

Vibration Frequencies and Normal Coordinates of Perylene with Different Molecular Charges A MINDO/3-Forces Treatment

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Abstract

The MINDO/3-FORCES method was applied for the calculation of the vibration frequencies and normal coordinates of the neutral aromatic perylene molecule and its radical cation and anion. The resulting frequency values were quite near the experimental values when available. Comparison of the results showed that for the C-H and C-C stretching vibrations the sym. mode shows higher frequency values than the asym. As for the δ CH and δ CC deformation the asym. vibrations where of higher frequency values than the sym. Comparing the frequencies of the three species with each other it was found that;

$$\nu_{\text{CH str.}}(\text{C}_{20}\text{H}_{12})^{\cdot+} > \nu_{\text{CH str.}}(\text{C}_{20}\text{H}_{12}) > \nu_{\text{CH str.}}(\text{C}_{20}\text{H}_{12})^{\cdot-}$$

and,

$$\nu_{\text{sym CC str.}} > \nu_{\text{sym CC str.}}^{\cdot-} > \nu_{\text{sym CC str.}}^{\cdot+}$$

$$\nu_{\text{asym CC str.}}^{\cdot+} > \nu_{\text{asym CC str.}} > \nu_{\text{asym CC str.}}^{\cdot-}$$

These relations are discussed in terms of the change of the σ electron densities at the C atoms of the C-H bonds and the changes in the C-C bond orders of the related bonds.

(3N-6)

MINDO/3-FORCES

(δ CC) (δ CH)

C-C C-H

:

$$\nu_{\text{CH str.}}(\text{C}_{20}\text{H}_{12})^{\cdot+} > \nu_{\text{CH str.}}(\text{C}_{20}\text{H}_{12}) > \nu_{\text{CH str.}}(\text{C}_{20}\text{H}_{12})^{\cdot-}$$

كذلك:

$$\nu_{\text{sym CC str.}} > \nu_{\text{sym CC str.}}^{\cdot-} > \nu_{\text{sym CC str.}}^{\cdot+}$$

$$\nu_{\text{asym CC str.}}^{\cdot+} > \nu_{\text{asym CC str.}} > \nu_{\text{asym CC str.}}^{\cdot-}$$

علت النتائج من خلال علاقة الترددات بقيمة كثافة الإلكترونات (σ) لذرة الكربون في الاصرة C-H و تغير رتب الاواصر CC جراء تغير الشحن الجزيئية.

Introduction

The IR-vibration spectrum of the aromatic Perylene molecule was a subject for many experimental works [1-3]. Later, the development of the isolated matrix technique allowed the remeasurement of the vibration spectrum of the molecule with a higher accuracy [4-9]. Langhoff et al. applied the ab initio quantum mechanical method for the theoretical analysis of its vibration spectrum [10]. However, in their work only the basic and most prominent frequencies were discussed.

As for perylene radical cation, various experimental studies of its vibration spectrum appeared [4-5]. The theoretical treatments were usually based on the ab initio SCF-MO method and limited to the discussion of the most relevant vibrations with no full analyses of the 3N-6 normal coordinates [10-11]. For the radical anion, no experimental vibration frequencies are known.

In the present work, we applied the MINDO/3-FORCES method which is

known to yield good frequency values for the polyaromatic hydrocarbons [12-18]. This method is used for evaluating vibration frequencies and for the complete analysis of all vibration frequencies and normal coordinates of perylene. The here reported vibration absorption intensities are to be viewed cautiously, due to the quantum mechanical approximate nature of the MINDO/3-FORCES method. For the analysis of the normal coordinates of the molecule we applied the DRAW.MOL [19] program, and the Herzberg [20] scheme for their classification.

Results and discussion

Figure 1 shows a descriptive prototype of the molecular motion of a normal coordinate of perylene. In this figure two vibrations are shown; a- an in plane and b- an out of plane vibration mode.

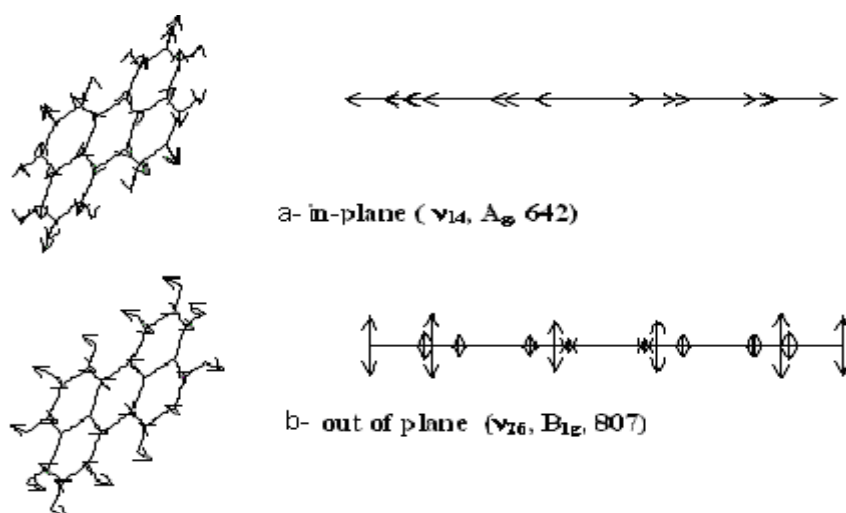


Fig. 1. DRAW.MOL pictures of two vibration modes of Perylene; a- in plane and b- out of plane vibration.

Perylene shows D_{2h} symmetry, with three C_2 rotation axes. The C_z axis falls conventionally in the plane of the

molecule and passing through the biggest number atoms.

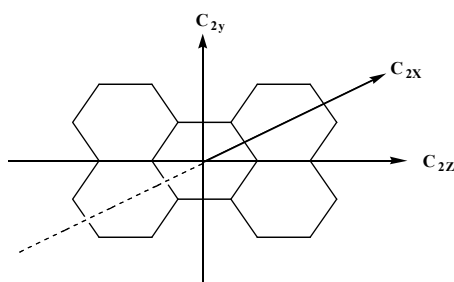


Fig. 2. Choice of the Cartesian coordinate as applied for the perylene molecule.

The IUPAC numbering of atoms was adopted for the molecule, Fig. 3. The vibration frequencies were calculated for the MINDO/3-FORCES equilibrium geometry of the molecule, Table 1. Totally 90 modes of vibrations are expected for the molecule. They are classified according to the following representations;

$$\Gamma_{\text{vib.}} = \Gamma_{\text{tot.}} - (\Gamma_{\text{rot.}} + \Gamma_{\text{tran.}}) = 16A_g + 6B_{1g} + 8B_{2g} + 15B_{3g} + 7A_u + 15B_{1u} + 15B_{2u} + 8B_{3u}$$

Γ_{ip} = In-plane modes of vibrations

$$\Gamma_{\text{ip}} = 2N - 3 = (2 \times 32) - 3 = 61 = 16A_g + 15B_{1u} + 15B_{2u} + 15B_{3g}$$

Γ_{op} = Out of plane modes of vibrations

$$\Gamma_{\text{op}} = N - 3 = 32 - 3 = 29 = 6B_{1g} + 8B_{2g} + 7A_u + 8B_{3u}$$

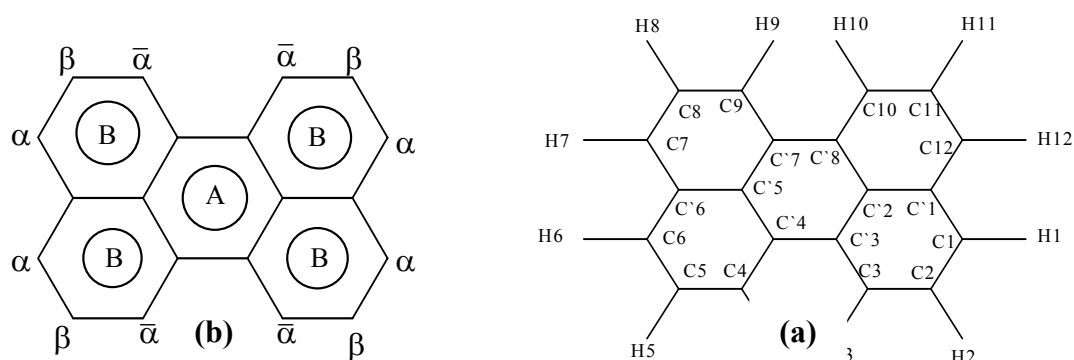


Fig. 3. Structure of the Perylene molecule showing a-the different designations of the C and H atoms as used normally by the organic chemist; b- the numbering of the atoms according to the IUPAC convention.

Table (1): Calculated geometry for perylene (neutral, cation and anion) molecule.

Bond length (Å) & Bond angles (deg.)		MINDO/ 3-FORCES	other work (neutral)		this work MINDO/ 3-FORCES	
		neutral	Exptl. [22]	calcd. [21]	cation	anion
	C ₃ C ₄	1.507	1.471	1.476	1.477	1.480
	C ₂ C ₃	1.478	1.425	1.432	1.467	1.471
	C ₃ C ₃	1.402	1.397	1.390	1.438	1.431
	C ₁ C ₂	1.460	1.424	1.415	1.480	1.477
	C ₁ C ₁	1.446	1.400	1.425	1.437	1.437
	C ₁ C ₂	1.377	1.370	1.375	1.395	1.392
	C ₂ C ₃	1.424	1.418	1.416	1.401	1.401
	H ₁ C ₁	1.106	-----	-----	1.105	1.108
	H ₂ C ₂	1.105	-----	-----	1.103	1.110
	H ₃ C ₃	1.107	-----	-----	1.106	1.108
	< C ₄ C ₃ C ₂	119.422	-----	-----	119.6	119.6
	< C ₄ C ₃ C ₃	123.368	-----	-----	123.4	123.4
	< C ₂ C ₁ C ₁	118.713	-----	-----	118.4	118.5
	< C ₁ C ₁ C ₂	121.423	-----	-----	121.7	121.2
	< H ₁ C ₁ C ₁	118.502	-----	-----	118.8	119.1
	< H ₂ C ₂ C ₁	121.150	-----	-----	120.5	119.9
	< H ₃ C ₃ C ₃	120.374	-----	-----	119.0	119.9

Table (2): Vibrational frequencies for perylene (neutral, anion and cation) molecule.

Symmetry & distription		Scaled	Raman & IR	calc.	This work		Cation
		MINDO/3-FORCES	[3, 8, 4]	[10]	anion	cation	Exp.[20]
A_g							
v ₁	CH _β str.	3063	-----	-----	3032	3086	-----
v ₂	CH _α str.	3041	-----	-----	3016	3059	-----
v ₃	CH _α str.	3034	-----	-----	2999	3048.3	-----
v ₄	ring (CC str.)	1627	1620	-----	1577	1564	1748
v ₅	ring (CC str.)	1583	1579	-----	1554.6	1557	1601
v ₆	ring (CC str.)	1406	-----	-----	1443	1442	-----
v ₇	ring (CCC str.)	1387	1373	-----	1363	1371	1387
v ₈	ring (CCC str.)	1355	1367	-----	1353	1353	-----
v ₉	δCH _{α,β} + ring(CCC str.)	1239	1291	-----	1254	1246	-----
v ₁₀	δCH _{α,β}	1218	1222	-----	1222	1216	-----
v ₁₁	δCH _α	1182	1140	-----	1185	1180	-----
v ₁₂	δ ring (δCCC) + δCH _β	1020	1045	-----	1025	1020	1094
v ₁₃	δ ring (δCCC)	793	784	-----	796	791	-----
v ₁₄	δ ring (δCCC)	642	548	-----	647	646	532
v ₁₅	δ ring (δCCC)	444	-----	-----	449	444	434
v ₁₆	δ ring (δCCC)	368	-----	-----	367	368	357
B_{1u}							
v ₃₀	CH _β str.	3062	3065 ^{a,b}	3068	3028	3085.4	-----
v ₃₁	CH _α str.	3040	-----	-----	3015	3058.9	-----
v ₃₂	CH _α str.	3031	-----	-----	2997.4	3046.9	-----
v ₃₃	ring (CC str.)	1623	-----	-----	1562	1552.5	1597
v ₃₄	ring (CC str.)	1586	1597 ^{a,b}	1586	1545	1534	-----
v ₃₅	ring (CCC str.)	1435	1385 ^{a,b}	1387	1417	1411.3	-----

Table (2); continue

v ₃₆	ring (CCC str.)	1371	-----	-----	1330	1332	-----
v ₃₇	ring (CCC str.)	1315	-----	-----	1287	1304	1298
v ₃₈	$\delta\text{CH}\alpha, \acute{\alpha}$	1221	1218 ^{a,b}	1217	1222.6	1222	1223
v ₃₉	$\delta\text{CH}\alpha, \acute{\alpha}$	1184	1157 ^{a,b}	1157	1191	1185	-----
v ₄₀	$\delta\text{CH}\beta + \delta$ ring (δCCC)	1091	1088 ^{a,b}	1091	1159	1148	-----
v ₄₁	δ ring(δCCC)(ring AClock wise)	983	-----	-----	980	980	969
v ₄₂	δ ring (δCCC)	773	791 ^{a,b}	793	779	770	-----
v ₄₃	δ ring (δCCC)	581	583 ^b	579	580	578	-----
v ₄₄	δ ring (δCCC)	482	-----	-----	482	479	-----
B_{2u}							
v ₅₃	$\text{CH}\beta$ str.	3061	3069 ^a	3069	3026	3085.35	-----
v ₅₄	$\text{CH}\alpha$ str.	3039	3057 ^a	3049	3016	3057.6	-----
v ₅₅	$\text{CH}\acute{\alpha}$ str.	3034	-----	-----	2998	3048	-----
v ₅₆	ring (CC str.)	1628	1614 ^{a,b}	1596	1541	1559	1589
v ₅₇	ring (CC str.)	1521	1501 ^{a,b}	1495	1494	1476	-----
v ₅₈	ring (CC str.)	1471	-----	-----	1400	1411.4	-----
v ₅₉	ring (CCC str.)	1383	1335 ^{a,b}	1329	1354	1362	-----
v ₆₀	ring (CCC str.)+ $\delta\text{CH}\alpha+\beta$	1264	1280 ^{a,b}	1272	1253	1253	-----
v ₆₁	$\delta\text{CH}\acute{\alpha}$	1241	-----	-----	1229	1250	-----
v ₆₂	$\delta\text{CH}\alpha + \delta$ ring (δCCC)	1223	-----	-----	1227	1212	-----
v ₆₃	$\delta\text{CH}\alpha,\beta$	1177	1186 ^b	1200	1179	1171	-----
v ₆₄	δ ring (δCCC) + $\delta\text{CH}\beta$	1041	1047 ^{a,b}	1043	1042	1038	-----
v ₆₅	δ ring (δCCC)	764	-----	775	762	785	-----
v ₆₆	δ ring (δCCC)	534	-----	-----	531	523	-----
v ₆₇	δ ring (δCCC)	255	-----	-----	256	252	-----
B_{3g}							
v ₆₈	$\text{CH}\beta$ str.	3061	-----	-----	3023	3085.31	-----

a: ref. (3), b: ref. (7)

Table (2); continue

v ₆₉	CH α str.	3038	-----	-----	3013	3057.5	-----
v ₇₀	CH $\acute{\alpha}$ str.	3030	-----	-----	2997	3046.8	-----
v ₇₁	ring (CC str.)	1629	-----	-----	1555	1558.7	-----
v ₇₂	ring (CC str.)	1523	-----	-----	1506	1492	-----
v ₇₃	ring (CC str.)	1425	-----	-----	1468	1458	-----
v ₇₄	ring (CCC str.)	1357	-----	-----	1305	1313	-----
v ₇₅	δ CH $\acute{\alpha}$, α , β (rocking)	1229	-----	-----	1225	1240	-----
v ₇₆	ring (CCC str.) + δ CH	1194	-----	-----	1222.9	1218	1207
v ₇₇	δ CH α , β	1175	-----	-----	1183	1173	-----
v ₇₈	δ CH β , $\acute{\alpha}$, α	1169	-----	-----	1178	1167	-----
v ₇₉	δ ring (δ CCC) (ring A Clockwise)	890	-----	-----	886	885	-----
v ₈₀	δ ring (δ CCC) (ring A anti clockwise)	622	-----	-----	621	617	-----
v ₈₁	δ ring (δ CCC)	540	-----	-----	545	534	-----
v ₈₂	δ ring (δ CCC) (rings B anti clockwise)	367	-----	-----	371	371	-----
	Out of plane						
A_u							
v ₁₇	γ CH α , β	962	-----	-----	949	970	-----
v ₁₈	γ CH $\acute{\alpha}$, α	926	-----	-----	837	962	-----
v ₁₉	γ CH β , $\acute{\alpha}$, α	833	-----	-----	787	841	-----
v ₂₀	γ CC (ring A)	654	-----	-----	640	692	-----
v ₂₁	γ CC (rings B)	484	-----	-----	464	456	-----
v ₂₂	γ CC (rings B)	228	-----	-----	214	225	-----
v ₂₃	γ CC (rings B)	27	-----	-----	33	38	-----
B_{1g}							
v ₂₄	γ CH β , α	963	-----	-----	950	970	-----
v ₂₅	γ CH α , $\acute{\alpha}$	926	-----	-----	827	959	-----
v ₂₆	γ CH α , β , $\acute{\alpha}$	807	-----	-----	779	805	-----
v ₂₇	γ CC	551	-----	-----	541	545	-----

Table (2); continue

v ₂₈	γ CC	403	-----	-----	388	390	-----
v ₂₉	γ CC	188	-----	-----	181.5	183	-----
B_{2g}							
v ₄₅	γ CH β,α	968	-----	-----	953	984	-----
v ₄₆	γ CH $\alpha,\acute{\alpha}$	938	-----	-----	857	966	-----
v ₄₇	γ CC	853	-----	-----	843	890	-----
v ₄₈	γ CH $\acute{\alpha},\beta$ + γ CC(ring A)	770	-----	-----	790	810	-----
v ₄₉	γ CC	685	-----	-----	632	623	-----
v ₅₀	γ CC	441	-----	-----	463	437	-----
v ₅₁	γ CC(ring A)	294	-----	-----	289	278	-----
v ₅₂	γ CC (rings B)	126	-----	-----	138	132	-----
B_{3u}							
v ₈₃	γ CH β,α	969	970 ^{a,b}	982	955	982	-----
v ₈₄	γ CH $\alpha,\acute{\alpha}$	940	-----	-----	847	964	-----
v ₈₅	γ CH $\beta,\acute{\alpha}$	815	815 ^{a,b}	815	815	851	-----
v ₈₆	γ CC (ring A)	745	772 ^{a,b}	765	797	757	-----
v ₈₇	γ CC	546	544 ^b	545	589	533	-----
v ₈₈	γ CC	445	-----	-----	457	436.8	-----
v ₈₉	γ CC	173	-----	-----	181.8	169	-----
v ₉₀	γ CC	87	-----	-----	86	83	-----

Scaling factors: 0.876 (CH str.); 0.96 (ring (CC) str.); 1.06 (δ CH); 1.08 (ring(δ CCC)); 1.11 (γ CH); 1.11 (γ CCC); 1.03 (γ CC).

Special scaling factors were used for vibration modes with overlaps of different types of motion; 1.06 (ring (CCC) str. + δ CH); 1.11 (γ CCC + γ CH) or (γ CC + γ CH); 1.03 (γ CH + γ CC) ^[23].

γ : out of plane bending vibration.

δ : in-plane bending vibration.

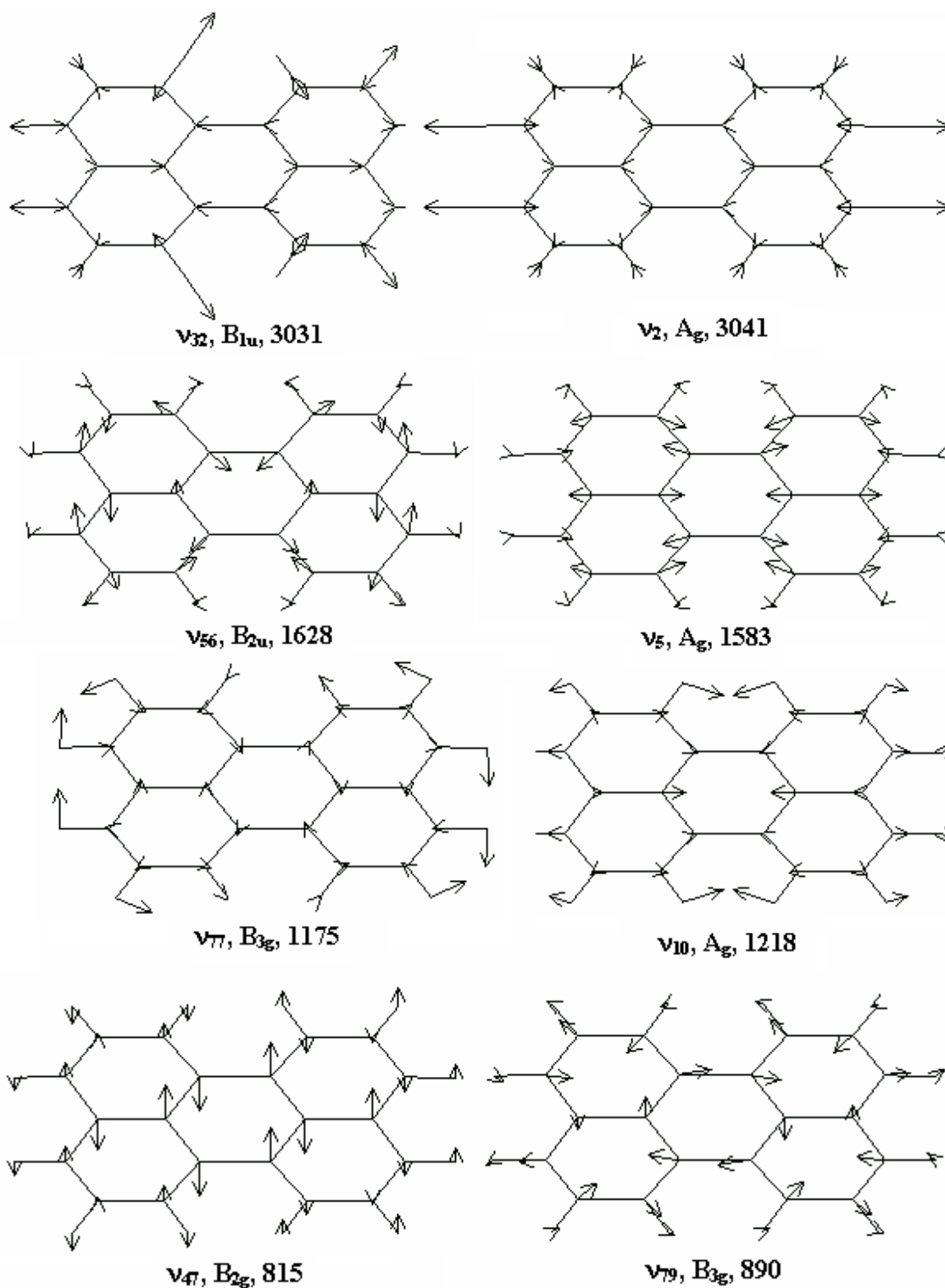


Fig.4. The graphical pictures of some vibration modes for neutral Perylene molecule as drawn applying the DRAW. MOL. routine.

Table (3): Calculated IR absorption intensities for neutral Perylene molecule.

Symmetry & description		Intensity (km/mol)	
		Scaled MINDO /3-FORCES	Calcd. [10]
In-plane			
A_g			
v ₁	CH _β str.	0.00	-----
v ₂	CH _α str.	0.00	-----
v ₃	CH _á str.	0.00	-----
v ₄	ring (CC str.)	0.00	-----
v ₅	ring (CC str.)	0.00	-----
v ₆	ring (CC str.)	0.00	-----
v ₇	ring (CCC str.)	0.00	-----
v ₈	ring (CCC str.)	0.00	-----
v ₉	δCH _{á,β} + ring (CCC str.)	0.00	-----
v ₁₀	δCH _{á,β}	0.00	-----
v ₁₁	δCH _α	0.00	-----
v ₁₂	δ ring (δCCC) + δCH _β	0.00	-----
v ₁₃	δ ring (δCCC)	0.00	-----
v ₁₄	δ ring (δCCC)	0.00	-----
v ₁₅	δ ring (δCCC)	0.00	-----
v ₁₆	δ ring B (δCCC)	0.00	-----
B_{1u}			
v ₃₀	CH _β str.	174.3	134.5
v ₃₁	CH _α str.	89.3	-----
v ₃₂	CH _á str.	51.0	-----
v ₃₃	ring (CC str.)	0.60	-----
v ₃₄	ring (CC str.)	0.00	23.8
v ₃₅	ring (CCC str.)	0.26	36.0
v ₃₆	ring (CCC str.)	0.00	-----
v ₃₇	ring (CCC str.)	0.18	-----
v ₃₈	δCH _{α, á}	1.95	5.9
v ₃₉	δCH _{α, á}	0.57	1.06
v ₄₀	δCH _β + δ ring (δCCC)	4.22	2.5
v ₄₁	δ ring(δCCC)(ring A clockwise)	0.64	-----
v ₄₂	δ ring (δCCC)	4.27	7.7
v ₄₃	δ ring (δCCC)	0.72	3.0
v ₄₄	δ ring (δCCC)	0.00	-----
B_{2u}			

Table (3); continue

v ₅₃	CH β str.	201.6	34.7
v ₅₄	CH α str.	12.6	7.8
v ₅₅	CH $\acute{\alpha}$ str.	45.3	-----
v ₅₆	ring (CC str.)	0.03	9.5
v ₅₇	ring (CC str.)	0.01	6.2
v ₅₈	ring (CC str.)	0.03	-----
v ₅₉	ring (CCC str.)	0.00	8.7
v ₆₀	ring (CCC str.) + δ CH $\alpha+\beta$	0.00	2.8
v ₆₁	δ CH $\acute{\alpha}$	0.42	-----
v ₆₂	δ CH α + δ ring (δ CCC)	3.96	-----
v ₆₃	δ CH α,β	1.09	1.1
v ₆₄	δ ring (δ CCC) + δ CH β	0.29	3.1
v ₆₅	δ ring (δ CCC)	0.02	2.7
v ₆₆	δ ring (δ CCC)	0.42	-----
v ₆₇	δ ring (δ CCC)	0.00	-----
B_{3g}			
v ₆₈	CH β str.	0.00	-----
v ₆₉	CH α str.	0.00	-----
v ₇₀	CH $\acute{\alpha}$ str.	0.00	-----
v ₇₁	ring (CC str.)	0.00	-----
v ₇₂	ring (CC str.)	0.00	-----
v ₇₃	ring (CC str.)	0.00	-----
v ₇₄	ring (CCC str.)	0.00	-----
v ₇₅	δ CH $\acute{\alpha},\alpha,\beta$ (clockwise rocking)	0.00	-----
v ₇₆	rings (CCC str.) + δ CH	0.00	-----
v ₇₇	δ CH α,β	0.00	-----
v ₇₈	δ CH $\beta,\acute{\alpha},\alpha$	0.00	-----
v ₇₉	δ ring (δ CCC)(ring A clockwise)	0.00	-----
v ₈₀	δ ring(δ CCC)(ring A anticlockwise)	0.00	-----
v ₈₁	δ ring (δ CCC)	0.00	-----
v ₈₂	δ ring (δ CCC) (rings B anticlockwise)	0.00	-----
	Out of plane		
A_u			
v ₁₇	γ CH α,β	0.00	-----
v ₁₈	γ CH $\acute{\alpha},\alpha$	0.00	-----
v ₁₉	γ CH $\beta,\acute{\alpha},\alpha$	0.00	-----
v ₂₀	γ CC (ring A)	0.00	-----

Table (3); continue

v ₂₁	γCC (rings B)	0.00	-----
v ₂₂	γCC (rings B)	0.00	-----
v ₂₃	γCC (rings B)	0.00	-----
B_{1g}			
v ₂₄	γCH _{β,α}	0.00	-----
v ₂₅	γCH _{α,á}	0.00	-----
v ₂₆	γCH _{α,β,á}	0.00	-----
v ₂₇	γCC	0.00	-----
v ₂₈	γCC	0.00	-----
v ₂₉	γCC	0.00	-----
B_{2g}			
v ₄₅	γCH _{β,α}	0.00	-----
v ₄₆	γCH _{α,á}	0.00	-----
v ₄₇	γCC	0.00	-----
v ₄₈	γCH _{á,β} + γCC(ring A)	0.00	-----
v ₄₉	γCC	0.00	-----
v ₅₀	γCC	0.00	-----
v ₅₁	γCC(ring A)	0.00	-----
v ₅₂	γCC(ring B)	0.00	-----
B_{3u}			
v ₈₃	γCH _{β,α}	0.00	2.6
v ₈₄	γCH _{α,á}	0.08	-----
v ₈₅	γCH _{β,á}	2.91	119.8
v ₈₆	γCC (ring A)	0.12	63.0
v ₈₇	γCC	0.10	8.1
v ₈₈	γCC	0.01	-----
v ₈₉	γCC	0.08	-----
v ₉₀	γCC	0.01	-----

Totally twelve C-H vibration frequencies are calculated and included in Table 2. The DRAW.MOL pictures show that the motion of these modes is localized completely on the H atoms. For all the C-H vibrations the sym. modes are of higher frequency values than their corresponding asym. Modes, i.e.

$$v_{\text{sym}}(\text{CH}\alpha_{\text{str.}})(3041 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CH}\alpha_{\text{str.}})(3040 \text{ cm}^{-1})$$

$$v_{\text{sym}}(\text{CH}\beta_{\text{str.}})(3063 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CH}\beta_{\text{str.}})(3062 \text{ cm}^{-1})$$

$$v_{\text{sym}}(\text{CH}\acute{\alpha}_{\text{str.}})(3034 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CH}\acute{\alpha}_{\text{str.}})(3031 \text{ cm}^{-1})$$

Comparing all the C-H modes, the following correlation is detected;

$$v_{\text{sym}}(\text{CH}\beta_{\text{str.}}) > v_{\text{asym}}(\text{CH}\beta_{\text{str.}}) > v_{\text{sym}}(\text{CH}\alpha_{\text{str.}}) > v_{\text{asym}}(\text{CH}\alpha_{\text{str.}}) > v_{\text{sym}}(\text{CH}\acute{\alpha}_{\text{str.}}) > v_{\text{asym}}(\text{CH}\acute{\alpha}_{\text{str.}}).$$

As for the C-C stretching vibrations the asym. modes are usually of higher frequency than the sym. e.g.

$$v_{\text{asym}}(\text{CC}_{\text{str.}})(1629 \text{ cm}^{-1}) > v_{\text{sym}}(\text{CC}_{\text{str.}})(1627 \text{ cm}^{-1})$$

Similar relation is found for the CCC ring vibration; e.g.;

$$v_{\text{asym}}(\text{CC str.})(1435 \text{ cm}^{-1}) > v_{\text{sym}}(\text{CC str.})(1387 \text{ cm}^{-1})$$

For all in plane vibrations, $\delta\text{C-H}$ as well as $\delta\text{C-C}$, the asym. Vibration frequencies are higher than the sym.; e.g.

$$v_{\text{asym}}(\delta\text{CH})(1241 \text{ cm}^{-1}) > v_{\text{sym}}(\delta\text{CH})(1239 \text{ cm}^{-1})$$

$$v_{\text{asym}}(\delta\text{CCC})(1041 \text{ cm}^{-1}) > v_{\text{sym}}(\delta\text{CCC})(1020 \text{ cm}^{-1}).$$

Table 2 includes the frequencies of all out of plane C-H and C-C vibration modes too.

The calculated IR absorption intensities in the table allows a qualitative distinction between the IR active ($\neq 0.0$) and the IR inactive ($= 0.0$) vibration mode

Vibration frequencies and normal coordinates for the positive and negative radical ions of perylene.

For both ions of perylene, the MINDO/3-FORCES treatment yielded bond distances of minor changes from those of the neutral molecule, Table 1, but retained the D_{2h} symmetry. For this reason the symmetry considerations of the vibration spectrum of neutral perylene apply for its radical cation and anion too.

As for the stretching C-H and C-C vibrations the symmetric modes are of higher frequencies than their corresponding asymmetric modes in a similar manner as in the neutral perylene molecule; e.g.

$$v_{\text{sym}}(\text{CH}_{\alpha} \text{ str.})(3059 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CH}_{\alpha} \text{ str.})(3058 \text{ cm}^{-1})$$

$$v_{\text{sym}}(\text{CH}_{\beta} \text{ str.})(3086 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CH}_{\beta} \text{ str.})(3085 \text{ cm}^{-1})$$

$$v_{\text{sym}}(\text{CH}_{\alpha'} \text{ str.})(3048 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CH}_{\alpha'} \text{ str.})(3047 \text{ cm}^{-1})$$

The sequence of the C-H frequencies follows the following order:

$$v_{\text{sym}}(\text{CH}_{\beta} \text{ str.}) > v_{\text{asym}}(\text{CH}_{\beta} \text{ str.}) > v_{\text{sym}}(\text{CH}_{\alpha} \text{ str.}) > v_{\text{asym}}(\text{CH}_{\alpha} \text{ str.}) > v_{\text{sym}}(\text{CH}_{\alpha'} \text{ str.}) > v_{\text{asym}}(\text{CH}_{\alpha'} \text{ str.}).$$

Similarly for the C-C stretching vibrations, e.g. ;

$$v_{\text{sym}}(\text{CC str.})(1564 \text{ cm}^{-1}) > v_{\text{asym}}(\text{CC str.})(1553 \text{ cm}^{-1})$$

As for the in plane deformation vibrations, the asym. modes show higher frequencies than the sym. modes, e.g.

$$v_{\text{asym}}(\delta\text{CH})(1250 \text{ cm}^{-1}) > v_{\text{sym}}(\delta\text{CH})(1246 \text{ cm}^{-1})$$

and,

$$v_{\text{asym}}(\delta \text{ CCC})(980 \text{ cm}^{-1}) > v_{\text{sym}}(\delta \text{ CCC})(791 \text{ cm}^{-1}).$$

All out of plane C-H and C-C vibration frequencies for both radical ions are included in the table too.

General correlation.

Of major interest is the discussion of the influence of the molecular charge on the vibration frequencies of perylene molecule. As for the CH stretching vibrations, it is found, on inspecting the frequency values of Table 2 and 4 that, the frequencies of the cation are higher than those for the neutral and these are higher than the frequency values of the radical anion.

$$v_{\text{sym}} \text{CH}_{\beta} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot+} > v_{\text{sym}} \text{CH}_{\beta} \text{ str. } (\text{C}_{20}\text{H}_{12}) > v_{\text{sym}} \text{CH}_{\beta} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

$$v_{\text{sym}} \text{CH}_{\alpha} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot+} > v_{\text{sym}} \text{CH}_{\alpha} \text{ str. } (\text{C}_{20}\text{H}_{12}) > v_{\text{sym}} \text{CH}_{\alpha} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

$$v_{\text{sym}} \text{CH}_{\acute{\alpha}} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot+} > v_{\text{sym}} \text{CH}_{\acute{\alpha}} \text{ str. } (\text{C}_{20}\text{H}_{12}) > v_{\text{sym}} \text{CH}_{\acute{\alpha}} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

This relation applies for all three types of C-H bonds in the molecule α β $\acute{\alpha}$.

A similar relation holds for the asym. C-H vibrations of perylene.

$$v_{\text{asym}} \text{CH}_{\beta} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot+} > v_{\text{asym}} \text{CH}_{\beta} \text{ str. } (\text{C}_{20}\text{H}_{12}) > v_{\text{asym}} \text{CH}_{\beta} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

$$v_{\text{asym}} \text{CH}_{\alpha} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot+} > v_{\text{asym}} \text{CH}_{\alpha} \text{ str. } (\text{C}_{20}\text{H}_{12}) > v_{\text{asym}} \text{CH}_{\alpha} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

$$v_{\text{asym}} \text{CH}_{\acute{\alpha}} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot+} > v_{\text{asym}} \text{CH}_{\acute{\alpha}} \text{ str. } (\text{C}_{20}\text{H}_{12}) > v_{\text{asym}} \text{CH}_{\acute{\alpha}} \text{ str. } (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

To explain this result one may draw the following argument;

The C-H bond is formed through the interaction of 1s AO of H

with the 2s, 2p_x and 2p_y AO s of the C atom. No contribution from the 2p_z AO is expected, since this is orthogonal to the H_{1s} AO. Calculating the electron densities of the σ -electrons for all three charged and neutral perylenes and inspecting their correlation with the corresponding C-H stretching frequencies an almost linear correlation is found, Fig. 5.

$$\sigma \text{CH}_{\beta} (\text{C}_{20}\text{H}_{12})^{\cdot+} > \sigma \text{CH}_{\beta} (\text{C}_{20}\text{H}_{12}) > \sigma \text{CH}_{\beta} (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

$$\sigma \text{CH}_{\alpha} (\text{C}_{20}\text{H}_{12})^{\cdot+} > \sigma \text{CH}_{\alpha} (\text{C}_{20}\text{H}_{12}) > \sigma \text{CH}_{\alpha} (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

$$\sigma \text{CH}_{\acute{\alpha}} (\text{C}_{20}\text{H}_{12})^{\cdot+} > \sigma \text{CH}_{\acute{\alpha}} (\text{C}_{20}\text{H}_{12}) > \sigma \text{CH}_{\acute{\alpha}} (\text{C}_{20}\text{H}_{12})^{\cdot-}$$

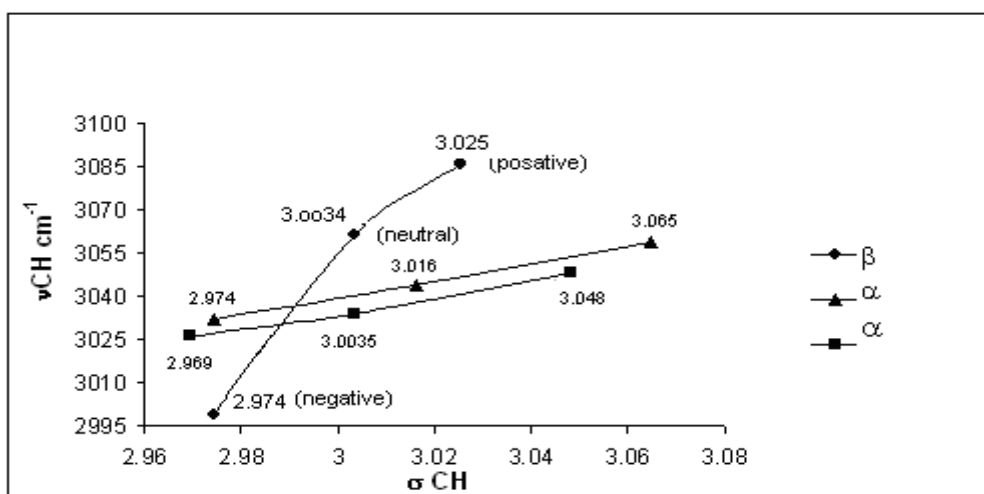


Fig. 5 Calculated change of the C-H vibration frequency of Perylene as a function of the σ electron densities of the carbon atoms.

A similar conclusion has been drawn on studying the vibration frequencies of the neutral, cation and anion radicals of benz@anthracene^[17] and phenanthrene^[18].

The CC stretching vibrations

Different is the change of the vibration frequencies of the CC bonds due to the change in the charge of the molecule. It is not similar for the sym. and asym. vibrations. For the sym. modes the following order is calculated;

$$v_{\text{sym}} \text{CC}_{\text{str.}} > v_{\text{sym}} \text{CC}_{\text{str.}}^{\cdot -} > v_{\text{sym}} \text{CC}_{\text{str.}}^{\cdot +}$$

The highest frequency is calculated for the neutral molecule, followed by that of the radical anion and then the radical cation. As for the asym. vibrations, the radical cation possess the highest vibration frequency, followed by the neutral and then the radical anion species.

$$v_{\text{asym}} \text{CC}_{\text{str.}}^{\cdot +} > v_{\text{asym}} \text{CC}_{\text{str.}} > v_{\text{asym}} \text{CC}_{\text{str.}}^{\cdot -}$$

The obvious reason for this change in the vibration frequency is the change in the bond orders of the related bonds due to the radical ion formation. According to the pairing theorem, adding an electron to the neutral molecule, i.e. forming the radical anion causes the occupation of LUMO with coefficient values different from those of the HOMO of perylene, where as removing an electron, to form a radical cation, does not change the coefficients of the singly occupied HOMO. The difference in the MO coefficient changes the bond orders of the CC bonds and consequently their vibration frequencies. Fig. 6. shows the change in the vibration frequencies of the double bond and single bond in Perylene due to the change in the charge of the molecule.

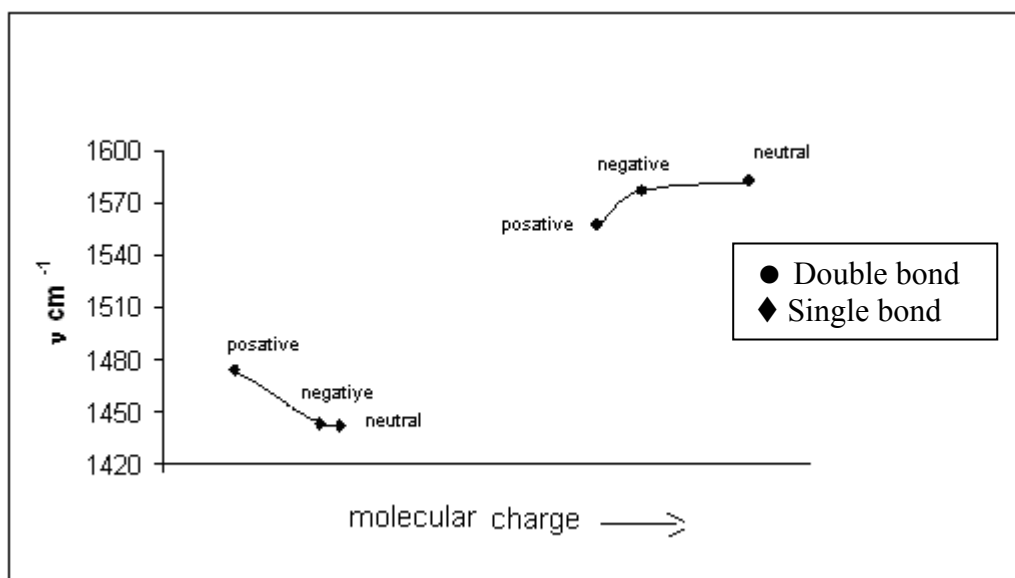


Fig. 6. Calculated change of the C-C vibration frequency of Perylene due to the change in the molecular charge.

As for the in-plane deformations the following correlations were found;

$$\begin{aligned} \delta_{\text{sym}} \text{CH} (\text{C}_{20}\text{H}_{12})^{\cdot -} &> \delta_{\text{sym}} \text{CH} \\ (\text{C}_{20}\text{H}_{12}) &> \delta_{\text{sym}} \text{CH} (\text{C}_{20}\text{H}_{12})^{\cdot +} \\ \delta_{\text{asym}} \text{CH} (\text{C}_{20}\text{H}_{12})^{\cdot -} &> \delta_{\text{asym}} \text{CH} \\ (\text{C}_{20}\text{H}_{12})^{\cdot +} &> \delta_{\text{asym}} \text{CH} (\text{C}_{20}\text{H}_1 \text{ and} \\ \delta_{\text{sym}} \text{CCC} (\text{C}_{20}\text{H}_{12})^{\cdot -} &> \delta_{\text{sym}} \text{CCC} \\ (\text{C}_{20}\text{H}_{12}) &> \delta_{\text{sym}} \text{CCC} (\text{C}_{20}\text{H}_{12})^{\cdot +} \\ \delta_{\text{asym}} \text{CCC} (\text{C}_{20}\text{H}_{12}) &> \delta_{\text{asym}} \text{CCC} \\ (\text{C}_{20}\text{H}_{12})^{\cdot +} &> \delta_{\text{asym}} \text{CCC} (\text{C}_{20}\text{H}_{12})^{\cdot -} \end{aligned}$$

And for the out of plane modes of vibrations

$$\begin{aligned} \gamma_{\text{CH}} (\text{C}_{20}\text{H}_{12})^{\cdot +} &> \gamma_{\text{CH}} (\text{C}_{20}\text{H}_{12}) > \\ \gamma_{\text{CH}} (\text{C}_{20}\text{H}_{12})^{\cdot -} \\ \gamma_{\text{CC}} (\text{C}_{20}\text{H}_{12})^{\cdot -} &> \gamma_{\text{CC}} (\text{C}_{20}\text{H}_{12}) > \\ \gamma_{\text{CC}} (\text{C}_{20}\text{H}_{12})^{\cdot +} \end{aligned}$$

Conclusion

The MINDO/ 3-FORCES computed vibration frequencies of perylene show good agreement with the available experimental frequencies. The study of the obtained frequencies show the same correlation between the sym. and assym. modes as was found for other PHD molecules. Interesting relations is shown between the frequencies of neutral perylene and its charged ions. These relations may be extended for other PAH molecules. The results may be useful for the reactivity of this class of organic molecule.

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