2v} conformation. Upon the excitation to the first-excited triplet state, the C_1-C_2, C_2-C_3, C_4-C_{11}, C_{10}-C_{11} and O_9-C_{10} bonds elongate by 0.055, 0.023, 0.076, 0.080 and 0.010 Å, respectively, at the HF level and by 0.048, 0.010, 0.055, 0.047 and 0.004 Å, respectively, at the B3LYP level. However the C_1-C_{10}, C_3-C_4, and C_{11}-C_{12} bonds become shorter by 0.025, 0.003 and 0.124 Å, respectively, at the HF level and by 0.036, 0.014 and 0.077 Å, respectively, at the B3LYP level. This geometrical change is consistent with BP's suggestion - based on the analysis of the transient Raman spectra - that, the molecular structure distorts from a benzene-like to a quinone-like form when going from the ground to the lowest triplet state.

The designation for the triplet state is $^3B_2$. All calculated (de)excitation energies are calculated at the (U)B3LYP/6-31G* level. The vertical and adiabatic excitation energies are calculated to be 3.60 and 3.17 eV, respectively. We believe there are no experimental data available for comparison. The calculated vertical deexcitation energy from the lowest triplet state to the ground state is 2.75 eV. The corresponding experimental one is 3.04 eV, and is derived from the phosphorescence spectra of DBF.[6] The calculated energy is lower than the experimental one by 0.3 eV. The size and direction of the error in the excitation energy is similar to other density functional theory calculations employing hybrid functionals for valence excited states.[24]

Vibrational Frequencies of Dibenzofuran in the Ground State. DBF in the ground state has 57 fundamentals with the various symmetries of 20 a_1+ 9 a_2 + 9 b_1 + 19 b_2. According to the group theoretical analysis of the selection rules for DBF in infrared and Raman spectra, all the symmetric modes are Raman active but only the a_1, b_1, and b_2 symmetric modes are infrared active. Two sets of scaled vibrational frequencies including relative infrared intensities, relative Raman activities, and depolarization ratio that are obtained from the B3LYP calculation for DBF are listed in Table 2. The most intense bands from calculated infrared and Raman spectra are made to have 100.0 relative infrared intensities and Raman scattering activities. The experimental vibrational frequencies reported by BVZ[7] and KC[1] are also included for comparison. The frequencies noted in **boldface** under the experiment column are newly assigned to fundamental vibrational frequencies. Since almost all the vibrational modes are delocalized over the whole molecule, they cannot be ascribed to several local vibrational motions. This is a characteristic feature of cyclic compounds, particularly aromatic compounds. Thus, the modes for DBF are described approximately in Table 2. The calculated B3LYP frequencies are in good agreement with experimental values. The root-mean-square (rms) deviations of vibrational frequencies of DBF calculated with the first and the second sets of scaling factors from experiment are remarkably low, 6.31 and 5.29 cm^{-1}, respectively. The assignments of fundamental mode can be made with confidence.

a_1 symmetry: On the basis of the computational results and the symmetry assigned peaks in infrared and Raman spectra reported by BVZ and KC, we have made a reliable one-to-one correspondence between our fundamentals and

Table 2. Comparison of calculated and experimental vibrational frequencies of Dibenzofuran in the ground state

Sym	Scale 1[a]	Scale 2[b]	I_{IR}[c]	I_{raman}[d]	DP[e]	Exp.[f]	Exp.[g]	Exp.[h]	Approx. Mode Descrition[h]
a_1 symmetry									
ν_1	215	216	0.695	0.191	0.30	218	217	217	RB+str(CC,CO)+ip(CH)
ν_2	420	422	0.990	2.222	0.30	425	424	424	RB+str(CC,CO)+ip(CH)
ν_3	657	660	0.528	0.127	0.12	659	660	660	RB+str(CC,CO)+ip(CH)
ν_4	739	740	0.010	6.726	0.10	746	746	746	RB+str(CC,CO)+ip(CH)
ν_5	844	848	5.265	5.262	0.17	851	850	850	RB+str(CC,CO)+ip(CH)
ν_6	1008	1006	0.158	11.012	0.12	1010	1010	1010	RB+str(CC,CO)+ip(CH)
ν_7	1097	1099	4.001	2.993	0.16	1102	1103	1103	RB+str(CC,CO)+ip(CH)
ν_8	1147	1148	2.331	4.457	0.15	1149	1148	1148	RB+str(CC,CO)+ip(CH)
ν_9	1192	1193	0.201	1.880	0.46	–	1170	1195	RB+str(CC,CO)+ip(CH)
ν_{10}	1240	1246	8.143	37.258	0.26	1242	1245	1245	RB+str(CC,CO)+ip(CH)

Table 2. Continued

Sym	Scale 1[a]	Scale 2[b]	I_{IR}[c]	I_{raman}[d]	DP[e]	Exp.[f]	Exp.[g]	Exp.[h]	Approx. Mode Descrition[h]
ν_{11}	1308	1310	1.061	28.359	0.24	1308	1309	1309	RB+str(CC,CO)+ip(CH)
ν_{12}	1357	1357	2.184	6.505	0.54	1350	1348	1348	RB+str(CC,CO)+ip(CH)
ν_{13}	1444	1446	23.586	5.505	0.53	1445	1448	1448	RB+str(CC,CO)+ip(CH)
ν_{14}	1492	1494	0.182	10.282	0.30	1489	1495	1495	RB+str(CC,CO)+ip(CH)
ν_{15}	1593	1595	0.311	2.106	0.72	1596	1595	1595	RB+str(CC,CO)+ip(CH)
ν_{16}	1632	1636	0.021	100.000	0.40	1633	1636	1636	RB+str(CC,CO)+ip(CH)
ν_{17}	3059	3052	0.205	0.138	0.07	3016	3040	3040	str(CH)
ν_{18}	3069	3062	7.207	53.384	0.73	3048	3061	3061	str(CH)
ν_{19}	3080	3074	18.748	65.310	0.13	3066	3082	3082	str(CH)
ν_{20}	3093	3087	3.508	90.940	0.12	3085	3096	3096	str(CH)
a_2 symmetry									
ν_{1}	150	152	0.000	0.011	0.75	–	150	150	RT+oop(CH)
ν_{2}	290	285	0.000	2.127	0.75	293	287	287	RT+oop(CH)
ν_{3}	444	440	0.000	0.182	0.75	446?	440	440	RT+oop(CH)
ν_{4}	561	573	0.000	0.001	0.75	–	576	576	RT+oop(CH)
ν_{5}	741	744	0.000	0.678	0.75	–	769	–	RT+oop(CH)
ν_{6}	759	763	0.000	0.272	0.75	768	855	769	RT+oop(CH)
ν_{7}	851	864	0.000	0.143	0.75	–	890	855	RT+oop(CH)
ν_{8}	916	928	0.000	0.378	0.75	–	931	931	RT+oop(CH)
ν_{9}	955	970	0.000	0.049	0.75	–	967	967	RT+oop(CH)
b_1 symmetry									
ν_{1}	108	103	0.924	0.098	0.75	130	103	103	RT+oop(CH)
ν_{2}	311	314	0.138	0.704	0.75	312	310	310	RT+oop(CH)
ν_{3}	418	428	2.102	0.005	0.75	421	419	419	RT+oop(CH)
ν_{4}	557	560	0.827	0.007	0.75	564	562	562	RT+oop(CH)
ν_{5}	713	722	8.576	0.066	0.75	723	724	724	RT+oop(CH)
ν_{6}	751	759	69.534	0.105	0.75	751	752	752	RT+oop(CH)
ν_{7}	849	864	0.579	2.205	0.75	783?	849	849	RT+oop(CH)
ν_{8}	916	929	2.103	0.008	0.75	930	930	930	RT+oop(CH)
ν_{9}	957	971	0.031	0.001	0.75	1152?	967	967	RT+oop(CH)
b_2 symmetry									
ν_{1}	514	516	0.051	0.668	0.75	517	516	516	RB+str(CC,CO)+ip(CH)
ν_{2}	554	556	2.079	2.016	0.75	554	556	556	RB+str(CC,CO)+ip(CH)
ν_{3}	614	617	4.041	0.003	0.75	616	617	617	RB+str(CC,CO)+ip(CH)
ν_{4}	841	845	14.863	0.200	0.75	840	849	849	RB+str(CC,CO)+ip(CH)
ν_{5}	993	995	0.156	0.059	0.75	999	1005	1005	RB+str(CC,CO)+ip(CH)
ν_{6}	1019	1020	6.609	0.014	0.75	1022	1024	1024	RB+str(CC,CO)+ip(CH)
ν_{7}	1108	1109	8.005	1.442	0.75	1116	1114	1114	RB+str(CC,CO)+ip(CH)
ν_{8}	1154	1156	0.937	0.475	0.75	1159	1153	1153	RB+str(CC,CO)+ip(CH)
ν_{9}	1191	1201	100.000	1.618	0.75	1193	1201	1201	RB+str(CC,CO)+ip(CH)
ν_{10}	1281	1284	7.808	0.802	0.75	1285	1286	1286	RB+str(CC,CO)+ip(CH)
ν_{11}	1330	1328	8.483	0.896	0.75	1324	1319	1319	RB+str(CC,CO)+ip(CH)
ν_{12}	1458	1460	18.691	0.089	0.75	1451	1458	1458	RB+str(CC,CO)+ip(CH)
ν_{13}	1475	1477	25.298	2.355	0.75	1471	1477	1477	RB+str(CC,CO)+ip(CH)
ν_{14}	1586	1584	3.122	1.363	0.75	1589	1593	1593	RB+str(CC,CO)+ip(CH)
ν_{15}	1600	1600	5.901	1.101	0.75	–	1599	1599	RB+str(CC,CO)+ip(CH)
ν_{16}	3058	3052	0.553	21.546	0.75	3045	3048	3048	str(CH)
ν_{17}	3068	3061	6.965	1.711	0.75	3058?	3061	3061	str(CH)
ν_{18}	3080	3073	19.317	16.781	0.75	3069	3074	3074	str(CH)
ν_{19}	3093	3086	10.321	12.516	0.75	3090?	3096	3096	str(CH)

[a] Vibrational Frequencies in cm^{-1}. The scaling factors are derived from benzene and furan cases. [b] The optimized scaling factors for DBF are employed. [c] Relative Infrared Intensities. The most intense peak has the absolute intensity of 144.87 KM/mole. [d] Relative Raman Scattering Activities. The most intense peak has the absolute Raman scattering activity of 408.05 $Å^4$/AMU. [e] Raman Depolarization Ratios. [f] Reference 7. [g] Reference 1. [h] Present Assignment. [i] RB, ring in-plane bending; RT, ring out-of-plane torsion; str, stretching; oop, out-of-plane; ip, in-plane.

the experimental data. The a_1 symmetric fundamental modes for DBF are observed at 217, 424, 600, 746, 850, 1010, 1103, 1148, 1245, 1309, 1348, 1448, 1495, 1636, 3040, 3060, 3082 and 3070 cm^{-1}. These assignments are the same as those made by BVZ and by KC. The only remaining mode, the 9th a_1 - that BVZ did not assign-should be located between 1148 and 1245 cm^{-1}. The peaks attributed to an a_1 symmetric mode in that range are observed at 1170 and 1190 cm^{-1}. KC selected the peak at 1170 cm^{-1} as the 9th a_1 fundamental mode, based on the scaled, quantum-mechanical force-field calculation at the AM1 level. The 9th a_1 mode are calculated to be located at 1193 cm^{-1} and have the depolarization ratio of 0.46 in this work. Since the peak observed at 1195 cm^{-1} is matched well with the present calculation in the wavenumber and has the experimental depolarization ratio of 0.4, the peak at 1195 cm^{-1} should be the remaining fundamental mode. The peak observed at 1170 cm^{-1} may originate from the combination of the 2nd and the 4th mode of a_1 symmetry. These two modes are observed at 424 and 746 cm^{-1}, respectively. These symmetry modes are totally symmetric vibrations. The fundamental modes below 1650 cm^{-1} consist of ring bendings, CC stretchings, CO stretchings and CH in plane bendings. The higher frequencies are from CH stretchings.

a_2 symmetry: Although these modes are Raman active, their Raman scattering activities are calculated to be relatively low. Fundamentals attributable to a_2 for DBF are observed at 150, 287, 440, 576, 769, 855 and 931 cm^{-1}. The unobserved fundamental 5th a_2 is predicted to be located at 744 cm^{-1} and may be overlapped with the 4th a_1 mode that is predicted to be at 741 cm^{-1} and observed at 746 cm^{-1}. The peak at 890 cm^{-1} - that was ascribed to a fundamental - turns out to be not a real-fundamental mode. These symmetry modes are below 1600 cm^{-1} and consist of interring out-of-plane bending, ring deformations, and CH out-of-plane bendings.

b_1 symmetry: Nine fundamentals that are assigned to the b_1 mode are at 103, 310, 419, 562, 724, 752, 849, 930 and 967 cm^{-1}. There are conflicts between BVZ's and KC's assignments to the 7 b_1 and 9 b_1 modes. But the present study supports KC's assignments. These symmetry modes are below 1600 cm^{-1} and consist of interring out of plane bending, ring deformations, and CH out-of-plane bendings.

b_2 symmetry: Nineteen fundamentals that are attributable to the b_2 mode are observed at 516, 556, 617, 849, 1005, 1024, 1114, 1153, 1201, 1286, 1319, 1458, 1477, 1593, 1599, 3048, 3061, 3074, and 3096 cm^{-1}. The modes whose frequencies are smaller than 1600 cm^{-1} consist of in-plane ring bendings, CC stretchings, CO stretchings and CH bendings. The other modes are CH stretchings.

Table 3. Comparison of calculated and experimental vibrational frequencies of Dibenzofuran in the lowest triplet state

Sym.	DBF S_0		DBF T_1		
	Cal[a]	Exp.[b]	Cal[a]	Exp.[c]	Exp.[d]
a_1 symmetry					
ν_1	212	217	210	–	–
ν_2	415	424	411	–	–
ν_3	646	660	626	–	–
ν_4	732	746	694	–	–
ν_5	833	850	805	818	818
ν_6	1003	1010	953	964	964
ν_7	1088	1103	1053	–	–
ν_8	1138	1148	1091	1154	–
ν_9	1182	1195	1155	–	1154
ν_{10}	1233	1245	1202	–	–
ν_{11}	1296	1309	1316	1345	1320
ν_{12}	1350	1348	1350	1320	1345
ν_{13}	1434	1448	1384	1440	–
ν_{14}	1480	1495	1457	1454	1454
ν_{15}	1586	1595	1588	1470	1586
ν_{16}	1624	1636	1653	1586	–
ν_{17}	3071	3040	3073	–	–
ν_{18}	3081	3061	3095	–	–
ν_{19}	3093	3082	3103	–	–
ν_{20}	3105	3096	3113	–	–

[a] Vibrational Frequencies in cm^{-1}. Frequencies are scaled by a factor of 0.963. [b] Reference 1. [c] Reference 3. [d] Present Assignments.

Vibrational Frequencies of DBF in the First Triplet State. Buntinx and Poizat observed nine bands in the transient Raman spectra of DBF. They assigned all the peaks to be fundamental modes of a_1 symmetry based on comparisons with the vibrational frequencies of the ground state and with the assignments for the biphenyl triplet state. The calculated and observed vibrational frequencies of only a_1 symmetric mode for DBF in the triplet state are also listed at Table 3. The corresponding frequencies for the ground state are included for comparison. The peaks observed at 818, 964, 1154, 1320, 1345, 1345, 1454 and 1586 cm^{-1} are assigned to be the 5th, 6th, 9th, 11th, 12th, 14th and 15th a_1 modes respectively, and are based on the comparison with the calculated frequencies for the triplet state. The remaining two peaks observed at 1440 and 1470 cm^{-1} could not be assigned to any fundamental mode. They may be ascribed to overtones or combinations of fundamental modes of the triplet state or vibrations of other transient species. The rms deviation of the calculated frequencies from the observed ones is only about 6.7 cm^{-1} for DBF in the first triplet state. The assignment of fundamental modes is slightly different from that made by BP. BP noticed from the analysis of Raman spectra that the vibrational frequencies decrease for the ring vibrational modes but increase for the inter-ring vibrational modes on going from the ground state to the triplet state. The hypothesis comes from the observation that the geometry changes from a benzene-like to a quinone-like form when there is an excitation to the triplet state. The same pattern they observed in the vibrational frequencies for an excitation can be seen in the calculated frequencies. Although their assignment of fundamental modes differs slightly from the present work, their suggestion about the change in the geometry upon excitation is confirmed here, as is observed seen in the molecular structure section.

Summary

The molecular structure of dibenzofuran in the ground and the first-excited triplet state and their vibrational spectra are calculated by using the B3LYP with the 6-31G* basis set. Upon the excitation to the first triplet state, the structural change occurs from a benzene-like to a quinone-like form. Based on the calculated and the experimental vibrational frequencies, a few fundamental frequencies are newly assigned.

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