Molecular Structure and Vibrational Spectra of 9-Fluorenone Density Functional Theory Study

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Received June 12, 1996

The molecular geometry and vibrational frequencies of 9-fluorenone have been calculated using the Hartree-Fock and Becke-3-Lee-Yang-Parr(B3LYP) density functional methods with 6-31G* basis set. Harmonic vibrational frequencies obtained from the B3LYP calculation show good agreement with the available experimental data. A few vibrational fundamentals are newly assigned based on the B3LYP results. The B3LYP calculation is reconfirmed to be useful in the assignment of the fundamental vibrational frequencies.

Introduction

Although the density functional theory was shown to have sound theoretical foundation and is efficient in cost,[1~3] its accuracy was not so high compared to those of the Hartree-Fock (HF) and post-Hartree-Fock methods because of the lack of the reliable density functionals. Many new density functionals have been proposed and tested. Among them, the functionals including "gradient corrections" have turned out to show the high accuracy that *ab initio* methods can provide.[4~7] Since density functional theory methods are very efficient, they have been successfully employed to study even the large systems to which standard *ab initio* methods cannot be applied easily.

Density functional theory calculations[8~15] are 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 that the vibrational frequencies and intensities from the density functional calculations are better than those from the second order Möller-Plesset perturbation theory calculation.

Rauhut and Pulay[14] calculated the vibrational spectra of thirty one molecules by using the Becke-Lee-Yang-Parr (BLYP)[6] and Becke-3-Lee-Yang-Parr(B3LYP)[7] functionals with 6-31G* basis set. Both functionals employed contain "gradient corrections". They could reproduce 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, the 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 B3 LYP functional with 6-31G* basis can be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra.

The spectroscopic properties and photochemistry of 9-fluorenone (FLO) and its derivatives have been extensively studied.[16~19] The complete vibrational analysis is necessary for the interpretation of the absorption and fluorescence spectra. Although the symmetry assignments of observed vibrational frequencies of 9-fluorenone by Zwarich, Bree and Vilkos (ZBV)[20] on the basis of the polarized infrared and Raman spectra are 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. Also there is some missing in the assignment of a_2 modes due to the forbidden infrared and Raman selection rules.

By using the HF/6-31G* and B3LYP/6-31G* methods, we calculated the vibrational frequencies of FLO to distinguish the fundamentals from the many experimental vibrational frequencies and to predict the spectral positions of the missing lines.

Calculations

The molecular structure of FLO is optimized at the levels of Hartree-Fock and B3LYP with the 6-31G* basis set. Two sets of vibrational frequencies are calculated with the HF and B3LYP methods at each corresponding optimized geometry and then scaled by 0.8929 and 0.963, respectively. The scaling factor for the B3LYP frequencies is recommended by RP.[14] Two different symmetry designations for FLO are possible due to the different spatial orientations of the molecule. To avoid the confusion, it should be emphasized that the calculations are performed for the molecule in the YZ plane. All the calculations are performed by using the Gaussian 94 program.[21]

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Table 1. Optimized and Experimental Geometries of 9-Fluorenone

Parameter[a]	HF/6-31G*	B3LYP/6-31G*	Exp.[b]
r(C_2-C_1)	1.392	1.401	1.385
r(C_3-C_2)	1.386	1.398	1.376
r(C_4-C_3)	1.394	1.403	1.389
r(C_{4a}-C_4)	1.379	1.390	1.380
r(C_{4b}-C_{4a})	1.488	1.484	1.475
r(C_{9a}-C_1)	1.376	1.387	1.379
r(C_{9a}-C_{4a})	1.395	1.410	1.390
r(C_{9a}-C_9)	1.497	1.500	1.486
r(O-C_9)	1.191	1.219	1.220
r(C_1-H)	1.075	1.087	1.02
r(C_2-H)	1.075	1.086	1.00
r(C_3-H)	1.076	1.087	0.99
r(C_4-H)	1.075	1.087	1.02
∠C_1-C_2-C_3	120.2	120.3	120.6
∠C_2-C_3-C_4	121.4	121.3	121.7
∠C_3-C_4-C_{4a}	118.3	118.5	118.0
∠C_4-C_{4a}-C_{4b}	131.4	131.6	131.1
∠C_2-C_1-C_{9a}	118.2	118.3	118.0
∠C_4-C_{4a}-C_{9a}	120.1	119.9	120.2
∠C_{4b}-C_{4a}-C_{9a}	108.5	108.5	108.8
∠C_1-C_{9a}-C_{4a}	121.8	121.8	121.7
∠C_{8a}-C_9-C_{9a}	104.8	105.0	105.8
∠C_1-C_{9a}-C_9	129.1	129.2	130.0
∠C_{4a}-C_{9a}-C_9	109.1	109.0	108.4
∠C_{9a}-C_9-O	127.6	127.5	127.1
∠C_{9a}-C_1-H	120.5	120.2	120.5
∠C_1-C_2-H	120.0	120.0	119.3
∠C_2-C_3-H	119.4	119.4	119.3
∠C_3-C_4-H	120.2	120.2	122.4

[a] bond lengths in Angstrom, bond angles in degree. [b] X-ray structure. Reference.[22]

Results and Discussion

Molecular Geometry. The FLO molecule has C_{2v} symmetry. The optimized geometries at the levels of HF and B3LYP with 6-31G* are listed at Table 1 with an experimental geometry obtained from an X-ray experiment.[22] The atomic numbering in 9-fluorenone is shown in Figure 1.

The CC bond lengths obtained from the B3LYP calculation are larger than those from the HF ones by about 0.01 Å except the C_{4a}-C_{4b} bond length. The B3LYP C_{4a}-C_{4b} bond is shorter than the corresponding one by marginally small 0.004 Å. The C-O bond length at the B3LYP level is also larger than the HF one by 0.03 Å. It is well known that the HF calculation with the 6-31G* basis set underestimates bond lengths and the inclusion of correlation makes them larger. This elongation usually makes the agreement better between the optimized and the experimental geometric parameters. This pattern is also observed here. The optimized bond lengths at both levels are in good agreement with the corresponding bond lengths from the X-ray diffraction but the detailed comparison between them is somewhat meaningless due to the existence of crystal packing force in the solid phase. The bond angles from either of calculations and the experiment are in good accord with each other.

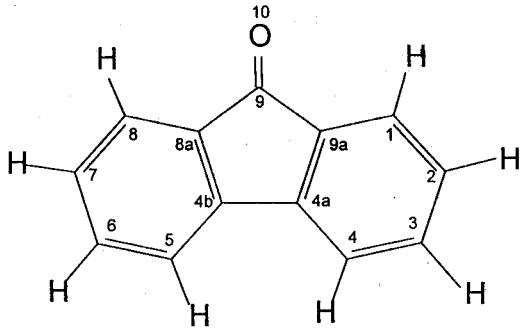

Figure 1. The atomic numbering in 9-Fluorenone.

Vibrational Frequencies. The FLO molecule has 60 fundamentals with the various symmetries of 21 a_1+9 a_2+10 b_1+20 b_2. According to the group thoretical analysis of selection rule for FLO in infrared and Raman spectra, all the symmetry modes are Raman active but only the a_1, b_1, and b_2 symmetry modes are infrared active. Calculated and scaled vibrational frequencies, infrared intensities, Raman activities, and depolarization ratio obtained from the HF calculation are listed in Table 2. Also the calculated frequencies with the infrared intensities from the B3LYP calculation are represented in Table 2. The experimental vibrational frequencies reported by ZBV are also included for comparison. The frequencies noted in boldface under the experiment column are newly assigned fundamental vibrational frequencies. The frequencies in italics were assigned to be fundamental modes but are not the ones based on the present calculations.

Since almost all the vibrational modes are delocalized over 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 are described approximately in Table 2.

When the HF and B3LYP calculated frequencies are compared, almost all the frequencies are in good accord with each other. However, the HF frequencies of 17a_1, 7a_2, 8a_2, 9a_2, 8b_1, 9b_1, and 10b_1 modes are larger than the corresponding B3LYP ones while the HF frequencies of 9b_2 and 11b_2 modes are smaller. All these modes are thought to have nonnegligible correlation contributions.

The calculated B3LYP frequencies are in good agreement with experiment. The rms deviations of vibrational frequencies from experiment is 31.6 (HF) and 16.9 cm^{-1} (B3LYP).

***a_1* symmetry.** On the basis of the computational results and the symmetry assigned peaks in the infrared and Raman spectra reported by ZBV, we have made a reliable one-to-one correspondence between our fundamentals and the experimental data. The a_1 fundamental modes are observed at 204, 411, 566, 726, 776, 1019, 1084, 1132, 1155, 1198, 1293, 1375, 1447, 1481, 1540, 1606, 1721, 3028, 3050, 3072, and 3082 cm^{-1}. The observed frequencies at 1084 and 1132 cm^{-1} are newly assigned to the 7th and 8th modes, respectively. The observed peak at 1540 cm^{-1} is tentatively assigned to the 15th mode. The peak at 1214 cm^{-1} that was ascribed to a fundamental turns out to be not the real fundamental.

These symmetry modes are totally symmetric vibrations

Table 2. Comparison of calculated and experimental vibrational frequencies

Symmetry	HF/6-31G*				B3LYP/6-31G*		Exp.[a]	Approx. Mode Description[b]
Mode	Freq[c]	I_{IR}[d]	I_{Raman}[e]	DP[f]	Freq	I_{IR}[d]	Freq	
a_1								
ν_1	197	0.28	0.59	0.63	196	0.23	204	RB+str(CC)+ip(CH)
ν_2	392	0.09	7.13	0.25	398	0.09	411	RB+str(CC)+ip(CH)
ν_3	539	0.95	7.70	0.12	544	0.69	566	RB+str(CC)+ip(CH)
ν_4	704	0.03	17.82	0.15	711	0.01	726	RB+str(CC)+ip(CH)
ν_5	752	0.38	6.96	0.53	759	0.17	776	RB+str(CC)+ip(CH)
ν_6	994	0.23	69.88	0.14	1008	0.13	1019	RB+str(CC)+ip(CH)
ν_7	1055	0.23	3.30	0.62	1063	0.16	**1084**	RB+str(CC)+ip(CH)
ν_8	1103	0.00	36.26	0.43	1135	11.54	**1132**	RB+str(CC)+ip(CH)
ν_9	1133	8.46	30.36	0.13	1150	0.23	1155	RB+str(CC)+ip(CH)
ν_{10}	1165	0.05	59.08	0.19	1189	0.00	1198	RB+str(CC)+ip(CH)
							1214	
ν_{11}	1267	2.85	5.37	0.30	1272	1.93	1293	RB+str(CC)+ip(CH)
ν_{12}	1294	0.09	105.72	0.22	1365	0.84	1375	RB+str(CC)+ip(CH)
ν_{13}	1436	5.44	8.72	0.39	1434	0.82	1447	RB+str(CC)+ip(CH)
ν_{14}	1471	0.32	33.75	0.28	1464	0.27	1481	RB+str(CC)+ip(CH)
ν_{15}	1590	9.29	0.41	0.74	1583	15.82	**1540**	RB+str(CC)+ip(CH)
ν_{16}	1615	28.44	188.49	0.54	1593	28.01	1606	RB+str(CC)+ip(CH)
ν_{17}	1811	376.39	82.13	0.14	1738	230.03	1721	str(CO)
ν_{18}	3002	1.42	5.53	0.45	3067	0.00	3028	str(CH)
ν_{19}	3015	4.14	192.13	0.74	3078	6.57	3050	str(CH)
ν_{20}	3023	41.14	102.28	0.11	3086	33.74	3072	str(CH)
ν_{21}	3032	0.03	444.23	0.11	3095	0.29	3082	str(CH)
a_2								
ν_1	127	0.00	0.00	0.75	128	0.00	129	RT+oop(CH)
ν_2	265	0.00	9.61	0.75	263	0.00	274	RT+oop(CH)
ν_3	423	0.00	1.23	0.75	423	0.00	422	RT+oop(CH)
ν_4	552	0.00	0.72	0.75	548	0.00		RT+oop(CH)
ν_5	739	0.00	2.18	0.75	728	0.00		RT+oop(CC,CH)
ν_6	782	0.00	0.02	0.75	767	0.00		RT+oop(CH)
ν_7	894	0.00	1.82	0.75	865	0.00		RT+oop(CH)
ν_8	969	0.00	1.58	0.75	922	0.00		RT+oop(CH)
ν_9	1005	0.00	0.59	0.75	956	0.00		RT+oop(CH)
b_1								
ν_1	93	3.05	1.18	0.75	96	2.14	120	RT+oop(CH)
ν_2	146	1.03	1.82	0.75	147	0.87	159	RT+oop(CO,CH)
ν_3	401	0.38	0.58	0.75	396	0.22	392	RT+oop(CO,CH)
ν_4	446	5.74	1.23	0.75	440	3.68	436	RT+oop(CO,CH)
							551?	
ν_5	667	11.73	0.82	0.75	660	9.70	672	RT+oop(CH)
ν_6	743	140.57	0.52	0.75	728	92.82	741	RT+oop(CH)
ν_7	812	5.46	0.04	0.75	795	5.03	812	RT+oop(CH)
ν_8	893	0.53	3.90	0.75	865	0.10	880?	RT+oop(CH)
ν_9	972	2.49	0.99	0.75	925	2.07		RT+oop(CH)
ν_{10}	1006	0.05	0.28	0.75	958	0.01	952?	RT+oop(CH)
b_2								
ν_1	273	8.46	2.51	0.75	271	5.52	278	RB+str(CC)+ip(CO,CH)
ν_2	490	1.62	2.48	0.75	492	2.20	501	RB+str(CC)+ip(CH)
ν_3	604	1.70	0.77	0.75	608	1.54	619?	RB+str(CC)+ip(CO,CH)
ν_4	637	9.06	0.52	0.75	640	5.30	652	RB+str(CC)+ip(CO,CH)
ν_5	897	56.12	5.22	0.75	899	47.24	919	RB+str(CC)+ip(CH)
ν_6	975	0.49	2.70	0.75	987	1.42	1008	RB+str(CC)+ip(CH)

Table 2. Continued.

Symmetry	HF/6-31G*				B3LYP/6-31G*		Exp.[a]	Approx. Mode [b]Description[b]
Mode	Freq[c]	I_{IR}[d]	I_{Raman}[e]	DP[f]	Freq	I_{IR}[d]	Freq	
ν_7	1008	0.74	3.73	0.75	1021	0.00	**1018**	RB+str(CC)+ip(CH) %
ν_8	1073	0.07	23.18	0.75	1080	24.74	1100	RB+str(CC)+ip(CH)
ν_9	1077	15.23	0.55	0.75	1146	3.92		RB+str(CC)+ip(CH)
ν_{10}	1167	31.57	12.45	0.75	1170	45.21	1192	RB+str(CC)+ip(CH)
							1237	
ν_{11}	1211	18.62	3.76	0.75	1278	39.66	**1278**	RB+str(CC)+ip(CH)
ν_{12}	1287	60.89	0.64	0.75	1299	13.89	1300	RB+str(CC)+ip(CH)
							1325	
							1394?	
ν_{13}	1446	65.81	1.00	0.75	1444	45.85	1455	RB+str(CC)+ip(CH)
ν_{14}	1469	0.00	4.50	0.75	1462	1.82	1475	RB+str(CC)+ip(CH)
							1524?	
ν_{15}	1603	12.77	0.00	0.75	1588	3.05		RB+str(CC)+ip(CH)
ν_{16}	1622	78.72	46.03	0.75	1605	73.68	1614	RB+str(CC)+ip(CH)
ν_{17}	3000	4.78	96.83	0.75	3066	3.80	3028	str(CH)
ν_{18}	3012	10.20	0.04	0.75	3076	3.87	3050	str(CH)
ν_{19}	3022	11.60	80.51	0.75	3085	4.10	3072	str(CH)
ν_{20}	3032	45.12	21.27	0.75	3094	50.40	3082	str(CH)

[a]Reference.[20] [b]RB, ring in-plane bending; RT, ring out-of-plane torsion; str, stretching; bend, in-plane bending; tors, out-of-plane torsion; oop, out-of-plane bending; ip, in-plane bending. [c]Vibrational Frequencies in cm^{-1}. [d]Infrared Intensities in KM/mole. [e]Raman Scattering Activities in $Å^4$/AMU. [f]Raman Depolarization Ratios.

in molecular plane. The fundamental modes below 1650 cm^{-1} consist of ring bendings, CC stretchings, and CH bendings. The frequency at 1721 cm^{-1} originates from the CO stretching while 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. Only three lowest fundamentals attributable to a_2 are observed at 129, 274 and 422 cm^{-1}. The unobserved fundamentals are predicted to locate at 548, 728, 767, 865, 922, 958 cm^{-1}. These symmetry modes are asymmetrically out-of-plane vibrations and consist of ring torsions, CC stretchings, and CH bendings.

b_1 symmetry. Nine fundamentals assigned to b_1 mode are at 120, 159, 392, 436, 672, 741, 812, 880 and 952 cm^{-1}. The peak observed at 551 cm^{-1} has tentatively been assigned to be a fundamental but it is not the case. The remaining one fundamental unobserved is predicted to locate at 925 cm^{-1}. These symmetry modes are symmetrically out-of-plane vibrations, and consist of ring torsions, CC stretchings, and CH bendings.

b_2 symmetry. Eighteen fundamentals attributable to b_2 mode are observed at 278, 501, 619, 652, 919, 1008, 1018, 1100, 1192, 1278, 1300, 1455, 1475, 1614, 3028, 3050, 3072, and 3082 cm^{-1}. Two remaining fundamentals could not be correlated with any observed peaks. They are predicted to locate at 1146 and 1588 cm^{-1}. The observed peaks at 1018 and 1278 cm^{-1} are newly assigned to 7th and 11th modes, respectively. Three observed peaks at 1237, 1394, and 1524 cm^{-1} that were considered to be fundamental modes are not the ones. The symmetry modes are asymmetric vibrations in molecular plane. The modes whose frequencies are smaller than 1650 cm^{-1} consist of ring bendings, CC stretchings, and CH bendings. The other modes are CH stretchings.

Summary

The vibrational spectra of 9-fluorenone are calculated by using the B3LYP with 6-31G* basis set. Based on the calculated and the experimental vibrational frequencies, the five fundamental frequencies are newly assigned. The density functional theory calculation employing the B3LYP functional that contains "gradient correction" turns out again to be very useful and efficient to predict vibrational fundamentals.

Acknowedgment. The present study was supported in part by NON DIRECTED FUND, Korea Research Foundation, 1995-1996, Project No. 01-D-0307, and by the Basic Science Research Institute Program, Ministry of Education, Korea, 1995-1996, Project No. BSRI-95-3432. S.Y.L. thanks the Center for Molecular Science (CMS) for a postdoctoral fellowship. B.H.B. is grateful to the CMS for partial financial support.

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