Molecular structure and vibrational spectroscopic studies of 2-(4-methoxyphenyl)-4H-chromen-4-one

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Abstract
2-(4-methoxyphenyl)-4H-chromen-4-one is synthesized from (2E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one. The density functional theory (DFT), MP2 and RHF calculation of this molecule is performed using Gaussian 03 W program package. Quantum mechanical calculations of energy, dipole moment, optimized geometry and fundamental vibrational frequency are evaluated using the DFT, MP2 and RHF with standard B3LYP method employing the 6-311++G(d,p) basis set.

The experimental vibrational frequencies were compared with those obtained theoretically from DFT, MP2 and RHF and ^{1}H NMR from DFT calculations. The difference between the observed and scaled frequencies was small. The frequencies were calculated with B3LYP/6-311++G(d,p) method which are in good agreement with the experimental ones.

Keywords: 2-(4H-methoxyphenyl)-4-H-Chromene-4-one, FT-IR, DFT calculation, ^{1}H NMR.

Introduction
The flavones are naturally occurring heterocyclic compounds belonging to the flavonoid group. These are accumulating in almost any part of plant from the roots to the flower petal and used as dyes for wool[1]. Flavonoids have gained recent interest because of their broad pharmaceutical and biological activities[2-5]. Theoretical investigations of the physical and chemical properties of flavones are very important to know the exact geometry, bond length, bond angels and other properties. Santiago Aparicio[6] studied the flavones derivatives at B3LYP/6-311++G(d,p) theoretical level. Lau et al[7] reported the ab initio and DFT conformational analysis of 5,7-dihydroxyflavone and 7,8-dihydroxyflavone. Raman and surface-enhanced Raman spectra of flavones and several hydroxy derivatives were studied by Teslova et al.[8]

Anbarasu et al[9] studied the DFT using standard B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) basis sets. The structure of 2-(4-methoxyphenyl)-4*H*-chromen-4-one is confirmed by IR, UV, ^{1}H NMR and elemental analysis[10]. Literature survey shows that no theoretical studies have been done so far on the title compound. The main objective of this investigation is to present theoretically more accurate vibrational assignments, ^{1}H NMR, energy and dipole moment of 2-(4-chlorophenyl)-4*H*-chromen-4-one.

Material and Methods
Computational details: The DFT, MP2 and RHF calculations of flavones were performed on an Intel (R) Pentium (R) Dual Core personal computer using the Gaussian-03W program package[11] without any constraint on the geometry. MP2 calculations were performed at Physical Chemistry Division, National Chemical Laboratory, Pune. Geometries of the 2-(4-methoxyphenyl)-4*H*-chromen-4-one compounds were first optimized at 6-311++G(d,p) basis set. Optimized structural parameters were used in the vibrational frequency calculations at DFT level to confirm the structure as minima. Using Gauss View 4.1.2 molecular visualization program, the vibrational frequency assignments and other parameters were made.

Vibrational frequency assignments of the 2-(4-methoxyphenyl)-4*H*-chromen-4-one has been made on the recorded FT-IR (solid phase) and theoretically predicted wave numbers by DFT/ B3LYP, MP2 and HF method using 6-311++G(d,p) basis set and compared with experimental vibrational frequencies.

None of the predicted vibrational frequencies have any imaginary frequency, implying that the optimized geometry is located at the local minimum point on the potential energy surface. The observed values show slight disagreement between theory and experiment, which could be a consequence of the anharmonicity and the general tendency of the quantum mechanical methods to overestimate the force constants at the exact equilibrium geometry. Therefore, in order to improve the calculated values in agreement with the experimental ones, it is necessary to scale the calculated harmonic frequencies. The scaling factor of 0.9427, 0.9631 and 0.8929 is used for MP2, DFT and HF for getting theoretical vibrational frequencies. All the calculations were done for the optimized structures in gas phase.

Results and Discussion
Mullikan atomic charges: We know that the atomic charges are very much dependent on how the atoms are defined. It also plays an important role in the application of quantum chemical calculations to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure and a lot of more properties of molecular systems. The Mullikan atomic charges calculated at DFT/ B3LYP, MP2 and RHF level with 6-311++G(d,p) basis set are listed in table 1. As seen in table 1, because of methoxy group in ring B at para position, the atomic charge distribution is different. The highest

positive charge on C3 carbon is 2.3946 e⁻, 2.3744 e⁻ and 2.3103 e⁻ for 2-(4-methoxyphenyl)-4*H*-chromen-4-one calculated at HF, DFT and MP2 level respectively. The more negative charge on C2 carbon of this compound is -1.4578 e⁻, -1.4479 e⁻ and -1.4692 e⁻ calculated by HF, DFT and MP2 level respectively. All hydrogen carries positive charge.

HOMO-LUMO: Figure 1 shows optimized geometries of 2-(4-methoxyphenyl)-4*H*-chromen-4-one at DFT/ B3LYP/6-311++G(d,p) level. Figure 2 shows the HOMO-LUMO of 2-(4-methoxyphenyl)-4*H*-chromen-4-one.

It shows that the frontier molecular orbital of this compound is mainly composed of p atomic orbital, so electronic transition corresponds to above electronic spectra assigned to n → π* and π → π* electronic transitions.

The highest occupied molecular orbital (HOMO) and the lowest lying unoccupied molecular orbital (LUMO) are named as frontier molecular orbital (FMO). The FMO plays an important role in the optical and electric property as well as quantum chemistry and UV-VIS spectra.
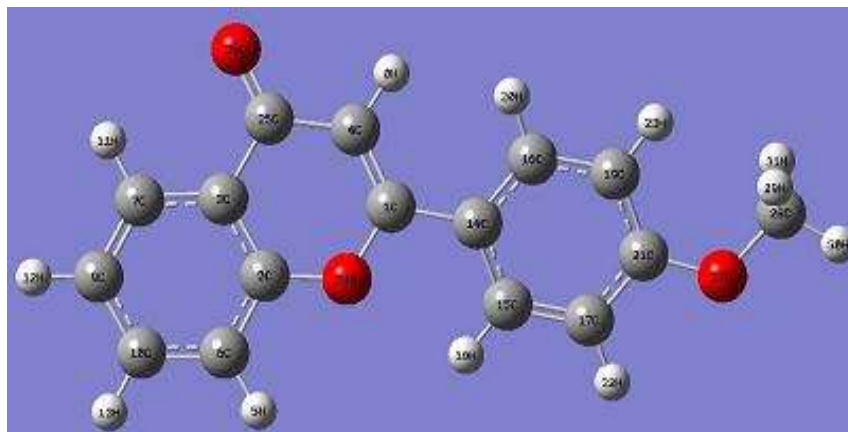

Figure 1: Optimized geometries of 2-(4-methoxyophenyl)-4*H*-chromen-4-one by DFT method at B3LYP level using 6-311++G(d,p) basis set.
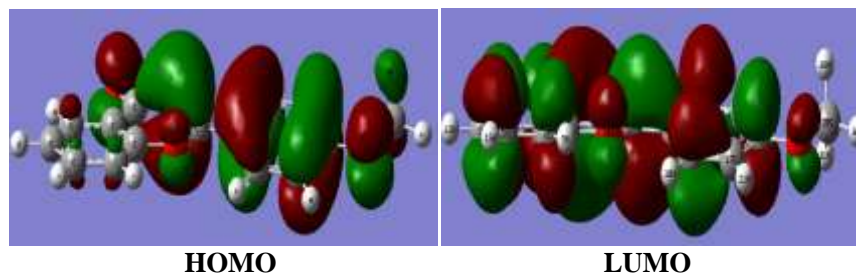

HOMO **LUMO**

Figure 2: HOMO and LUMO plots for Title compound by DFT method atB3LYP level using 6-311++G(d,p) basis set.

Table 1
Mullikan atomic charges (e⁻) of 2-(4-methoxyphenyl)-4*H*-chromen-4-one calculated by DFT method using 6-311++G(d,p) basis set.

Atom	DFT (e⁻)	Atom	DFT (e⁻)	Atom	DFT (e⁻)
C1	0.4608	H12	0.1708	H23	0.1984
C2	-1.4387	H13	0.1749	O24	0.0350
C3	2.3695	C14	0.9278	C25	-1.4440
C4	-0.2269	C15	0.0701	O26	-0.3060
H5	0.1714	C16	-0.3400	O27	-0.146
C6	-0.3741	C17	-0.447	C28	-0.3200
C7	0.1203	H18	0.1630	H29	0.1547
H8	0.1876	C19	0.0117	H30	0.1796
C9	-0.1591	H20	0.1264	H31	0.1568
C10	-0.4385	C21	-0.4270	-	-
H11	0.1907	H22	0.1994	-	-

HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron, energy gap (ΔE) between HOMO and LUMO determines the kinetic stability, chemical reactivity. The calculated energy value of HOMO and LUMO are: -0.23352 a.u. and -0.07508 a.u. respectively having energy gap 0.15844 a.u.

Experimental and theoretical vibrational frequencies:
Fundamental modes of vibrations are calculated by using the formula (3N-6) where N is the number of atoms. There are 31 atoms in 2-(4-methoxyphenyl)-4*H*-chromen-4-one, having 87 normal modes of fundamental vibrations. Computed C-H stretching for this compound is in between 3090 - 3050 cm^{-1}, 3060 -3020 cm^{-1} and 3020 - 2970 cm^{-1} by DFT/B3LYP, MP2 and HF method using 6-311++G(d,p) basis set and experimentally observed at 3067 cm^{-1} . The C-H in plane bending vibrations and C-H out of plane bending vibrations were calculated in between 1580 - 1010, 1560 - 970, 1490 - 1040 cm^{-1} and 960 - 730, 850 - 710, 990 - 720 cm^{-1} by DFT, MP2 and HF respectively and the experimental values were observed within the range 1510 - 1020 cm^{-1} and 949 cm^{-1} and listed in table 2, 2.1 and 2.2 respectively.

The C=O stretching mode was observed at 1645 cm^{-1} in FT-IR spectrum for 2-(4-methoxyphenyl)-4*H*-chromen-4-one and the theoretical value of C=O band was computed at 1635, 1615 and 1706 cm^{-1} by DFT, MP2 and HF respectively. The DFT/B3LYP method shows a very good agreement with experimental value than MP2 and HF. The C-O stretching mode was computed in between 1330 - 980 cm^{-1}, 1310 - 970 cm^{-1} and 1340 - 1180 cm^{-1} by DFT, MP2 and HF respectively and experimentally reported within the range 1370 - 1020 cm^{-1}. The C=C stretching vibrations were found within the range 1600 - 1510 cm^{-1} and the calculated frequencies were in between 1590 - 1530, 1570 - 1450 and 1610 - 1560 cm^{-1} by DFT, MP2 and HF respectively for this compound.

NMR Spectra Analysis: Comparison between the experimental and theoretical ^{1}H NMR chemical shifts (δ) in ppm of title compound calculated at B3LYP/6-311++G(d,p) level using gauge independent atomic orbital (GIAO) method, given in table 3. The NMR calculations have been carried out using the optimized geometries at the same level of theory and using TMS as reference. All aromatic protons are observed at 8.25 to 7.02 δ and theoretically calculated at 5.83 to 7.35 δ where as H$_8$ proton is experimentally observed at 6.76 δ and theoretically at 5.55 δ.

Thermodynamic properties: On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions such as Zero point vibrational energy (Kcal/mol), Rotational Constant, Total energy E (Thermal) kcal/mol (Translational, Rotational and Vibration al), Molar capacity at constant volume (CV) cal/mol-Kelvin (Translational, Rotational and Vibrational) are performed for title compound using HF, DFT/B3LYP and MP2 method with 6-311++G(d,p) basis set. The results obtained on the basis of vibrational analysis are listed in table 4.

Table 2
Observed and computational vibrational assignments (cm^{-1}) along with their intensities of 2-(4-methoxyphenyl)-4*H*-chromen-4-one at DFT/ B3LYP/6-311++G(d,p) level.

S.N.	Scaled frequency	Intensity	Observed frequency	Assignment
1	3095	3	-	C3-H str
2	3088	3	-	Ar-H str
3	3087	6	-	Ar-H str
4	3077	11	-	Ar-H sym str
5	3073	03	-	Ar-H asym str
6	3068	2	3067	Ar-H sym str
7	3064	7	-	Ar-H sym str
8	3062	8	-	Ar-H sym str
9	3050	3	-	Ar-H sym str
10	3018	21	3005	CH$_3$ asym str
11	2954	32	2949	CH$_3$ asym str
12	2894	63	2839	CH$_3$ sym str
13	1635	526	1645	C=O str
14	1589	62	1607	C=C str
15	1585	185	-	C=C str, aromatic CH ip
16	1576	215	-	C-H ip
17	15466	43	-	C=C str, aromatic CH ip
18	1538	20	1512	C=C str, aromatic CH ip
19	1482	170	-	aromatic CH ip,
20	1446	54	-	CH$_3$ ip
21	1442	11	-	aromatic CH ip

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22	1436	10	-	CH₃ ip
23	1434	96	-	aromatic CH ip
24	1419	8	-	CH₃ ip
25	1395	17	-	aromatic CH ip
26	1332	479	1373	C-O str, aromatic CH ip
27	1306	23	1313	ring def, aromatic CH ip
28	1289	6	-	ring def, aromatic CH ip
29	1283	18	-	ring def, aromatic CH ip
30	1256	1	-	ring A,B aromatic CH ip
31	1236	384	1263	C-OCH₃ str
32	1224	106	-	C-C str, aromatic CH ip
33	1208	10	-	C-C str, aromatic CH ip
34	1188	35	1188	C-O str, ring def
35	1156	6	-	CH₃ str
36	1155	192	-	ring B, aromatic CH ip
37	1129	1	-	aromatic CH ip, C-O str
38	1123	1	-	aromatic CH₃ oop
39	1102	29	-	aromatic CH ip
40	1097	37	-	aromatic CH ip
41	1066	2	-	ring def
42	1022	8	1020	O-CH₃ str, aromatic CH ip
43	1012	936	-	O-CH₃ str, aromatic CH ip
44	994	9	-	C-O, O-CH₃ str, ring def
45	982	5	-	C-O str, ring def
46	963	1	-	aromatic CH oop
47	944	1	949	aromatic CH oop
48	939	1	-	aromatic CH oop
49	918	1	-	aromatic CH oop
50	884	17	-	ring def
51	846	1	-	aromatic CH oop
52	835	15	-	ring def
53	829	15	-	ring def
54	818	64	-	aromatic CH oop
55	788	5	-	aromatic CH oop
56	775	6	764	ring def
57	754	33	-	aromatic CH oop
58	737	22	-	aromatic CH oop
59	720	5	-	ring def
60	624	4	-	ring def

Table 2.1
Assignments of frequencies (cm⁻¹) and their intensities of 2-(4-methoxyphenyl)-4*H*-chromen-4-one by MP2/6-311++G(d,p) method.

S. N.	Scaled frequency	Intensity	Observed frequency	Assignments
1	3061	5	-	Ar-H str
2	3059	1	-	Ar-H str
3	3051	10	-	Ar-H str
4	3049	2	-	Ar-H str
5	3045	3	3067	Ar-H asym str
6	3036	3	-	Ar-H asym str
7	3035	2	-	Ar-H asym str
8	3027	3	-	Ar-H asym str
9	3025	3	-	Ar-H asym str

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10	3020	19	3005	CH$_3$ asym str
11	2959	29	2949	CH$_3$ asym str
12	2883	53	2839	CH$_3$ sym str
13	1615	483	1645	C=O str
14	1571	109	1607	C=C str
15	1561	107	-	C=C str, aromatic CH ip
16	1557	16	-	aromatic CH ip
17	1525	8	-	ring def, aromatic CH ip
18	1521	4	1512	ring def, aromatic CH ip, C=C str
18	1457	93	-	C=C str, aromatic CH ip
19	1444	69	-	CH$_3$ ip
20	1422	9	-	CH$_3$ ip
21	1418	9	-	ring def, aromatic CH ip
22	1409	34	-	CH$_3$ ip
23	1408	84	-	aromatic CH ip
24	1399	17	-	trigonal ring def, aromatic CH ip
25	1391	50	-	trigonal ring def
26	1345	165	-	C=C str, aromatic CH ip
27	1311	286	1373	C-O, aromatic CH ip
28	1256	5	-	aromatic CH ip
29	1246	42	-	aromatic CH ip
30	1229	352	1236	aromatic CH ip, C-OCH$_{3\ str}$
31	1206	2	-	aromatic CH ip
32	1196	4	-	aromatic CH ip
33	1180	71	1188	aromatic CH ip, C-O str
34	1149	13	-	CH$_3$ ip
35	1132	71	-	aromatic CH ip
36	1119	1	-	CH$_3$ ip
37	1108	1	-	aromatic CH ip
38	1082	36	-	aromatic CH ip
39	1068	15	-	aromatic CH ip
40	1041	1	-	aromatic CH ip
41	1020	32	1020	aromatic CH ip, C-OCH$_3$ str
42	1000	43	-	aromatic CH ip, C-O str
43	978	6	-	aromatic CH ip, C-O str
44	961	7	-	ring def
45	856	1	-	aromatic CH oop
46	849	1	949	aromatic CH oop
47	842	1	-	aromatic CH oop
48	823	4	-	aromatic CH oop
49	809	5	-	ring def
50	785	9	-	aromatic CH oop
51	780	9	-	aromatic CH oop
52	758	23	-	aromatic CH oop
53	757	7	764	ring def
54	739	39	-	aromatic CH oop
55	710	70	-	aromatic CH oop
56	700	8	-	ring def
57	626	9	-	ring def
58	616	7	-	ring def
59	603	9	-	ring def
60	570	12	-	ring def

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Table 2.2

Theoretical HF/ 6-311++G(d,p) and experimental vibrational frequencies (cm^{-1}) along with their intensities of 2-(4-methoxyphenyl)-4*H*-chromen-4-one.

S.N.	Scaled frequency	Intensity	Observed frequency	Assignments
1	3026	3	-	Ar-H str
2	3013	7	-	Ar-H sym str
3	3011	6	3067	Ar-H asym str
4	3008	7	-	Ar-H str
5	3001	5	-	Ar-H asym str
6	2993	2	-	Ar-H asym str
7	2990	10	-	Ar-H asym str
8	2988	14	-	Ar-H asym str
9	2973	4	-	Ar-H asym str
10	2936	38	3005	CH$_3$ str
11	2885	44	2949	CH$_3$ str
12	2829	56	2839	CH$_3$ sym str
13	1706	776	1645	C=O str
14	1614	234	1607	C=C str
15	1606	45	-	C=C str
16	1603	331	-	C=C str, ring def
17	1568	34	-	C=C str, ring def
18	1561	3	1512	C=C str, ring def
19	1495	233	-	ring def, aromatic CH ip
20	1454	28	-	aromatic CH ip, CH$_3$ ip
21	1448	8	-	CH$_3$ ip
22	1446	228	-	aromatic CH ip
23	1434	22	-	CH$_3$ ip
24	1394	39	-	aromatic CH ip
25	1349	516	1373	C-O str, aromatic CH ip
26	1291	15	-	aromatic CH ip
27	1274	220	-	C-OCH$_3$ str
28	1264	213	1263	aromatic CH ip, C-O str, C-OCH$_3$ str
29	1232	29	-	C-O str, aromatic CH ip
30	1235	150	-	aromatic CH ip
31	1203	4	-	aromatic CH ip
32	1182	50	1188	C-O str, aromatic CH ip
33	1177	15	-	aromatic CH ip, CH$_3$ str
34	1153	128	-	aromatic CH ip
35	1143	3	-	aromatic CH ip
36	1134	3	-	aromatic CH ip
37	1101	33	-	aromatic CH ip
38	1082	22	-	aromatic CH ip
39	1072	4	-	aromatic CH ip
40	1057	10	-	aromatic CH ip
41	1045	66	-	aromatic CH ip
42	1016	44	-	aromatic CH ip, ring def
43	995	1	-	aromatic CH oop
44	985	10	-	CH ip, ring def
45	981	1	-	aromatic CH oop
46	978	1	-	aromatic CH oop
47	977	12	-	ring def
48	956	1	949	aromatic CH oop
49	886	19	-	ring def
50	868	4	-	aromatic CH oop
51	850	16	-	aromatic CH oop

52	836	88	-	aromatic CH oop
53	825	7	-	ring def
54	817	5	-	aromatic CH oop
55	773	11	764	ring def
56	769	60	-	aromatic CH oop
57	756	29	-	aromatic CH oop
58	726	1	-	aromatic CH oop
59	712	7	-	ring def
60	657	3	-	ring def

Abbreviations: str – stretching; sym – symmetric; asym – asymmetric; def – deformation;

ip – in plane bending, oop - out of plane bending.

Table 3
Comparison between the experimental and theoretical ^{1}H NMR chemical shifts (δ) in ppm of title compound calculated at B3LYP/6 -311++G(d,p) level using GIAO method.

Experimental ^{1}H NMR	Calculated ^{1}H NMR
7.53 (d, 1H, H_5),	6.50 (d, 1H, H_5),
7.23 (dt, 1H, H_{13})	6.53 (dt, 1H, H_{13}),
7.44 (t, 1H H_{12})	6.40 (t, 1H, H_{12}),
8.25 (dd, 1H, H_{11}),	7.35 (dd, 1H, H_{11}),
7.89 (d, 2H, H_{18}, H_{20}),	6.95 (d, 2H, H_{18}, H_{20}),
7.02 (d, 2H, H_{22}, H_{23}).	5.83 (d, 2H, H_{22}, H_{23}).
6.76 (s, 1H, H_8),	5.55 (s,1H, H_8),

Table 4
Thermodynamic properties of title compound by different theoretical methods using B3LYP/6-311++G (d,p) basis set.

Parameter	Theoretical methods		
	HF	DFT	MP2
Zero point vibrational energy (kcal/mol)	161.1017	150.3884	149.5947
Rotational constant (GHZ)	1.1447 0.1689 0.1486	1.1282 0.1671 0.1463	1.1185 0.1670 0.1475
Total energy E(Thermal) kcal/mol	169.970	159.882	159.572
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	168.193	158.105	157.795
Total Molar capacity at constant volume (CV) cal/mol-K	55.194	59.724	62.224
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	49.233	53.763	56.262
Total entropy (S) cal/mol-K	121.274	125.323	128.227
Translational	42.474	42.474	42.474
Rotational	33.681	33.721	33.722
Vibrational	45.119	49.128	52.031
Dipole moment (Debye)	4.4282	4.755	4.5829

Conclusion

The selected normal mode of frequencies, corresponding vibrational assignments and ^{1}HNMR of 2-(4-methoxyphenyl)-4*H*-chromen-4-one is examined theoretically using the Gaussian 03package. The optimized geometries, vibrational analysis and ^{1}HNMR chemical shifts were performed by using the DFT method with 6-311++G(d,p) basis set. It was found that the vibrational frequencies and chemical shifts were in good agreement with the experimental results. The DFT/B3LYP method shows a very good agreement with experimental stretching vibrations of C-H, C=O, C=C and C-O than MP2 and HF.

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