Carbon σ-Electron Densities and C-H Stretching Vibration Frequencies of Phenanthrene

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Abstract

MINDO/3-FORCES calculations were carried out for the vibration frequencies and IR absorption intensities of phenanthrene radical ions. The obtained frequency values were compared with the experimental values when possible. It was found that the C-H stretching frequencies are directly related to the carbon σ-electron densities of the relevant atoms.

الخلاصة

أجريت حسابات MINDO/3-FORCES الترددات اهتزاز وشدة امتصاص الأشعة تحت الحمراء لجذور جزيئة الفينانثرين الأيونية، و كذلك تمت مقارنة الترددات المحسوبة مع القيم التجريبية المتوفرة لها، وجدت تبين ان تردد مط الأصرة C-H يعتمد مباشرة مع كثافة الألكترونات نوع σ لذرات الكاربون العائدة لها.

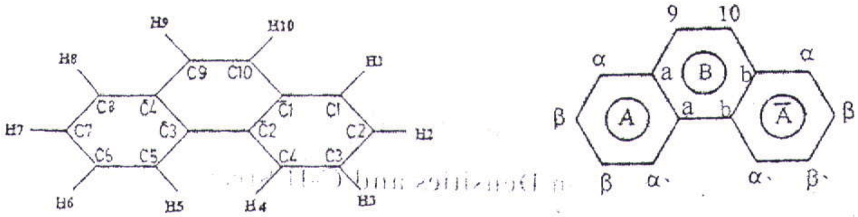
Introduction

The vibration spectra of polyaromatic hydrocarbon cations gain increasing importance due to their assumed presence in the interstellar spaces and their expected ecological importance. Efforts were done to study their spectra both experimentally and theoretically. As for the phenanthrene radical cation, Hudgins et al. [1] studied its vibration spectrum, applying the isolated matrix technique. Langhoff [2] and Yang Ling et al. [3] studied its spectrum theoretically, applying quantum mechanical methods. The phenanthrene radical cation was generated then through γ-irradiation of the neutral molecule [4,5] or of the molecule in isolation matrix [6]. It is known to undergo electron transfer reactions [7,8].

In former papers we applied the MINDO/3-FORCES method [9] for the calculation of molecular geometries, vibration frequencies and IR absorption intensities of different aromatic hydrocarbons as well as their radical cations and anions. Both valance and symmetry assignments of the vibration modes could be accomplished applying group theoretical considerations [10] and the so-called atomic partial participation (APP) values [11]. Graphical representations of the vibration motion of the atoms for each mode could be obtained applying the DRAW.MOL routine [12]. As for the phenanthrene radical anion no such study had been reported, neither experimentally nor theoretically.

Results and Discussions

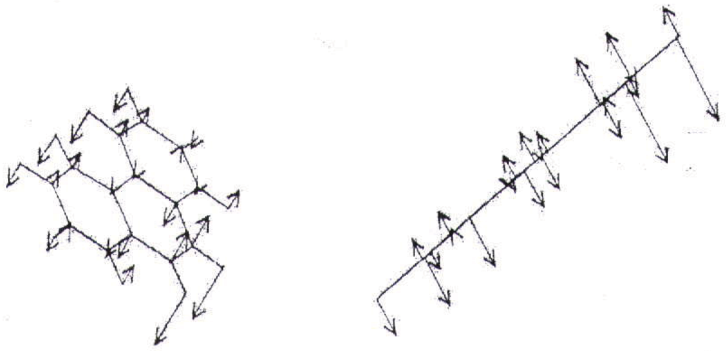
According to former theoretical and experimental results [1-3] the phenanthrene radical cation shows C_{2v} symmetry, similar to the neutral molecule. Fig. 1 shows the numbering of the atoms as followed in this paper.



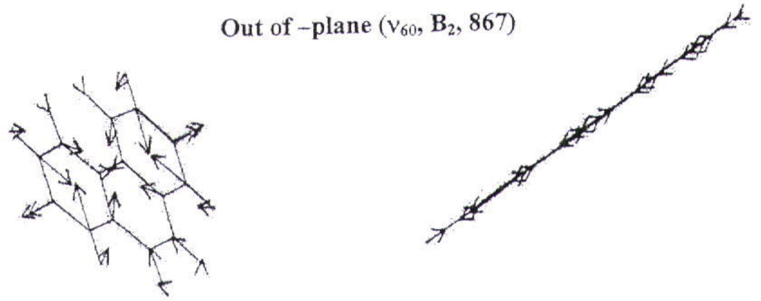
(a) (b)

Fig.1. Structure of the phenanthrene radical cation. Showing; (a-) the numbering of the C and H atoms; and (b-) the designation of the atoms in the molecule.

The C_Z axes falls in the molecular plane and does not pass through any of its atoms. The number of its vibration modes is 66 (3N-6). They are classified symmetrically according to the following picture, ($23A_1$ + $22B_1$) inplane, and ($11A_2$+ $10B_2$) out of plane vibration modes. According to the group theoretical considerations, 55 modes are expected to be Raman and IR active ($10B_2$ + $22B_1$, $23A_1$) and eleven modes ($11A_2$) should be IR inactive and Raman active. The present calculations agree with these expectations fully. Fig. 2 shows DRAW.MOL plotted graphical pictures of two vibration modes of phenanthrene radical cation.



Out of -plane (ν_{60}, B_2, 867)



In -plane (ν_{20}, A_1,766)

Fig. 2. DRAW- MOL plotted graphical pictures of two vibration modes of phenanthrene radical cation.

Table 1 includes the MINDO/3-FORCES calculated equilibrium geometry of phenanthrene radical cation, anion and neutral molecule compared with other calculated geometric values.The calculated equilibrium geometry of both cation and anion were applied then for the evaluation of their vibration frequencies, Table 2, and normal coordinates coefficients,. The so obtained coefficient values were supplied then to the DRAW.MOL program to draw the graphical picture of each vibration mode, Fig. 3.

Table 1. MINDO/3-FORCES calculated geometry of phenanthrene radical cation, radical anion and neutral molecule compared with some calculated and experimental results available in the literature.

Length(Å)/angle (deg.)	*This work*	*Cation*		*Neutral Calcd.(13)*
		Calcd.(3)	*Anion*	
$C_1-C'_1$	1.455	1.4305	1.453	1.437
C_1-C_2	1.389	1.3828	1.387	1.388
C_2-C_3	1.413	1.4055	1.412	1.417
C_3-C_4	1.412	1.4050	1.409	1.389
$C_4-C'_2$	1.418	1.3988	1.419	1.440
C_9-C_{10}	1.412	1.4031	1.407	1.361
$C'_1-C'_2$	1.485	1.4393	1.486	1.456
C'_1-C_{10}	1.421	1.4078	1.421	1.464
$C'_2-C'_3$	1.499	1.4668	1.500	1.494
H_1-C_1	1.106	--------	1.109	1.107
H_2-C_2	1.102	--------	1.112	1.105
H_3-C_3	1.104	--------	1.107	1.105
H_4-C_4	1.106	--------	1.112	1.107
H10-C10	1.106	--------	1.110	1.107
$< C'_1\,C_1\,C_2$	122.4	--------	122.7	122.7
$< C_1\,C_2\,C_2$	118.8	--------	120.2	119.3
$< C_2\,C_3\,C_4$	120.8	--------	118.8	122.7
$< C'_1\,C_{10}\,C_9$	122.5	--------	122.5	122.0
$< C_1\,C'_1\,C'_2$	118.5	--------	117.4	118.7
$< C_4\,C'_2\,C'_1$	116.3	--------	116.5	116.1
$< C'_1\,C'_2\,C'_3$	119.0	--------	118.9	116.0
$< H_1\,C_1\,C_2$	119.9	--------	118.9	119.3
$< H_2\,C_2\,C_3$	120.4	--------	119.6	120.0
$< H_3\,C_3\,C_4$	119.1	--------	120.6	120.0
$< H_4\,C_4\,C'_2$	119.8	--------	119.6	119.3
$< H_4\,C_4\,C_3$	117.1	--------	116.0	117.4
$< H_{10}\,C_{10}\,C'_1$	119.4	--------	119.0	118.0

Table 2: Calculated vibration frequencies and normal modes of phenanthrene radical cation.

Symmetry And Description		Frequencies cm^{-1}			
		This work	Others		
A_1		Scaled	Calcd$^{(3)}$	Calcd.$^{(2)}$	Calcd$^{(1)}$. Exptl.
ν_1	CH_{β} str.	3091	-------	-------	-------
ν_2	$CH_{\beta'}$ str. +$CH_{\alpha'}$ str.	3076	-------	-------	-------
ν_3	$CH_{(9,10)}$ str.	3065	-------	-------	-------
ν_4	CH_{α} str.+$CH_{\alpha'}$ str.	3062	-------	-------	-------
ν_5	$CH_{\alpha'}$ str.	3059	-------	-------	-------
ν_6	ring(C-C) str.	1606	1607	1583	1558
ν_7	$(C_9\text{-}C_{10})$str.+ $(C_{\alpha}\text{-}C_{\beta})$str.	1550	1550	1533	1551
ν_8	$(C_{\beta'}\text{-}C_{\beta})$str.+ $(C_a\text{-}C_b)$str.	1505	1515	1513	1513
ν_9	$(C_a\text{-}C_b)$str.+ $(C_9\text{-}C_{10})$str.	1381	-------	-------	-------
ν_{10}	$(C_a\text{-}C_a)$str.&$(C_b\text{-}C_b)$str.	1355	-------	-------	-------
ν_{11}	$(C_{\alpha'}\text{-}C_{\beta'})$ str.+ $(C_{\alpha}\text{-}C_{\beta})$str.	1296	-------	-------	-------
ν_{12}	ring(CCC) str.	1295	-------	-------	1267
ν_{13}	ring(CCC) str.+ $\delta CH_{(\beta',9,10)}$	1249	1249	1263	1259
ν_{14}	$\delta CH_{\alpha'}$ +δCH_{α}	1248	1207	1218	1228
ν_{15}	$\delta CH_{(9,10)}$ + $\delta CH_{(\alpha,\beta')}$	1175	-------	-------	-------
ν_{16}	δCH_{α} + $\delta CH_{\alpha'}$	1169	-------	-------	-------
ν_{17}	$\delta CH_{\beta'}$+ δCH_{β}	1161	-------	-------	-------
ν_{18}	δCH_{β}+ $\delta CH_{(9,10)}$ + δ(CCC)	1061	-------	-------	-------
ν_{19}	ring(δCCC)	858	-------	-------	-------
ν_{20}	ring (δCCC)	766	-------	-------	-------
ν_{21}	ring (δCCC)	556	-------	-------	-------
ν_{22}	ring $(\delta C_a C_{\alpha} C_{\beta})$ &$(C_b C_{\alpha} C_{\beta})$	417	-------	-------	-------
ν_{23}	ring (δCCC)	244	-------	-------	-------
B_1					
ν_{35}	CH_{β} str.	3090	-------	-------	-------
ν_{36}	$CH_{\beta'}$ str.+ $CH_{\alpha'}$ str.	3075	-------	-------	-------
ν_{37}	CH_{α} str.+ $CH_{\alpha'}$ str.	3061	-------	-------	-------
ν_{38}	$CH_{\alpha'}$ str.	3058	-------	-------	-------
ν_{39}	$CH_{(9,10)}$ str.	3055	-------	-------	-------
ν_{40}	$(C_{\alpha}\text{-}C_{\beta})$str.+ $(C_{\beta'}\text{.}C_{\alpha'})$str.	1559	1570	1565	1565
ν_{41}	$(C_a\text{-}C_9)$ &$(C_b\text{-}C_{10})$str.	1521	1521	-------	-------
ν_{42}	ring(CCC)str.	1512	1505	1496	-------
ν_{43}	ring(CCC)str.	1408	1424	1419	-------
ν_{44}	ring(CCC)str.	1377	1415	-------	-------
ν_{45}	ring(CCC)str.+ $\delta CH_{(9,10)}$	1299	1316	1309	-------

Table 2 con.

ν_{46}	$\delta CH_{\alpha'}$ + $\delta CH_{(9,10,\alpha)}$	1260	1272	1292	1299

ν_{47}	$\delta CH_{(9,10)} + \delta CH_{\alpha}$	1221	1213	1230	-------
ν_{48}	. $\delta CH_{\beta'} + \delta CH_{\alpha'} + \delta(CCC)$	1170	-------	-------	-------
ν_{49}	$\delta CH_{\alpha} + \delta CH_{\beta'}$	1159	-------	-------	-------
ν_{50}	$\delta CH_{\beta} + \delta CH_{\beta'}$	1155	1132	1154	-------
ν_{51}	ring) $\delta CCC) + \delta CH_{(9,10,\alpha')}$	990	978	986	-------
ν_{52}	ring) $\delta CCC)$	860	855	-------	-------
ν_{53}	ring (δCCC)	711	-------	-------	-------
ν_{54}	ring (δCCC)	595	581	597	582
ν_{55}	ring (δCCC)	500	-------	-------	-------
ν_{56}	ring (δCCC)	447	-------	-------	-------
A_2					
ν_{24}	. $\gamma CH_{\beta'} + \gamma CH_{\alpha}$	991	-------	-------	-------
ν_{25}	$\gamma CH_{(9,10)} + \gamma CH_{(\beta',\beta)}$	984	-------	-------	-------
ν_{26}	$\gamma CH_{\beta} + \gamma CH_{\alpha}$	962	-------	-------	-------
ν_{27}	$\gamma CH_{\alpha'}$ + ring(γCCC)	859	-------	-------	-------
ν_{28}	$\gamma(C_a\text{-}C_b) + \gamma CH_{\alpha'}$	814	-------	-------	-------
ν_{29}	$\gamma CH_{\beta} + \gamma CH_{\beta'} + \gamma CH_{\alpha}$	805	-------	-------	-------
ν_{30}	ring(γCCC) + γCH_{α}	539	-------	-------	-------
ν_{31}	ring(γCCC) + $\gamma CH_{(9,10)}$	477	-------	-------	-------
ν_{32}	$\gamma(C_9\text{-}C_{10}) + \gamma CH_{(9,10)}$	376	-------	-------	-------
ν_{33}	ring(γCCC)	242	-------	-------	-------
ν_{34}	ring(γCCC)	72			
B_2					
ν_{57}	$\gamma CH_{\beta'} + \gamma CH_{\alpha'}$	988	1120	1139	-----
ν_{58}	$\gamma CH_{\beta} + \gamma CH_{\alpha}$	972	1033	-----	-----
ν_{59}	$\gamma CH_{\alpha'} + \gamma CH_{\beta}$	920	885	-----	-----
ν_{60}	$\gamma CH_{(9,10)} + \gamma CH_{\alpha'}$	867	840	839	836
ν_{61}	$\gamma CH_{(9,10)} + \gamma CH_{(\beta,\alpha',\beta')}$	791	760	759	756
ν_{62}	$\gamma(C_a\text{-}C_b) + \gamma CH_{\alpha}$	707	703	693	695
ν_{63}	ring(γCCC) + $\gamma CH_{\beta'}$	478	-----	-----	-----
ν_{64}	ring(γCCC) + $\gamma CH_{(\alpha,\alpha')}$	437	406	407	-----
ν_{65}	/ring(γCCC)	209	212	-----	-----
ν_{66}	ring (γCCC)	102	-----	-----	-----

Scaling factors: 0.876 (CH str.); 0.96 (ring (CC) str.); 1.00 (ring (CCC) str); 1.06 (δCH); 1.08 (ring(δCCC); 1,11 (γCH); 1.11 (γCCC); 1.03 (γCC).

Special scaling factors were used for vibration modes with overlaps of different types of motion; 1.00(ring (CC) str. + δCH); 1.00 (δCH + ring(CCC str.)); 1.00 (ring δCCC + δCH); 1.06 (ring (CCC) str. + δCH); 1.11 (γCCC + γCH) or (γCC + γCH); 1.03 (γCH + γCC).

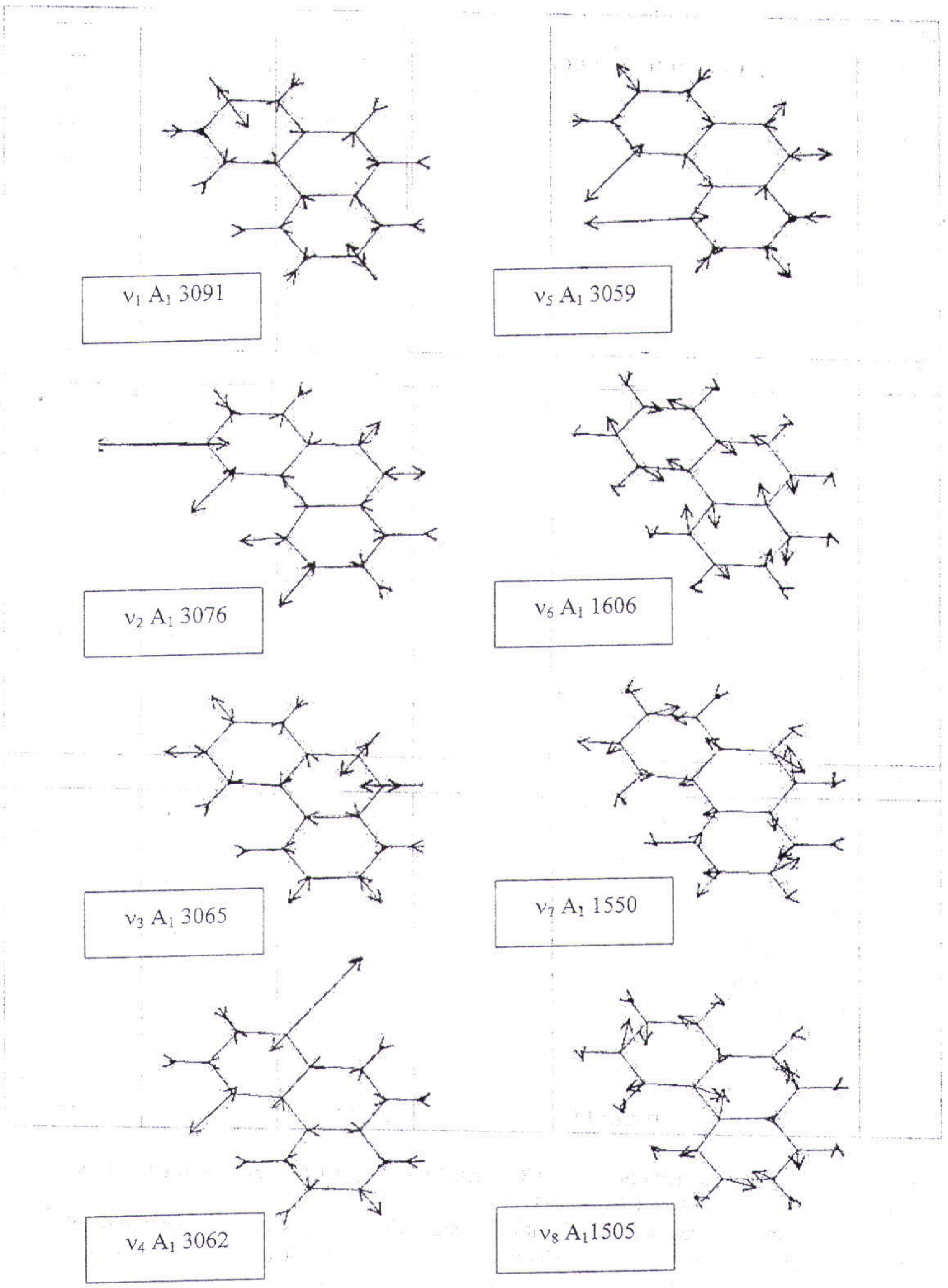


Fig. 3. Graphical pictures of some vibration modes of phenanthrene radical cation as drawn through the DRAW. MOL routine.

Similar to the calculated frequencies of the neutral molecule [13], those of its radical cation show a close agreement with both experimental and ab initio calculated frequencies. No such comparison could be done for the radical anion. The numbering of the vibration modes was done according to the Herzberg convention [14] their frequency assignments according to their APP values and DRAW.MOL pictures, Fig.3. Table 3 includes the calculated IR absorption intensities of the radical cation. Table 4 shows both vibration frequencies and IR absorption intensities for the radical anion as calculated with the MINDO/3-FORCES method.

Table 3: Calculated IR absorption intensities and normal modes of phenanthrene radical cation.

Symmetry And Description		*Intensities km/mol*		
		This work	*Others*	
		Calcd.	*Calcd.* (3)	*Calcd.* (2)
A_1				
ν_1	δCH_{β} str.	0.88	-------	-------
ν_2	$CH_{\beta'}$ str. +$CH_{\alpha'}$ str.	23.10	-------	-------
ν_3	$CH_{(9,10)}$ str.	30.12	-------	-------
ν_4	CH_{α} str.+ $CH_{\alpha'}$ str.	2.65	-------	-------
ν_5	$CH_{\alpha'}$ str.	19.46	-------	-------
ν_6	ring(C-C) str.	20.47	19.8	23.1
ν_7	$(C_9\text{-}C_{10})$str.+ $(C_{\alpha}\text{-}C_{\beta})$str.	47.81	108.9	112.7
ν_8	$(C_{\beta'}\text{-}C_{\beta})$str.+ $(C_a\text{-}C_b)$str.	0.02	6.97	10.8
ν_9	$(C_a\text{-}C_b)$str.+ $(C_9\text{-}C_{10})$str.	2.80	-------	-------
ν_{10}	$(C_a\text{-}C_a)$str.& $(C_b\text{-}C_b)$str.	12.14	-------	-------
ν_{11}	$(C_{\alpha'}\text{-}C_{\beta'})$ str.+ $(C_{\alpha}\text{-}C_{\beta})$str.	1.20	-------	-------
ν_{12}	ring(CCC) str.	32.14	-------	-------
ν_{13}	ring(CCC) str +$\delta CH_{(\beta',9,10)}$	3.61	9.9	16.1
ν_{14}	$\delta CH_{\alpha'} + \delta CH_{\alpha}$	0.00	40.9	30.1
ν_{15}	$\delta CH_{(9,10)} + \delta CH_{(\alpha,\beta')}$	0.04	-------	-------
ν_{16}	$\delta CH_{\alpha} + \delta CH_{\alpha'}$	1.71	-------	-------
ν_{17}	$\delta CH_{\beta'} + \delta CH_{\beta}$	0.00	-------	-------
ν_{18}	δCH_{β}.+ $\delta CH_{(9,10)}$ + δ (CCC)	2.46	-------	-------
ν_{19}	ring (δCCC)	0.05	-------	-------
ν_{20}	ring (δCCC)	0.07	-------	-------
ν_{21}	ring (δCCC)	0.06	-------	-------
ν_{22}	ring) $\delta C_aC_{\alpha}C_{\beta}$) &$(C_bC_{\alpha}C_{\beta})$	0.08	-------	-------
ν_{23}	ring (δCCC)	0.00	-------	-------
B_1				
ν_{35}	CH_{β} str.	28.87	--------	--------
ν_{36}	$CH_{\beta'}$ str.+ $CH_{\alpha'}$ str.	8.49	--------	--------
ν_{37}	CH_{α} str. + $CH_{\alpha'}$ str.	3.73	--------	--------
ν_{38}	$CH_{\alpha'}$ str.	7.27	--------	--------
ν_{39}	$CH_{(9,10)}$ str.	4.23	--------	--------
ν_{40}	$(C_{\alpha}\text{-}C_{\beta})$str.+ $(C_{\beta'}\ .C_{\alpha'})$str.	139.44	213.3	184.0
ν_{41}	$(C_a\text{-}C_9)$ &$(C_b\text{-}C_{10})$str.	124.02	16.4	--------

Table 3 cont.

ν_{42}	ring(CCC)str.	100.38	5.84	15.8
ν_{43}	ring(CCC)str.	8.18	74.9	80.8
ν_{44}	ring(CCC)str.	1.75	14.2	--------
ν_{45}	$(C_{\alpha'}$-$C_{\beta'})$str.+ $\delta CH_{(9,10)}$	213.13	228.2	186.4
ν_{46}	$\delta CH_{\alpha'} + \delta CH_{(9,10,\alpha)}$	6.24	1.5	61.3
ν_{47}	$\delta CH_{(9,10)} + \delta CH_{\alpha}$	0.00	54.1	44.8
ν_{48}	$\delta CH_{\beta'} + \delta CH_{\alpha'}$	7.01	--------	--------
ν_{49}	$\delta CH_{\alpha} + \delta CH_{\beta'}$	0.42	--------	--------
ν_{50}	$\delta CH_{\beta} + \delta CH_{\beta'}$	4.67	141.5	160.5
ν_{51}	ring (δCCC) + $\delta CH_{(9,10,\alpha')}$	13.13	21.9	31.3
ν_{52}	ring (δCCC)	1.40	5.9	--------
ν_{53}	ring (δCCC)	0.01	--------	--------
ν_{54}	ring (δCCC)	8.10	45.3	46.4
ν_{55}	ring) δCCC)	2.00	--------	--------
ν_{56}	ring) δCCC)	1.52	--------	--------
A_2				
ν_{24}	$\gamma CH_{\beta'} + \gamma CH_{\alpha}$	0.00	--------	--------
ν_{25}	$\gamma CH_{(9,10)} + \gamma CH_{(\beta',\beta)}$	0.00	--------	--------
ν_{26}	$\gamma CH_{\beta} + \gamma CH_{\alpha}$	0.00	--------	--------
ν_{27}	$\gamma CH_{\alpha'}$ + ring(γCCC)	0.00	--------	--------
ν_{28}	$\gamma(C_a$-$C_b) + \gamma CH_{\alpha'}$	0.00	--------	--------
ν_{29}	$\gamma CH_{\beta} + \gamma CH_{\beta'} + \gamma CH_{\alpha}$	0.00	--------	--------
ν_{30}	ring(γCCC) + γCH_{α}	0.00	--------	--------
ν_{31}	ring(γCCC) + $\gamma CH_{(9,10)}$	0.00	--------	--------
ν_{32}	$\gamma(C_9$-$C_{10}) + \gamma CH_{(9,10)}$	0.00	--------	--------
ν_{33}	ring(γCCC)	0.00	--------	--------
ν_{34}	ring(γCCC)	0.00	--------	--------
B_2				
ν_{57}	$\gamma CH_{\beta'} + \gamma CH_{\alpha'}$	1.10	3.2	10.3
ν_{58}	$\gamma CH_{\beta} + \gamma CH_{\alpha}$	1.09	5.4	--------
ν_{59}	$\gamma CH_{\alpha'} + \gamma CH_{\beta}$	0.10	5.0	--------
ν_{60}	$\gamma CH_{(9,10)} + \gamma CH_{\alpha'}$	2.80	31.4	53.6
ν_{61}	$\gamma CH_{(9,10)} + \gamma CH_{(\beta,\alpha',\beta')}$	2.45	34.3	57.3
ν_{62}	$\gamma(C_a$-$C_b) + \gamma CH_{\alpha}$	4.95	34.5	38.6
ν_{63}	ring(γCCC) + $\gamma CH_{\beta'}$	0.17	--------	--------
ν_{64}	ring(γCCC) + $\gamma CH_{(\alpha,\alpha')}$	1.31	9.3	10.0
ν_{65}	ring(γCCC)	1.52	6.3	--------
ν_{66}	ring (γCCC)	0.22	--------	--------

Table 4: Calculated vibration frequencies and IR absorption intensities phenanthrene radical anion.

Symmetry And Description		*Frequencies cm^{-1}*	*Intensities km/mol*
		This work	
A_1			
ν_1	$\delta CH_{\beta'}$ str.	3035	72.46
ν_2	$CH_{(9,\alpha)}$ str. + $CH_{(10,\alpha)}$ str.	3014	289.55
ν_3	$CH_{(9,10)}$ str. + CH_{α} str.	3006	0.76
ν_4	$CH_{\alpha'}$ str.	2996	69.18
ν_5	CH_{β} str.	2985	6.63
ν_6	$(C_{\alpha'}-C_{\beta'})$ str.+ (C_a-C_b)str.	1616	32.11
ν_7	(C_9-C_{10})str.+ $(C_{\alpha}-C_{\beta})$str.	1570	31.40
ν_8	$(C_{\beta'}-C_{\beta})$str.+ (C_a-C_b)str.	1496	0.18
ν_9	ring((C_9-C_{10})str.+ (C_a-C_b)str.)	1454	0.00
ν_{10}	ring ((C_b-C_b)str.+ (C_a-C_a)str.)	1420	9.29
ν_{11}	ring(CCC) str.	1371	0.65
ν_{12}	ring ($(C_{\alpha'}-C_b)$ str.&$(C_{\alpha'}-C_a)$ str.)	1291	21.08
ν_{13}	(C_a-C_b)str.+ $\delta CH_{(9,10,\beta)}$	1244	9.00
ν_{14}	$\delta CH_{\alpha'} + \delta CH_{\alpha}$ ring (δCCC)	1190	0.35
ν_{15}	$\delta CH_{(9,10)} + \delta CH_{(\beta,\alpha)}$	1185	0.03
ν_{16}	$\delta CH_{\alpha} + \delta CH_{\alpha'}$	1178	0.10
ν_{17}	$\delta CH_{\beta'} + \delta CH_{\beta}$	1170	0.08
ν_{18}	$\delta CH_{(9,10)} + \delta CH_{\beta}$	1129	2.00
ν_{19}	ring (δCCC)	862	0.17
ν_{20}	ring ($\delta C_{\alpha}C_{\beta}C_{\beta'}$)	775	0.07
ν_{21}	ring ($\delta C_{\alpha}C_{\beta'}C_{\alpha'}$)	561	0.13
ν_{22}	ring ($\delta C_{\beta}C_{\alpha}C_a$)	423	0.03
ν_{23}	ring (δCCC) .	248	0.36
B_1			
ν_{35}	$CH_{\beta'}$ str.	3032	161.71
ν_{36}	CH_{α} str.	3009	162.42
ν_{37}	$CH_{(9,10)}$ str.	2990	16.65
ν_{38}	$CH_{\alpha'}$ str.	2987	88.66
ν_{39}	CH_{β} str.	2983	149.73

Table 4 cont.

ν_{40}	$(C_{\alpha'}-C_{\beta'})$str.+ $(C_{\alpha}-C_{\beta})$str.	1571	112.41
ν_{41}	$(C_{\alpha}-C_{a})$str. & $(C_{\alpha}-C_{b})$str.	1515	223.12
ν_{42}	$(C_{\alpha'}-C_{b})$str. & $(C_{\alpha'}-C_{a})$str.	1438	187.74
ν_{43}	ring $(C_{b}-C_{b})$str.& $(C_{a}-C_{a})$str.	1404	6.11
ν_{44}	ring(CCC)str.	1391	5.53
ν_{45}	$\delta CH_{(9,10)}$	1302	104.47
ν_{46}	$\delta CH_{\alpha'} + \delta CH_{\alpha}$	1255	32.35
ν_{47}	$\delta CH_{(9,10,\beta)}$ + ring(CCC)str.	1218	48.24
ν_{48}	$\delta CH_{\beta'} + \delta CH_{\alpha'}$	1175	1.93
ν_{49}	$\delta CH_{\beta} + \delta CH_{\alpha}$	1172	7.94
ν_{50}	$\delta CH_{\beta'} + \delta CH_{\beta}$	1165	0.11
ν_{51}	ring (δCCC) + $\delta CH_{(9,10)}$	999	15.52
ν_{52}	ring $(\delta C_{\alpha'} C_{\beta'} C_{\beta})$.	863	4.72
ν_{53}	ring (δCCC).	716	4.89
ν_{54}	ring $(\delta C_{\alpha} C_{\beta} C_{\alpha'})$.	611	0.38
ν_{55}	ring (δCCC).	506	0.54
ν_{56}	ring (δCCC).	450	0.01
A_2			
ν_{24}	γCH_{β}	954	0.00
ν_{25}	$\gamma CH_{\alpha'}$	912	0.00
ν_{26}	$\gamma CH_{(9,10)}$	849	0.00
ν_{27}	γCH_{α} + ring(γCCC)	755	0.00
ν_{28}	$\gamma(C_{a}-C_{b}) + \gamma CH_{\alpha}$	799	0.00
ν_{29}	$\gamma CH_{\beta'}$	756	0.00
ν_{30}	$\gamma(C_{a}-C_{b}) + \gamma CH_{\alpha}$	560	0.00
ν_{31}	ring(γCCC) + $\gamma CH_{\alpha'}$	525	0.00
ν_{32}	$\gamma(C_{9}-C_{10})$	357	0.00
ν_{33}	ring(γCCC)	260	0.00
ν_{34}	ring$(\gamma C_{\alpha} C_{\beta'} C_{\alpha'})$	83	0.00
B_2			
ν_{57}	γCH_{β}	955	3.91
ν_{58}	$\gamma CH_{\alpha'}$	913	1.18
ν_{59}	γCH_{α}	818	2.06
ν_{60}	$\gamma CH_{(9,10)} + \gamma CH_{\beta'}$	761	2.36
ν_{61}	$\gamma CH_{\beta'}$	0.03	ν_{61}
ν_{62}	$\gamma(C_{a}-C_{b}) + \gamma CH_{(9,10)}$	2.62	ν_{62}
ν_{63}	ring(γCCC) + γCH_{β}	0.75	ν_{63}
ν_{64}	ring(γCCC) + $\gamma CH_{\alpha} + \gamma CH_{\alpha'}$	0.46	ν_{64}
ν_{65}	ring(γCCC)	0.69	ν_{65}
ν_{66}	ring $(\gamma C_{\alpha} C_{\beta} C_{\alpha'})$	0.04	ν_{66}

Scaling factors: 0.876 (CH str.); 0.96 (ring (CC) str.); 1.00 (ring (CCC) str); 1.06 (δCH); 1.08 (ring(δCCC); 1.11 (γCH); 1.11 (γCCC); 1.03 (γCC).
Special scaling factors were used for vibration modes with overlaps of different types of motion; 1.00(ring (CC) str. + δCH); 1.00 (δCH + ring(CCC str.)); 1.00 (ring δCCC + δCH); 1.06 (ring (CCC) str. + δCH); 1.11 (γCCC + γCH) or (γCC + γCH); 1.03 (γCH + γCC).
Of interest is the comparison of the vibration freqüencies of the different C-H bonds, as well as the different C-C bonds of the three species, with each other. For the C-H stretching modes we find that, generally and for both ions, the symmetric vibration frequencies are higher than the corresponding antisymmetric vibration frequencies and for all C-H bonds. That is;

ν_{sym} CH str. > ν_{asym} CH str.

Further, different CH bonds exhibit different vibration frequencies i.e.

ν_{sym} CH_{β} str. > ν_{asym} CH_{β} str. > ν_{sym} $CH_{\beta'+\alpha'}$ str. > ν_{asym} $CH_{\beta'+\alpha'}$ str. >

$\nu_{sym}CH_{(9,10)}$ str. > ν_{sym} $CH_{\alpha+\alpha'}$ str. > ν_{asym} $CH_{\alpha+\alpha'}$ str. > ν_{sym} $CH_{\alpha'}$ str. >

$\nu_{asym}CH_{\alpha'}$ str. > ν_{sym} $CH_{\alpha'}$ str. > ν_{asym} $CH_{(9,10)}$str.

For the radical anion the following comparison holds;

$\nu_{sym}CH_{\beta}$ str.>$\nu_{asym}CH_{\alpha}$str.>$\nu_{sym}CH_{(9,10)}$ str.>$\nu_{sym}CH_{\alpha}$ str.>$\nu_{sym}CH_{\beta}$ str.

For the C-C frequencies different values are calculated for the different bonds of both cation and anion. As expected the differences in the vibration frequencies are due to the different C-C force constants;

ν_{sym} ring(C_a-C_a)&(C_b- C_b)str. > ν_{asym}ring(C_a-C_a)&(C_b- C_b)str.

ν_{sym}ring ($C_{\alpha'}$-$C_{\beta'}$) str. > ν_{asym} ring($C_{\alpha'}$-$C_{\beta'}$) str.

And for the anion similar correlation holds.
In general, comparative correlations of similar type might be concluded from the frequencies of Table 2 and 4 for the other types of vibration, i.e. δCH, γCH and γCC modes.

Interionic Correlation

The frequency values of the vibration modes in Tables 2 and 4 point out to systematic correlations between the frequencies of the different species. This fact is mostly obvious in the case of the C-H stretching vibration, for which the following general relation holds;

vsym CH str..+ > vasym CH str. > vasym CH str. –

This interesting result shows that in general the C-H str. Frequency of the radical cation are higher than those of the neutral molecule and these are higher than those of the radical anion.
This influence of the molecular charge might be explained in term of the following consideration; the excess charge is distributed among the carbon atoms of the ring. The negative charge repels the σelectrons of the corresponding carbon atoms and thus decreasing its C-H bond order and the C-H vibration frequency. The positive charge is also distributed among the electrons. The positive charge attracts the σelectrons of the carbon atoms increasing its σelectron density, and correspondinly its C-H force constant and vibration frequency.
In fact the calculation for the σelectrons densities for all carbon atoms shows the following order;

σρÇ.+ > σρC > σρÇ.-

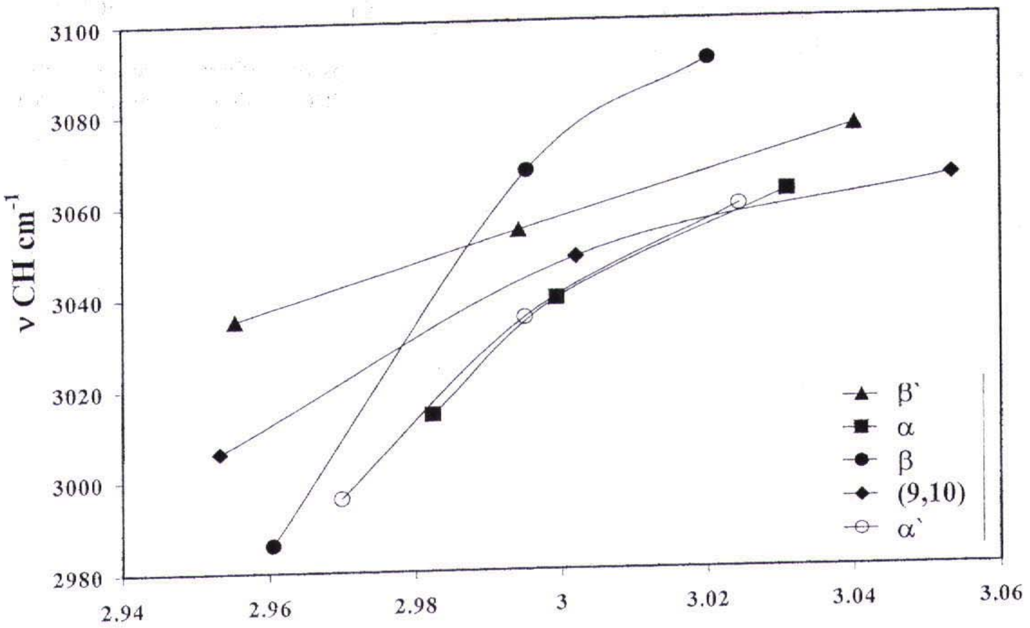


Fig. 4 shows the correlation curve between the σρcarbon and the C-H vibration frequencies for the different C-H bonds.

Fig 4. Graphical correlation of the calculated σ-ρC at different C atoms with the corresponding C-H vibration frequencies for each C atom in phenanthrene radical anion , neutral molecule and cation (C14H10) .-,(C14H10), and (C14H10) .+.
No general, systematic correlation could be established for the other valance modes of vibration. This fact indicates a variation of force constant values for the different vibration modes. Considering the C-C stretching vibrations the frequencies for the different charge species vary according to the following picture;

ν(C9 - C10) > ν(C9-C10).- > ν (C9-C10) .+
ν(Cα` - Cβ`) > ν(Cα` - Cβ`).- > ν (Cα` -Cβ`).+
ν(Cβ` - Cβ) > ν(Cβ` - Cβ).- > ν (Cβ` -Cβ).+
ν(Ca- Cb) > ν(Ca- Cb) .- > ν (Ca- Cb).+

It is seen that, generally that the frequencies of the neutral molecule are higher than those of the charged species. The result is different than that for the δCH deformation frequencies, which assigns the highest frequencies for the radical cation followed by those of the neutral molecule and then that radical cation.
δCH.- > δCH > δCH.+

The comparison for the other modes may be summarized in the following relations;
δCCC.- > δCCC > δCCC.+
γCH.+ > γCH > γCH.-
and
γCCC > γCCC .+ > γCCC.-

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