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

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

Key words: Phenanthrene; Vibration; σ-Electrons.

1. Introduction

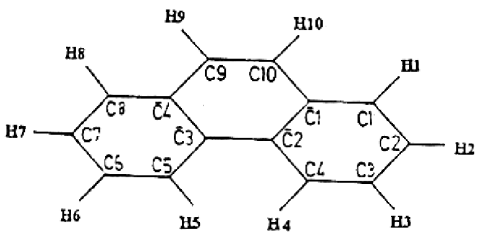
The vibration spectra of polyaromatic hydrocarbon cations gain increasing importance due to their presence in interstellar spaces and their expected ecological importance. Efforts were made to study their spectra both experimentally and theoretically. As for the phenanthrene radical cation, Hudgins and Allamandola [1] studied its vibration spectrum, applying the isolated matrix technique. Langhoff [2] and Ling et al. [3] studied its spectrum theoretically, applying quantum mechanical methods. The phenanthrene radical cation was generated through γ-irradiation of the neutral molecule [4, 5] or of the molecule in an 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 valence 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.

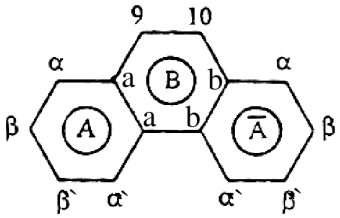
2. Results and Discussion

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

The C_Z axis 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, $(23A_1 + 22B_1)$ in-plane, and $(11A_2 + 10B_2)$ out of-plane vibration modes. According to 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



(a)



(b)

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

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

Length (Å)/ angle (deg.)	Cation		Anion	Neutral
	This work	Calcd. [3]		Calcd. [13]
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
H_{10}-C_{10}	1.106	—	1.110	1.107
$\angle C'_1\ C_1\ C_2$	122.4	—	122.7	122.7
$\angle C_1\ C_2\ C_2$	118.8	—	120.2	119.3
$\angle C_2\ C_3\ C_4$	120.8	—	118.8	122.7
$\angle C'_1\ C_{10}\ C_9$	122.5	—	122.5	122.0
$\angle C_1\ C'_1\ C'_2$	118.5	—	117.4	118.7
$\angle C_4\ C'_2\ C'_1$	116.3	—	116.5	116.1
$\angle C'_1\ C'_2\ C'_3$	119.0	—	118.9	116.0
$\angle H_1\ C_1\ C_2$	119.9	—	118.9	119.3
$\angle H_2\ C_2\ C_3$	120.4	—	119.6	120.0
$\angle H_3\ C_3\ C_4$	119.1	—	120.6	120.0
$\angle H_4\ C_4\ C'_2$	119.8	—	119.6	119.3
$\angle H_4\ C_4\ C_3$	117.1	—	116.0	117.4
$\angle H_{10}\ C_{10}\ C'_1$	119.4	—	119.0	118.0

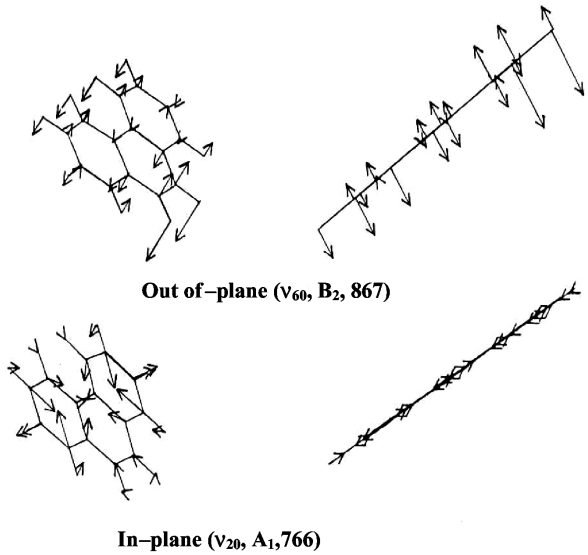


Fig. 2. DRAW.MOL plotted graphical pictures of two vibration modes of the phenanthrene radical cation.

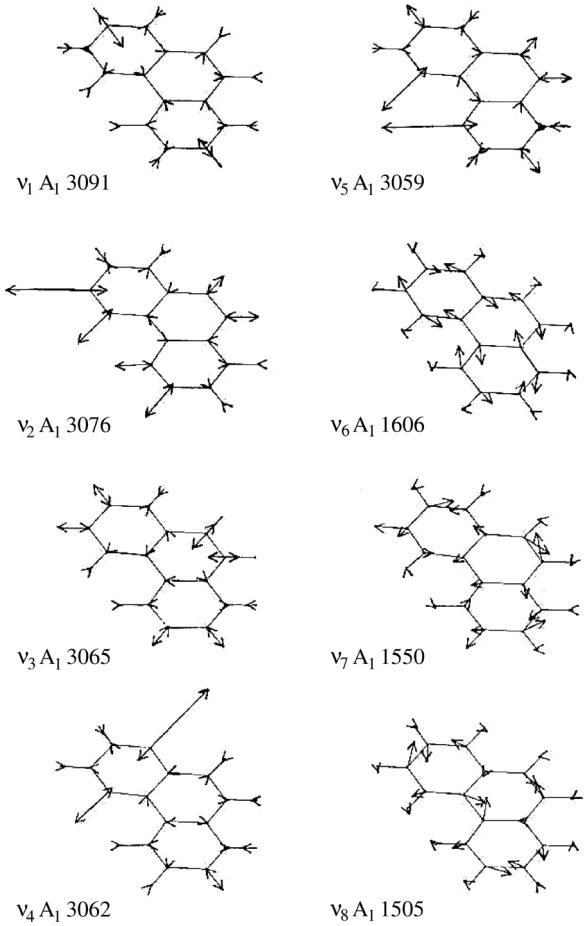


Fig. 3. Graphical pictures of some vibration modes of the phenanthrene radical cation as drawn through the DRAW.MOL routine.

present calculations agree fully with these expectations. Figure 2 shows DRAW.MOL plotted graphical pictures of two vibration modes of the phenanthrene radical cation.

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

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

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

Symmetry and description	Frequency in cm^{-1} This work Scaled	Others Calcd. [3]	Others Calcd. [2]	Others Calcd. Exptl. [1]
A_1				
ν_1 CH_βstr.	3091	—	—	—
ν_2 $CH_{\beta'}$str. + $CH_{\alpha'}$str.	3076	—	—	—
ν_3 $CH_{(9,10)}$str.	3065	—	—	—
ν_4 CH_αstr. + $CH_{\alpha'}$str.	3062	—	—	—
ν_5 $CH_{\alpha'}$str.	3059	—	—	—
ν_6 ring(C-C)str.	1606	1607	1583	1558
ν_7 (C_9-C_{10})str. + (C_α-C_β)str.	1550	1550	1533	1551
ν_8 ($C_{\beta'}$-C_β)str. + (C_a-C_b)str.	1505	1515	1513	1513
ν_9 (C_a-C_b)str. + (C_9-C_{10})str.	1381	—	—	—
ν_{10} (C_a-C_a)str. & (C_b-C_b)str.	1355	—	—	—
ν_{11} ($C_{\alpha'}$-$C_{\beta'}$)str. + (C_α-C_β)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_βstr.	3090	—	—	—
ν_{36} $CH_{\beta'}$str. + $CH_{\alpha'}$str.	3075	—	—	—
ν_{37} CH_αstr. + $CH_{\alpha'}$str.	3061	—	—	—
ν_{38} $CH_{\alpha'}$str.	3058	—	—	—
ν_{39} $CH_{(9,10)}$str.	3055	—	—	—
ν_{40} (C_α-C_β)str. + ($C_{\beta'}$-$C_{\alpha'}$)str.	1559	1570	1565	1565
ν_{41} (C_a-C_9) & (C_b-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	—	—

Symmetry and description	Frequency in cm^{-1} This work Scaled	Others Calcd. [3]	Others Calcd. [2]	Others Calcd. Exptl. [1]
ν_{45} ring(CCC)str. + $\delta CH_{(9,10)}$	1299	1316	1309	—
ν_{46} $\delta CH_{\alpha'}$ + $\delta CH_{(9,10,\alpha)}$	1260	1272	1292	1299
ν_{47} $\delta CH_{(9,10)}$ + δCH_α	1221	1213	1230	—
ν_{48} $\delta CH_{\beta'}$ + $\delta CH_{\alpha'}$ + δ(CCC)	1170	—	—	—
ν_{49} δCH_α + $\delta CH_{\beta'}$	1159	—	—	—
ν_{50} δCH_β + $\delta CH_{\beta'}$	1155	1132	1154	—
ν_{51} ring(δCCC) + $\delta CH_{(9,10,\alpha')}$	990	978	986	—
ν_{52} ring(δCCC)	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} $\gamma CH_{\beta'}$ + γCH_α	991	—	—	—
ν_{25} $\gamma CH_{(9,10)}$ + $\gamma CH_{(\beta',\beta)}$	984	—	—	—
ν_{26} γCH_β + γCH_α	962	—	—	—
ν_{27} $\gamma CH_{\alpha'}$ + ring(γCCC)	859	—	—	—
ν_{28} γ(C_a-C_b) + $\gamma CH_{\alpha'}$	814	—	—	—
ν_{29} γCH_β + $\gamma CH_{\beta'}$ + γCH_α	805	—	—	—
ν_{30} ring(γCCC) + γCH_α	539	—	—	—
ν_{31} ring(γCCC) + $\gamma CH_{(9,10)}$	477	—	—	—
ν_{32} γ(C_9-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} γCH_β + γCH_α	972	1033	—	—
ν_{59} $\gamma CH_{\alpha'}$ + γCH_β	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} γ(C_a-C_b) + γCH_α	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 (CHstr.); 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; 1.06 [ring(CCC)str. + δCH]; 1.11 (γCCC + γCH) or (γCC + γCH); 1.03 (γCH + γCC).

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 (Figure 3).

Table 3 includes the calculated IR absorption intensities of the radical cation. Table 4 shows both, the vibration frequencies and IR absorption intensities for the radical anion as calculated with the MINDO/3-FORCES method.

Figure 4 shows the correlation curve between the $\sigma\rho$-carbon and the C-H vibration frequencies for the different C-H bonds.

2.1. C-H and C-C Vibrations

Of interest is the comparison of the vibration frequencies of the different C-H bonds, as well as the different C-C bonds of the three species. For the C-H stretching modes we find that, generally and for both ions, the symmetrical vibration frequencies are higher than the corresponding antisymmetrical vibration frequencies. For all C-H bonds is

$$\nu_{sym}\text{CHstr.} > \nu_{asym}\text{CHstr.}$$

Further, different C-H bonds exhibit different vibration frequencies, i. e.

$$\begin{aligned}&\nu_{sym}CH_\beta\text{str.} > \nu_{asym}CH_\beta\text{str.} > \nu_{sym}CH_{\beta'+\alpha'}\text{str.}\\ &> \nu_{asym}CH_{\beta'+\alpha'}\text{str.} > \nu_{sym}CH_{(9,10)}\text{str.}\\ &> \nu_{sym}CH_{\alpha+\alpha'}\text{str.} > \nu_{asym}CH_{\alpha+\alpha'}\text{str.} > \nu_{sym}CH_{\alpha'}\text{str.}\\ &> \nu_{asym}CH_{\alpha'}\text{str.} > \nu_{sym}CH_{\alpha'}\text{str.} > \nu_{asym}CH_{(9,10)}\text{str.}\end{aligned}$$

For the radical anion the following comparison holds:

$$\begin{aligned}&\nu_{sym}CH_\beta\text{str.} > \nu_{asym}CH_\alpha\text{str.} > \nu_{sym}CH_{(9,10)}\text{str.}\\ &> \nu_{sym}CH_{\alpha'}\text{str.} > \nu_{sym}CH_\beta\text{str.}\end{aligned}$$

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

Symmetry and description	Intensity in km/mol This work Calcd.	Others Calcd. [3]	Others Calcd. [2]
A_1			
ν_1 δCH_βstr.	0.88	—	—
ν_2 $CH_{\beta'}$str. + $CH_{\alpha'}$str.	23.10	—	—
ν_3 $CH_{(9,10)}$str.	30.12	—	—
ν_4 CH_αstr. + $CH_{\alpha'}$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-C_{10})str. + (C_α-C_β)str.	47.81	108.9	112.7
ν_8 ($C_{\beta'}$-C_β)str. + (C_a-C_b)str.	0.02	6.97	10.8
ν_9 (C_a-C_b)str. + (C_9-C_{10})str.	2.80	—	—
ν_{10} (C_a-C_a)str. & (C_b-C_b)str.	12.14	—	—
ν_{11} ($C_{\alpha'}$-$C_{\beta'}$)str. + (C_α-C_β)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} $\delta CH_{\alpha'}$ + δCH_α	0.00	40.9	30.1
ν_{15} $\delta CH_{(9,10)}$ + $\delta CH_{(\alpha,\beta')}$	0.04	—	—
ν_{16} δCH_α + $\delta CH_{\alpha'}$	1.71	—	—
ν_{17} $\delta CH_{\beta'}$ + δCH_β	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($\delta C_a C_\alpha C_\beta$) & ($C_b C_\alpha C_\beta$)	0.08	—	—
ν_{23} ring(δCCC)	0.00	—	—
B_1			
ν_{35} CH_βstr.	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_α-C_β)str. + ($C_{\beta'}$-$C_{\alpha'}$)str.	139.44	213.3	184.0
ν_{41} (C_a-C_9) & (C_b-C_{10})str.	124.02	16.4	—
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} $\delta CH_{(9,10)}$ + δCH_α	0.00	54.1	44.8
ν_{48} $\delta CH_{\beta'}$ + $\delta CH_{\alpha'}$	7.01	—	—
ν_{49} δCH_α + $\delta CH_{\beta'}$	0.42	—	—
ν_{50} δCH_β + $\delta CH_{\beta'}$	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} $\gamma CH_{\beta'}$ + γCH_α	0.00	—	—
ν_{25} $\gamma CH_{(9,10)}$ + $\gamma CH_{(\beta',\beta)}$	0.00	—	—
ν_{26} γCH_β + γCH_α	0.00	—	—
ν_{27} $\gamma CH_{\alpha'}$ + ring(γCCC)	0.00	—	—
ν_{28} γ(C_a-C_b) + $\gamma CH_{\alpha'}$	0.00	—	—
ν_{29} γCH_β + $\gamma CH_{\beta'}$ + γCH_α	0.00	—	—
ν_{30} ring(γCCC) + γCH_α	0.00	—	—
ν_{31} ring(γCCC) + $\gamma CH_{(9,10)}$	0.00	—	—
ν_{32} γ(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} γCH_β + γCH_α	1.09	5.4	—
ν_{59} $\gamma CH_{\alpha'}$ + γCH_β	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} γ(C_a-C_b) + γCH_α	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	—	—

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

$$\nu_{sym}\text{ring}(C_a - C_a)\,\&\,(C_b - C_b)\text{str.} > \nu_{asym}\text{ring}(C_a - C_a)\,\&\,(C_b - C_b)\text{str.}$$

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

For the anion similar correlations hold.

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

2.2. Interionic Correlation

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

$$\nu_{sym}\text{CHstr.}^{\cdot+} > \nu_{asym}\text{CHstr.} > \nu_{asym}\text{CHstr.}^{\cdot-}.$$

This interesting result shows that in general the C-H stretching frequencies 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 terms of the following consideration: The

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

Symmetry and description	Frequency in cm^{-1}	Intensity in km/mol
	This work	
A_1		
ν_1 $CH_{\beta'}$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_{α}-C_{β})str.	1570	31.40
ν_8 ($C_{\beta'}$-C_{β})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} $\delta CH_{\alpha'}$ + δCH_{α} [f02b] ring(δCCC)	1190	0.35
ν_{15} $\delta CH_{(9,10)}$ + $\delta CH_{(\beta,\alpha)}$	1185	0.03
ν_{16} δCH_{α} + $\delta CH_{\alpha'}$	1178	0.10
ν_{17} $\delta CH_{\beta'}$ + δCH_{β}	1170	0.08
ν_{18} $\delta CH_{(9,10)}$ + δCH_{β}	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
ν_{40} ($C_{\alpha'}$-$C_{\beta'}$)str. + (C_{α}-C_{β})str.	1571	112.41
ν_{41} (C_{α}-C_a)str. & (C_{α}-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} $\delta CH_{\alpha'}$ + δCH_{α}	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} δCH_{β} + δCH_{α}	1172	7.94
ν_{50} $\delta CH_{\beta'}$ + δCH_{β}	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} γ(C_a-C_b) + γCH_{α}	799	0.00
ν_{29} $\gamma CH_{\beta'}$	756	0.00
ν_{30} γ(C_a-C_b) + γCH_{α}	560	0.00
ν_{31} ring(γCCC) + $\gamma CH_{\alpha'}$	525	0.00
ν_{32} γ(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} $\gamma CH_{\beta'}$	753	0.03
ν_{62} γ(C_a-C_b) + $\gamma CH_{(9,10)}$	706	2.62
ν_{63} ring(γCCC) + γCH_{β}	504	0.75
ν_{64} ring(γCCC) + γCH_{α} + $\gamma CH_{\alpha'}$	443	0.46
ν_{65} ring(γCCC)	223	0.69
ν_{66} ring($\gamma C_{\alpha}C_{\beta}C_{\alpha'}$)	107	0.04

Scaling factors: 0.876 (CHstr.); 0.96 [ring(CC)str.]; 1.00 [ring(CC)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; 1.06 [ring(CCC)str. + δCH]; 1.11 (γCCC + γCH) or (γCC + γCH); 1.03 (γCH + γCC).

excess charge is distributed among the carbon atoms of the ring. The negative charge repels the σ-electrons of the corresponding carbon atoms, 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 σ-electrons of the carbon atoms, increasing the σ-electron density, and correspondingly its C-H force constant and vibration frequency.

In fact the calculation for the σ-electron densities for all carbon atoms shows the order

$$\sigma\rho C^{\cdot+} > \sigma\rho C > \sigma\rho C^{\cdot-}.$$

No systematic correlation could be established for the other valence modes of vibration. This fact indicates a variation of force constants for the different vibration modes. Considering the C-C stretching vibrations, the frequencies for the different charge species vary as follows:

$$\nu(C_9 - C_{10}) > \nu(C_9 - C_{10})^{\cdot-} > \nu(C_9 - C_{10})^{\cdot+}$$

$$\nu(C_{\alpha'} - C_{\beta'}) > \nu(C_{\alpha'} - C_{\beta'})^{\cdot-} > \nu(C_{\alpha'} - C_{\beta'})^{\cdot+}$$

$$\nu(C_{\beta'} - C_{\beta}) > \nu(C_{\beta'} - C_{\beta})^{\cdot-} > \nu(C_{\beta'} - C_{\beta})^{\cdot+}$$

$$\nu(C_a - C_b) > \nu(C_a - C_b)^{\cdot-} > \nu(C_a - C_b)^{\cdot+}$$

It is seen that generally the frequencies of the neutral molecule are higher than those of the charged species.

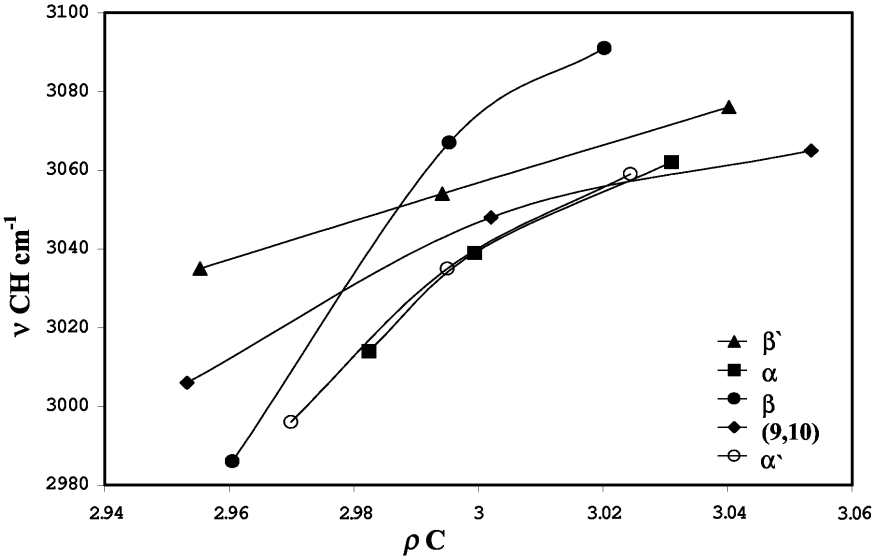


Fig. 4. Graphical correlation of the calculated σ-ρ_C at different carbon atoms with the corresponding C-H vibration frequencies, for each carbon atom in the phenanthrene radical anion, neutral molecule and cation $(C_{14}H_{10})^{\cdot -}$, $(C_{14}H_{10})$, and $(C_{14}H_{10})^{\cdot +}$.

The result is different for the δCH deformation frequencies, which assign the highest frequencies for the radical anion followed by those of the neutral molecule and then of the radical cation:

$$\delta CH^{\cdot -} > \delta CH > \delta CH^{\cdot +}.$$

The comparison for the other modes may be summarized in the following relations:

$$\delta CCC^{\cdot -} > \delta CCC > \delta CCC^{\cdot +},$$

$$\gamma CH^{\cdot +} > \gamma CH > \gamma CH^{\cdot -},$$

and

$$\gamma CCC > \gamma CCC^{\cdot +} > \gamma CCC^{\cdot -}.$$

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