

Theoretical Study of Vibration Spectroscopy for Neutral and Charged Fluoranthene Molecule

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Abstract:

The vibration frequencies and infrared absorption intensities for the fluoranthene molecule ($C_{16}H_{10}$) and their positive and negative radical ions have been calculated using ab initio method according to the density functional theory (DFT) at the B3LYP / 6-311G basis set, in addition to PM3 semi-empirical quantum chemical method. Although, the importance of this molecule due to their presence in interstellar space and their environmental contaminating properties, the literatures miss to a complete classification for (3N-6) vibration modes and the vibration frequencies and infrared absorption intensities calculations for the negative radical ion. For these reasons our calculation and classification considered to be assignment. All calculated vibration frequencies rearrangement as the Hertzberg convention, then classified symmetrically and assigned by valence for (3N-6) modes depending on graphical pictures obtained by using Hyperchem program. Generally, the calculated vibration frequencies values showed a good agreement and compatible with values measured experimentally and those calculated by other theoretical methods.

Key words: infrared spectra, fluoranthene, vibrations, interstellar.

Introduction:

Polycyclic aromatic hydrocarbons PAHs are important environmental carcinogens [1-2], these compounds are prevalent in our surrounding and play important role in the chemistry of fossil fuels, the nucleation and growth of soot particles, environmental pollutants [3], and even as interstellar molecules [4]. PAHs are expected to exist in a wide variety of interstellar environments, in a complex statistical equilibrium of different charge and hydrogenation states [5-6]. Ionized and neutral PAH molecules have been proposed as the carriers of a very common family of interstellar infrared fluorescence bands at (3050, 1615, 1310, 1150, and 885 cm^{-1}) [7]. As such, any specific modeling of specific interstellar PAHs must take into account all the ionization states

which may be relevant for a given astronomical environment. Several studies suggested that negatively charged PAHs play an important role in interstellar clouds [5, 6, 8]. However, despite intensive searches a complete normal coordinate analysis on the symmetry and the valence basis of all its 3N-6 vibration modes still missing to date, and as we know for negative radical ion no such studies have been reported in literatures. These reasons have led to renewed interest in a poly aromatic hydrocarbon known as fluoranthene fig. 1. The vibration spectrum of fluoranthene was measured experimentally applying the isolated matrix technique [9] and theoretically [10] as well as its positive radical ion [11-13].

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In this study we present the spectroscopic properties of fluoranthene as well as both ions, the geometries are optimized and all 3N-6 vibration frequencies and IR intensities computed using the Gaussian-based DFT module, the B3LYP [14] hybrid functional in conjunction with the (6-

311G Gaussian basis set), and PM3 semi-empirical method. Finally, graphical pictures obtained from Hyperchem program were used to describe the participation and direction of motion of the atoms in each vibration mode.

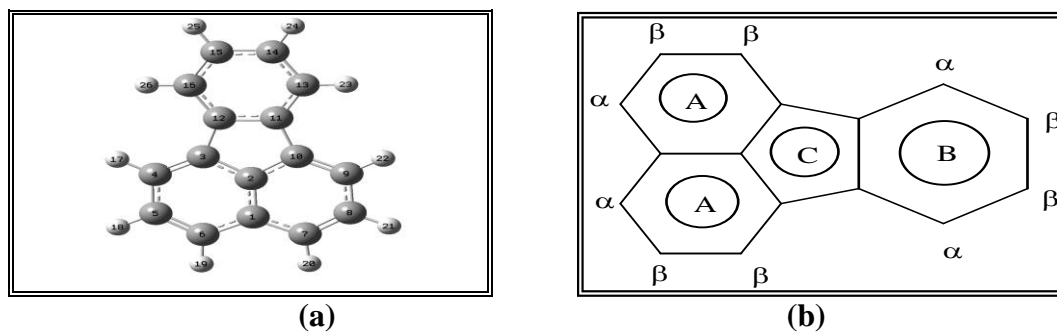


Fig.1. Structure of fluoranthene, showing (a) the designation of the atoms in the molecule, and (b) the numbering of the C and H atoms.

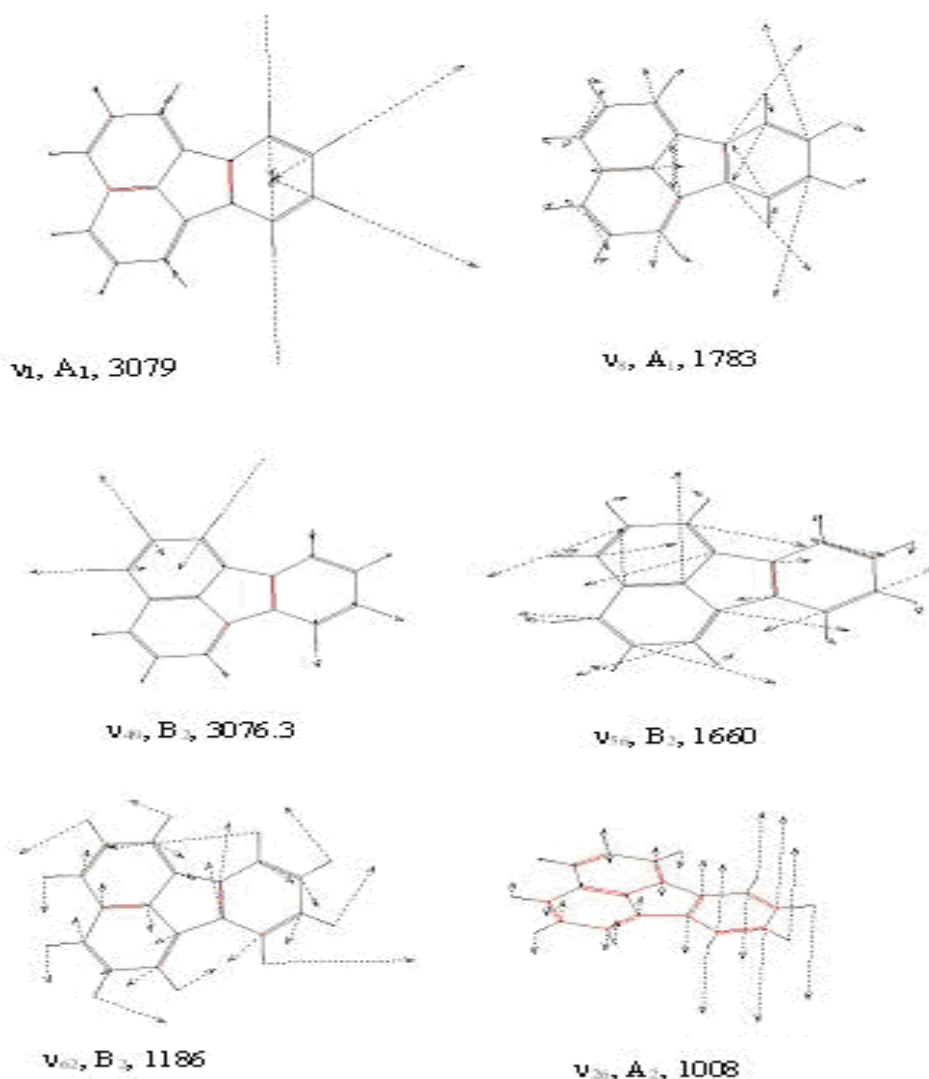


Fig. 2. Graphical pictures of some vibration modes of neutral fluoranthene molecule.

Table 1: calculated geometry of fluoranthene molecule (neutral, cation, and anion radical ions).

Bond length (Å) and Bond angles (deg.)	Neutral		Cation		Anion	
	DFT	PM3	DFT	PM3	DFT	PM3
C ₁ -C ₂	1.402	1.388	1.402	1.406	1.415	1.403
C ₁ -C ₆	1.427	1.423	1.421	1.412	1.427	1.416
C ₂ -C ₃	1.420	1.429	1.416	1.418	1.427	1.426
C ₃ -C ₄	1.380	1.366	1.404	1.402	1.413	1.400
C ₄ -C ₅	1.425	1.423	1.404	1.393	1.403	1.397
C ₅ -C ₆	1.385	1.374	1.408	1.406	1.408	1.400
C ₃ -C ₁₂	1.479	1.469	1.471	1.461	1.448	1.433
C ₁₁ -C ₁₂	1.432	1.432	1.431	1.446	1.461	1.452
C ₁₂ -C ₁₆	1.391	1.379	1.387	1.372	1.403	1.396
C ₁₅ -C ₁₆	1.402	1.400	1.422	1.421	1.395	1.382
C ₁₄ -C ₁₅	1.398	1.387	1.383	1.373	1.415	1.407
C ₆ -H ₁₉	1.082	1.095	1.081	1.097	1.085	1.092
C ₅ -H ₁₈	1.082	1.095	1.080	1.099	1.086	1.094
C ₄ -H ₁₇	1.082	1.094	1.080	1.097	1.085	1.092
C ₁₆ -H ₂₆	1.082	1.094	1.081	1.096	1.085	1.093
C ₁₅ -H ₂₅	1.081	1.095	1.080	1.097	1.085	1.093
< C ₂ C ₁ C ₆	116	116	116	116	116	116
< C ₆ C ₁ C ₇	127	127	127	127	127	127
< C ₁ C ₂ C ₃	124	124	124	124	124	124
< C ₃ C ₂ C ₁₀	111	111	111	111	111	111
< C ₂ C ₃ C ₄	118	118	118	118	118	117
< C ₂ C ₃ C ₁₂	106	105	106	106	106	106
< C ₃ C ₄ C ₅	118	118	118	118	118	118
< C ₃ C ₄ C ₁₇	121	121	121	120	121	120
< C ₄ C ₅ C ₆	122	122	122	123	122	123
< C ₁₁ C ₁₂ C ₁₆	120	120	120	120	119	119
< C ₁₄ C ₁₅ C ₁₆	120	121	120	121	120	121
< C ₆ C ₅ H ₁₈	119	119	118	118	118	118
< C ₁₂ C ₁₆ H ₂₆	120	120	121	121	120	119
< C ₁₄ C ₁₅ H ₂₅	119	119	120	120	119	118
< C ₁ C ₆ H ₁₉	119	118	120	119	119	119
Heat of formation (ΔH_f kcal/mol)	-----	79	-----	272	-----	40

Results and discussion:

The molecule considered here is shown in Figure 1, the geometries for the neutral, cation, and anion forms for this PAH are optimized, for all forms planer C_{2v} symmetry was obtained. The calculated distance and angles are shown in table (1), it is seen that the energy required for formation of the radical cation is much higher than that for the radical anion, this can explain in term of the fact; the formed

anion is expected to be thermodynamically more stable than the corresponding cation. For this reason, the change in the valence binding energies of the bonds of the anion, relative to the neutral molecule, is small than that of the radical cation [15]. The harmonic frequencies and IR intensities which are computed using the Gaussian 03 and Hyperchem programs are tabulated in (2, 3, and 4) tables.

Table 2: calculated vibration frequencies and IR absorption intensities for neutral fluoranthene molecule.

Symmetry and description	Frequencies (cm ⁻¹)			Intensities (km/mol)		
	DFT	PM3	Exp. ^[9]	DFT	PM3	Exp. ^[9]
A₁						
v ₁ CH _{α,β} str. (ring B)	3066	3079	3066	39.367	28.283	-----
v ₂ CH _{β,α} str. (rings A)	3061	3076	-----	71.752	1.401	-----
v ₃ CH _β str. (rings A)	3045	3065	-----	34.847	59.121	-----
v ₄ CH _α str. (ring B)	3039	3063	-----	6.278	8.184	-----
v ₅ CH _β str. (rings A)	3034	3049	-----	0.475	0.346	-----
v ₆ CC str.	1660	1862	1679	0.064	1.061	0.020
v ₇ CC str.	1643	1835	-----	2.413	0.033	-----
v ₈ CC str. (ring B)	1616	1783	1616	0.134	0.002	0.040
v ₉ CC str.	1496	1621	1492	55.331	36.229	0.020
v ₁₀ CC str.	1472	1546	1461	24.292	19.982	0.020
v ₁₁ CC str.	1453	1472	1444	3.698	2.497	0.130
v ₁₂ CC str. + δCH	1412	1450	1429	0.004	1.055	0.160
v ₁₃ CC str. + δCH	1354	1402	-----	0.397	3.310	-----
v ₁₄ CC str. + δCH	1305	1276	-----	0.063	0.214	-----
v ₁₅ δCH + CC str.	1229	1179	1230	2.568	0.011	0.020
v ₁₆ δCH	1210	1154	1217	0.732	0.705	0.020
v ₁₇ δCH (ring B)	1130	1148	1137	2.010	0.036	0.070
v ₁₈ δCH (rings A)	1067	1093	-----	5.408	0.058	-----
v ₁₉ δCH	1046	1078	1036	3.000	0.403	0.020
v ₂₀ δring (δCCC) + δCH	909	1023	1019	1.151	1.263	0.020
v ₂₁ δring (δCCC)	830	847	828	0.487	0.551	0.100
v ₂₂ δring (δCCC)	695	736	672	1.542	0.009	0.010
v ₂₃ δring (δCCC)	580.5	585	-----	2.282	0.432	-----
v ₂₄ δring (δCCC)	499	515	-----	1.743	0.822	-----
v ₂₅ δring (δCCC)	360	376	-----	0.167	0.021	-----
B₁						
v ₂₆ γCH (rings A)	1013	1008	-----	1.750	2.390	-----
v ₂₇ γCH + γCC (ring B)	974	962	-----	1.620	3.144	-----
v ₂₈ γCH (rings A) + γCC	950	938	936	0.036	0.272	0.020
v ₂₉ γCH + γCC (rings A)	851	863	-----	47.549	14.907	-----
v ₃₀ γCH + γCC	798	787	777	117.83	126.92	-----
v ₃₁ γCH	770	767	775	14.554	3.835	1.000
v ₃₂ γCC + γCH	642	604	-----	17.402	13.319	-----
v ₃₃ γCC + γCH (rings A)	478	421	-----	0.113	0.486	-----
v ₃₄ γCC + γCH	449	405	-----	0.952	0.774	-----
v ₃₅ γCC + γCH	306	279	-----	0.565	1.006	-----
v ₃₆ γCC + γCH (rings A)	172	158	-----	3.422	3.583	-----
v ₃₇ γCC + γCH	105	100	-----	2.897	2.104	-----
A₂						
v ₃₈ γCH + γCC (ring B)	1014	1008	-----	0.000	0.000	-----
v ₃₉ γCH + γCC (rings A)	1002	993	-----	0.000	0.000	-----
v ₄₀ γCH + γCC (rings A)	940	932	-----	0.000	0.000	-----
v ₄₁ γCH + γCC (ring B)	907	896	-----	0.000	0.000	--
v ₄₂ γCH + γCC	808	797	-----	0.000	0.002	-----
v ₄₃ γCH + γCC	762	750	762	0.000	0.000	0.010
v ₄₄ γCC + γCH	659	582	-----	0.000	0.000	-----
v ₄₅ γCC + γCH	584	506	-----	0.000	0.000	-----
v ₄₆ γCC + γCH	442	401	-----	0.000	0.000	-----
v ₄₇ γCC + γCH (rings A)	260	228	-----	0.000	0.000	-----
v ₄₈ γCC + γCH	124	112	-----	0.000	0.000	-----
B₂						
v ₄₉ CH _{β,α} str. (rings A)	3062	3076	3073	39.952	10.269	-----
v ₅₀ CH _{α,β} str. (ring B)	3051	3072	3052	35.544	26.917	-----
v ₅₁ CH _{α,β} str. (rings A)	3045	3066	-----	2.275	3.088	-----
v ₅₂ CH _β str. (ring B)	3034	3054	-----	0.084	0.386	-----
v ₅₃ CH _{α,β} str. (rings A)	3033	3050	-----	2.756	4.187	-----
v ₅₄ CC str.	1647	1849	-----	0.158	4.850	-----
v ₅₅ CC str.	1649	1827	-----	0.990	0.542	-----
v ₅₆ CC str.	1530	1660	-----	4.948	0.914	-----
v ₅₇ CC str.	1519	1632	-----	0.938	0.247	-----
v ₅₈ CC str.	1485	1566	1490	15.746	3.873	0.020
v ₅₉ CC str. + δCH	1405	1472	-----	0.588	9.287	-----
v ₆₀ CC str. + δCH (ring B)	1341	1270	-----	0.491	0.961	-----
v ₆₁ δCH + CC str.	1271	1231	-----	1.881	5.756	-----
v ₆₂ δCH (clockwise)	1246	1186	-----	1.214	0.077	-----
v ₆₃ δCH	1207	1154	1184	0.111	0.310	0.030
v ₆₄ δCH (rings A)	1179	1140	1159	9.885	0.803	0.020
v ₆₅ δCH (ring B)	1118	1103	1106	0.002	0.040	0.020
v ₆₆ δCH (rings A)	1043	1084	1034	1.683	0.000	0.010
v ₆₇ δring (δCCC) + δCH	1006	959	-----	0.146	0.134	-----
v ₆₈ δring (δCCC)	791	788	745	1.997	0.199	0.250
v ₆₉ δring (δCCC)	643	637	619	0.010	0.036	0.130
v ₇₀ δring (δCCC)	581	580	561	0.199	0.012	0.020
v ₇₁ δring (δCCC)	486	475	-----	0.562	0.083	-----
v ₇₂ δring (δCCC)	209	218	-----	0.135	0.019	-----

Scaling factor: (0.96) for CH str.

δ: In-plane of the molecule

γ: Out of plane of the molecule

Table 3: calculated vibration frequencies and IR absorption intensities for fluoranthene radical cation molecule.

Symmetry and description	Frequencies (cm ⁻¹)			Intensities (km/mol)		
	DFT	PM3	Exp ^[11]	DFT	PM3	Exp ^[11]
A₁						
v ₁	CH _{αβ} str. (ring B)	3091	3061	-----	12.390	23.036
v ₂	CH _β str. (rings A)	3086	3052	-----	4.158	4.929
v ₃	CH _β str. (ring B)	3071	3046	-----	1.583	33.982
v ₄	CH _{αβ} str. (rings A)	3064	3042	-----	0.094	48.280
v ₅	CH _{βα} str. (rings A)	3063	3025	-----	0.380	2.844
v ₆	CC str.	1651	1820	-----	4.876	147.56
v ₇	CC str.	1623	1809	-----	152.570	24.907
v ₈	CC str.	1583	1732	-----	28.557	0.826
v ₉	CC str.	1501	1592	-----	0.547	2.044
v ₁₀	CC str.	1481	1556	-----	138.330	198.300
v ₁₁	CC str. + δCH	1453	1492	1453	8.208	67.810
v ₁₂	CC str. + δCH (ring B)	1424	1468	-----	63.031	39.050
v ₁₃	CC str. + δCH (rings A)	1375	1439	-----	171.110	11.978
v ₁₄	CC str. + δCH	1311	1280	-----	43.346	42.096
v ₁₅	δCH (rings A)	1232	1173	-----	50.302	7.390
v ₁₆	δCH	1226	1149	1226	27.339	10.677
v ₁₇	δCH + δring (δCCC)	1116	1145	-----	44.534	7.804
v ₁₈	δCH _{αβ} + δring (δCCC)(rings A)	1081	1093	-----	11.405	11.488
v ₁₉	δCH _{αβ} + δring (δCCC)(rings A)	1036	1077	1010	18.888	0.854
v ₂₀	δCH + δring (δCCC)	911	1026	891	14.479	8.348
v ₂₁	δring (δCCC) + δCH	829	840	-----	69.040	3.482
v ₂₂	δring (δCCC)	684	730	-----	19.116	2.194
v ₂₃	δring (δCCC)	573	578	-----	0.000	0.151
v ₂₄	δring (δCCC) + δCH	498	513	-----	1.622	0.010
v ₂₅	δring (δCCC) + δCH	358	373	-----	0.028	0.001
B₁						
v ₂₆	γCH + γCC (rings A)	1035	1033	1020	0.462	0.005
v ₂₇	γCH + γCC (B ring)	995	987	-----	0.846	0.471
v ₂₈	γCH + γCC	979	960	-----	0.216	0.224
v ₂₉	γCC + γCH (rings A)	837	869	831	0.654	11.057
v ₃₀	γCC + γCH	788	783	-----	111.06	44.305
v ₃₁	γCH + γCC	734	758	766	0.053	0.302
v ₃₂	γCC + γCH (rings A)	613	586	-----	13.161	9.725
v ₃₃	γCC + γCH (rings A)	461	418	-----	1.539	1.774
v ₃₄	γCC + γCH	415	375	-----	1.801	1.257
v ₃₅	γCC + γCH	285	262	-----	0.698	0.873
v ₃₆	γCC + γCH (rings A)	168	160	-----	5.294	2.563
v ₃₇	γCC	101	98	-----	5.179	2.029
A₂						
v ₃₈	γCH + γCC (ring B)	1035	1030	-----	0.000	0.001
v ₃₉	γCH + γCC (rings A)	1029	1017	-----	0.000	0.000
v ₄₀	γCH + γCC	958	942	-----	0.000	0.000
v ₄₁	γCH + γCC	924	913	-----	0.000	0.000
v ₄₂	γCH + γCC	808	805	-----	0.000	0.011
v ₄₃	γCC + γCH	744	741	-----	0.000	0.000
v ₄₄	γCC + γCH	638	567	-----	0.000	0.000
v ₄₅	γCC + γCH	541	466	-----	0.000	0.000
v ₄₆	γCC + γCH	424	379	-----	0.000	0.005
v ₄₇	γCC + γCH	251	219	-----	0.000	0.000
v ₄₈	γCC + γCH	123	109	-----	0.000	0.000
B₂						
v ₄₉	CH _α str. (ring B)	3086	3056	-----	9.268	21.371
v ₅₀	CH _{βα} str. (rings A)	3077	3051	-----	5.891	68.323
v ₅₁	CH _{αβ} str. (rings A)	3071	3042	-----	1.254	0.044
v ₅₂	CH _β str. (ring B)	3064	3034	-----	0.215	4.528
v ₅₃	CH _{βα} str. (rings A)	3061	3024	-----	1.108	23.213
v ₅₄	CC str.	1567	1702	-----	6.782	0.180
v ₅₅	CC str.	1543	1635	-----	27.581	16.486
v ₅₆	CC str.	1523	1584	-----	11.954	118.37
v ₅₇	CC str. (rings A)	1492	1523	-----	43.780	58.985
v ₅₈	CC str. + δCH (rings A)	1439	1454	1434	15.067	21.139
v ₅₉	CC str. + δCH _β (rings A)	1369	1392	-----	0.403	26.936
v ₆₀	δCH + CC str.	1314	1227	1318	9.756	13.369
v ₆₁	δCH (anticlockwise)	1265	1183	1275	50.981	3.747
v ₆₂	δCH _{αβ}	1248	1161	-----	33.375	11.270
v ₆₃	δCH _β (rings A) + δring (δCCC)	1173	1134	1183	4.599	0.630
v ₆₄	δCH _β (ring B) + δring (δCCC)	1113	1101	-----	85.588	41.723
v ₆₅	δCH _{αβ} + δring (δCCC)(rings A)	1058	1084	-----	6.183	0.079
v ₆₆	δring (δCCC) + δCH	1002	956	-----	7.261	42.549
v ₆₇	δring (δCCC) + δCH	913	838	-----	511.56	56.945
v ₆₈	δring (δCCC) + δCH (rings A)	703	767	-----	323.98	76.425
v ₆₉	δring (δCCC) + δCH	632	626	-----	8.157	2.837
v ₇₀	δring (δCCC) + δCH	570	575	-----	0.713	2.623
v ₇₁	δring (δCCC) + δCH	331	400	-----	200.91	89.386
v ₇₂	δring (δCCC) + δCH	74	200	-----	218.81	15.554

Table 4: calculated vibration frequencies and IR absorption intensities for fluoranthene radical anion molecule.

Symmetry and description		Frequencies (cm ⁻¹)		Intensities (km/mol)	
		DFT	PM3	DFT	PM3
A₁					
v ₁	CH _{α,β} str. (ring B)	3028	3082	99.788	8.312
v ₂	CH _β str.	3019	3081	244.100	4.598
v ₃	CH _{α,β} str.	3005	3074	98.018	25.788
v ₄	CH _α str. (ring B)	2995	3062	7.3780	5.589
v ₅	CH _{β,α} str. (rings A)	2981	3050	4.8370	0.010
v ₆	CC str.	1617	1799	6.3790	5.957
v ₇	CC str.	1583	1768	0.6430	0.261
v ₈	CC str.	1557	1702	63.785	246.270
v ₉	CC str.	1482	1553	33.913	47.075
v ₁₀	CC str.	1470	1506	1.545	326.82
v ₁₁	CC str.	1414	1493	5.925	79.860
v ₁₂	CC str.	1391	1439	0.219	17.815
v ₁₃	CC str. + δCH	1342	1418	11.189	39.993
v ₁₄	CC str. + δCH	1317	1354	59.402	229.530
v ₁₅	δCH + CC str. (rings B and C)	1215	1183	36.884	1.407
v ₁₆	δCH + δring (δCCC)	1187	1152	22.133	0.763
v ₁₇	δCH _β (ring B) scissoring	1106	1150.6	40.213	10.056
v ₁₈	δCH + ring (δCCC)	1072	1090	22.586	9.816
v ₁₉	δCH rocking + δring (δCCC)	1024	1076	22.602	0.060
v ₂₀	δCH scissoring + rocking + δring (δCCC)	894	1016	16.860	0.205
v ₂₁	δring (δCCC) + δCH _β (rings A)	820	840	2.151	16.270
v ₂₂	δring (δCCC)	684	733	0.738	1.723
v ₂₃	δring (δCCC)	569	581	0.291	1.868
v ₂₄	δring (δCCC)	498	518	8.870	2.857
v ₂₅	δring (δCCC)	359	375	2.389	1.123
B₁					
v ₂₆	γCH + γCC (ring B)	925	930	0.862	0.428
v ₂₇	γCH + γCC (rings A)	920	915	1.530	2.607
v ₂₈	γCH + γCC (rings A)	835	846	10.249	4.112
v ₂₉	γCH + γCC (rings A)	814	818	0.228	5.383
v ₃₀	γCH _{β,α} (ring B)	745	744	180.730	123.01
v ₃₁	γCH _{α,β} (rings A)	735	723	2.892	23.624
v ₃₂	γCC + γCH _α (rings A)	623	564	9.044	4.247
v ₃₃	γCC + γCH (rings A)	509	434	0.140	0.253
v ₃₄	γCC + CH (ring B)	444	400	3.800	5.339
v ₃₅	γCC + γCH	302	266	0.584	0.793
v ₃₆	γCC + γCH (rings A)	183	166	2.860	1.965
v ₃₇	γCC + γCH	104	105	1.279	1.306
A₂					
v ₃₈	γCH + γCC (ring B)	949	956	0.000	0.000
v ₃₉	γCH + γCC (rings A)	914	910	0.000	0.000
v ₄₀	γCH + γCC (ring B)	847	854	0.000	0.000
v ₄₁	γCH + γCC (rings A)	806	823	0.000	0.000
v ₄₂	γCH	766	747	0.000	0.000
v ₄₃	γCH + γCC (ring C)(middle bond)	707	711	0.000	0.000
v ₄₄	γCC + γCH	632	553	0.000	0.000
v ₄₅	γCC + γCH	567	487	0.000	0.000
v ₄₆	γCC + γCH	389	365	0.000	0.000
v ₄₇	γCC + γCH	243	219	0.000	0.000
v ₄₈	γCC + γCH	128	116	0.000	0.000
B₂					
v ₄₉	CH _{α,β} str. (rings A)	3022	3081	142.94	18.557
v ₅₀	CH _{α,β} str.	3009	3075	87.281	2.151
v ₅₁	CH _{α,β} str. (ring B)	3003	3072	2.001	4.878
v ₅₂	CH _{α,β} str. (ring B)	2985	3055	0.449	6.397
v ₅₃	CH _β str. (rings A)	2981	3049	35.670	0.440
v ₅₄	CC str.	1593	1749	3.147	1.260
v ₅₅	CC str.	1540	1676	59.020	24.713
v ₅₆	CC str.	1510	1638	13.363	3.247
v ₅₇	CC str.	1504	1586	3.246	7.286
v ₅₈	CC str.	1445	1527	2.693	14.424
v ₅₉	CC str.	1397	1445	3.495	1.048
v ₆₀	CC str. + δCH	1341	1361	20.738	12.519
v ₆₁	δCH + CC str. (rings A)	1257	1232	31.397	123.550

The obtained results presented as shown below:

• **The C-H Stretching vibrations**

The number of C-H stretching frequencies is ten as C-H bonds, in which the participation of atomic are mainly localized at the C-H bonds as shown in fig. (2), the values range between (2900-3100 cm^{-1}), and comparing these vibrations for all species (neutral, cation, and anion) holds the following relations:

$$v_{\text{sym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10}) (3045) > v_{\text{asym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10}) (3034)$$

$$v_{\text{sym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet+} (3071) > v_{\text{asym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet+} (3064)$$

$$v_{\text{sym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet-} (3019) > v_{\text{asym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet-} (2981)$$

$$v_{\text{sym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet+} > v_{\text{sym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10}) > v_{\text{sym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet-}$$

$$v_{\text{asym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet+} > v_{\text{asym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10}) > v_{\text{asym}} \text{CH}_\beta \text{ str. (C}_{16}\text{H}_{10})^{\bullet-}$$

As we show the C-H stretching frequencies symmetric and asymmetric of the radical cation higher than radical anion through neutral molecule, the reason for this might be explained in term the change in the C-H force constants for the bonds, caused by the change of the electric charge of the molecules.

• **The C-C Stretching vibrations**

Vibration modes in the (1700-1400 cm^{-1}) region arises from pure CC stretching motions within the carbon skeleton of the PAH, and the compares of three species give the following orders:

$$v_{\text{sym}} \text{CC str. (C}_{16}\text{H}_{10}) (1660) > v_{\text{asym}} \text{CC str. (C}_{16}\text{H}_{10}) (1647)$$

$$v_{\text{sym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet+} (1651) > v_{\text{asym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet+} (1567)$$

$$v_{\text{sym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet-} (1617) > v_{\text{asym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet-} (1593)$$

The sequence of three species is found as:

$$v_{\text{sym}} \text{CC str. (C}_{16}\text{H}_{10}) > v_{\text{sym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet+} > v_{\text{sym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet-}$$

$$v_{\text{asym}} \text{CC str. (C}_{16}\text{H}_{10}) > v_{\text{asym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet-} > v_{\text{asym}} \text{CC str. (C}_{16}\text{H}_{10})^{\bullet+}$$

Tables (2, 3, and 4) showed a combination between CC stretching and δCH modes in the region (1300-1400 cm^{-1}).

• **The in-plane of the molecule C-H bending vibrations (δCH)**

The C-H and C-C bending frequencies followed the order:

$$\delta\text{CH}_{\text{sym}} (\text{C}_{16}\text{H}_{10})^{\bullet+} (1232) > \delta\text{CH}_{\text{sym}} (\text{C}_{16}\text{H}_{10})^{\bullet-} (1215) > \delta\text{CH}_{\text{sym}} (\text{C}_{16}\text{H}_{10}) (1210)$$

$$\delta\text{CH}_{\text{asym}} (\text{C}_{16}\text{H}_{10})^{\bullet+} (1265) > \delta\text{CH}_{\text{asym}} (\text{C}_{16}\text{H}_{10})^{\bullet-} (1257) > \delta\text{CH}_{\text{asym}} (\text{C}_{16}\text{H}_{10}) (1246)$$

• **The in-plane of the molecule C-C bending vibrations (δCCC)**

$$\delta_{\text{ring}} (\delta\text{CCC})_{\text{sym}}^{\bullet-} (1072) > \delta_{\text{ring}} (\delta\text{CCC})_{\text{sym}} (830) > \delta_{\text{ring}} (\delta\text{CCC})_{\text{sym}}^{\bullet+} (684)$$

$$\delta_{\text{ring}} (\delta\text{CCC})_{\text{asym}}^{\bullet-} (993) > \delta_{\text{ring}} (\delta\text{CCC})_{\text{asym}}^{\bullet+} (791) > \delta_{\text{ring}} (\delta\text{CCC})_{\text{asym}} (632)$$

• **The out of plane of the molecule C-H vibrations (γCH)**

$$\gamma\text{CH}_{\text{sym}} (\text{C}_{16}\text{H}_{10})^{\bullet+} (1036) > \gamma\text{CH}_{\text{sym}} (\text{C}_{16}\text{H}_{10}) (1013) > \gamma\text{CH}_{\text{sym}} (\text{C}_{16}\text{H}_{10})^{\bullet-} (925)$$

$$\gamma\text{CH}_{\text{asym}} (\text{C}_{16}\text{H}_{10})^{\bullet+} (1035) > \gamma\text{CH}_{\text{asym}} (\text{C}_{16}\text{H}_{10}) (1014) > \gamma\text{CH}_{\text{asym}} (\text{C}_{16}\text{H}_{10})^{\bullet-} (632)$$

• **The out of plane of the molecule C-C vibrations (γCC)**

$$\gamma\text{CC}_{\text{sym}} (\text{C}_{16}\text{H}_{10}) (642) > \gamma\text{CC}_{\text{sym}} (\text{C}_{16}\text{H}_{10})^{\bullet-} (623) > \gamma\text{CC}_{\text{sym}} (\text{C}_{16}\text{H}_{10})^{\bullet+} (613)$$

$$\gamma\text{CC}_{\text{asym}} (\text{C}_{16}\text{H}_{10}) (659) > \gamma\text{CC}_{\text{asym}} (\text{C}_{16}\text{H}_{10})^{\bullet+} (644) > \gamma\text{CC}_{\text{asym}} (\text{C}_{16}\text{H}_{10})^{\bullet-} (632)$$

Conclusion:

As a general conclusion, one could say that DFT calculations give fairly accurate results, and able to account the harmonic frequencies for the neutral as well as for cation, and anion forms of the PAHs. The geometries for

the neutral, cation, and anion forms for this PAH are optimized, for all forms planer C_{2v} symmetry was obtained. The obtained calculated frequencies, has shown that good agreement with available experimental data. The corresponding intensity values not fully agree with available experimental data. The DFT and PM3 methods allow a complete valence and symmetry assignment of all frequencies to their corresponding modes, and the graphical pictures help to describe the participation and direction of motion of the atoms in each vibration mode.

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دراسة نظرية للطيف الاهتزازي لجزيئة الفلورانثين وجذريها الايونيين الموجب والسالب

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الخلاصة:

تم حساب ترددات الاهتزاز الاساسية وشدت امتصاص الاشعة تحت الحمراء لجزيئة الفلورانثين (C₁₆H₁₀) وجذريها الايونيين الموجب و السالب باستخدام طريقة الحساب التام وفقا لنظرية دوال الكثافة Density Functional Theory (DFT) عند عناصر القاعدة (6-311G) وبأسلوب (B3LYP), فضلا عن إحدى طرائق ميكانيك الكم التقريبية (PM3) Semi-empirical method. وعلى الرغم من أهمية هذه الجزيئة كونها احد مصادر الاشعة تحت الحمراء المنبعثة في الاوساط الفضائية فضلا عن كونها مدرجة ضمن احد المصادر البيئية الخطرة لتلوث البيئة, تفتقر الادبيات للتصنيف المتكامل وبعده (3N-6), كما لم يتوفر في الادبيات ما يشير الى حساب ترددات الاهتزاز وشدة امتصاص الاشعة تحت الحمراء للجزر الايوني السالب لهذه الجزيئة, لذا يعد حسابنا وتصنيفنا لها تنبؤيا. تم ترتيب جميع ترددات الاهتزاز المحسوبة بحسب تقليد هيرتزرغ كما تم تصنيفها تماثليا وتشخيصها تكافؤيا وبعده (3N-6) اعتمادا على الاشكال البيانية التي تم الحصول عليها باستخدام برنامج Hyperchem. عموما كانت القيم العددية لترددات الاهتزاز التي نتجت عن الحساب جيدة و متوافقة مع القيم المقاسة تجريبيا وتلك المحسوبة بطرائق نظرية اخرى.