Vibration Frequencies Shifts of Naphthalene and Anthracene as Caused by Different Molecular Charges

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Semi-empirical SCF-MO calculations were carried out for the naphthalene and anthracene radical cations and anions. For all ions D_{2h} symmetry was obtained. All 3N-6 vibration frequencies for all species were calculated and assigned, applying the Herzberg convention. The valence assignment of the vibration modes was possible applying graphical pictures of each mode and the so called atomic partial participation (APP) values. Interesting relations between the frequencies of the ions were obtained, e. g. for the radical cation of naphthalene $\nu_{sym}(CH_\beta\ str.)^{\cdot+} > \nu_{asym}(CH_\beta\ str.)^{\cdot+} > \nu_{sym}(CH_\alpha\ str.)^{\cdot+} > \nu_{asym}(CH_\alpha\ str.)^{\cdot+}$, and for its anion $\nu_{sym}(CH_\alpha\ str.)^{\cdot-} > \nu_{asym}(CH_\alpha\ str.)^{\cdot-} > \nu_{sym}(CH_\beta\ str.)^{\cdot-} > \nu_{asym}(CH_\beta\ str.)^{\cdot-}$, as well as for both ions ν_{sym} ring (C_β-C_β) str. $> \nu_{asym}$ ring C_α-C_β) str. $> \nu_{sym}$ ring (C_9-C_{10}) str. Similar correlations were detected for the anthracene ions. Interionic correlations could be observed for the frequencies of similar modes for the ions and neutral molecules, e. g. for naphthalene $\nu_{sym}(CH_\beta\ str.)^{\cdot+} > \nu_{sym}(CH_\beta\ str.) > \nu_{sym}\ (CH_\beta\ str.)^{\cdot-}$ and $\nu_{sym}(CH_\alpha\ str.)^{\cdot+} > \nu_{sym}(CH_\alpha\ str.) > \nu_{sym}(CH_\alpha\ str.)^{\cdot-}$. Generally the calculated frequencies for the radical anions were nearer to those of the neutral molecule than those of the radical cations.

Key words: Vibration Frequencies; Naphthalene; Anthracene; Ions.

Introduction

Aromatic radical ions gained significant importance as intermediates in chemical reactions [1]. They were generated in most cases through irradiation of the parent molecules or through chemical reactions such as charge transfer reactions [1]. The vibration spectrum of the naphthalene radical cation was studied experimentally applying the isolated matrix technique [2 – 6] and theoretically applying the Hartree-Fock method [7] and density functional approach [8]. As far as we know, for the naphthalene radical anion no such studies have been reported, although it has chemical importance as reducing agent, as initiator of polymerization and for the synthesis of metal-organic complexes [9 – 12].

The anthracene radical cation was generated in an isolated matrix applying γ-radiation at 77 °K [13, 14]. It was found to participate in electronic charge transfer [15, 16]. It's vibration frequencies and absorption intensities were measured by various research groups, e. g. Szepanski *et al.* [17 – 20]. De Frees *et al.* [7] calculated its vibration frequencies applying the Hartree-Fock method. Yan Ling [21] and Langhoff [22] obtained the same results applying the density functional method.

Table 1. Bond distances (Å) and angles (deg.) of the naphthalene radical cation.

Atoms	This work calcd.	calcd. [7]	Neutral calcd. [21]
C_1'-C_2'	1.488	1.421	1.462
C_1'-C_1	1.434	1.401	1.449
C_1-C_2	1.418	1.398	1.380
C_2-C_3	1.398	1.378	1.430
C_1-H_1	1.106	1.072	1.107
C_2-H_2	1.103	1.070	1.105
$< C_1\ C_1'\ C_2$	117.600	119.100	118.000
$< C_1'\ C_1\ C_2$	122.300	120.600	122.000
$< C_1\ C_2\ C_3$	120.100	120.300	120.000
$< H_1\ C_1\ C_1'$	118.900	119.600	118.000
$< H_2\ C_2\ C_1$	119.300	119.500	120.000

Radical ions of polyaromatic hydrocarbons (PAH's) gained increasing importance due to their possible carcinogenic properties and their presence in the interstellar space. In this work we applied the MINDO/3-FORCES [23] method for the calculation of the vibration frequencies anbd IR absorption intensities of such molecules. The study should shed some light on the spectroscopic properties of these ions and allow a comparison between their vibration modes.

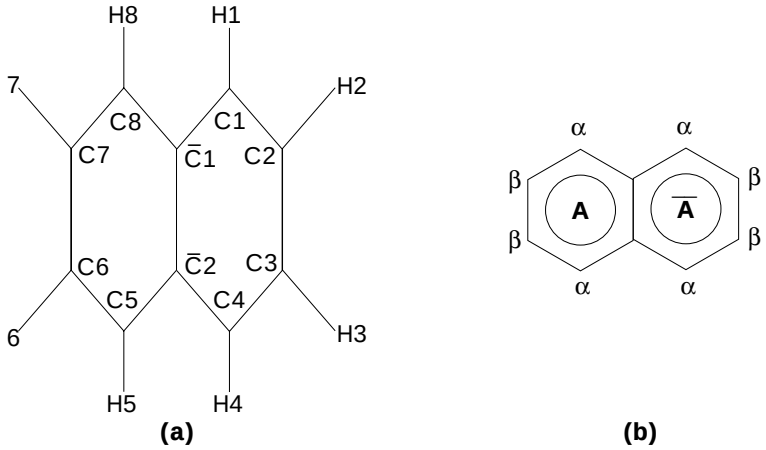

Fig. 1. Structure of the naphthalene radical cation, showing (a) the numbering of the C and H atoms and (b) the designation of the atoms in the molecule.

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

Symmetry and description	This work	Frequency cm^{-1} Others calcd. [7]	calcd. [21]	exptl. [5]
In-plane				
A_g				
ν_1 CH_β str.	3089	–	–	–
ν_2 CH_α str.	3064	–	–	–
ν_3 ring (CC str.)$_{(\beta-\beta),(9-10)}$	1576	–	–	–
ν_4 ring (CCC str.)	1448	–	–	–
ν_5 ring (C_9-C_{10}) str.	1337	–	–	–
ν_6 $\delta CH_{(\beta,\alpha)}$	1168	–	–	–
ν_7 $\delta CH_{(\alpha\&\beta)}$	1153	–	–	–
ν_8 ring(δCCC)	920	–	–	–
ν_9 ring(δCCC)	517	–	–	–
B_{1u}				
ν_{17} CH_β str.	3081	3094	–	–
ν_{18} CH_α str.	3062	3072	–	–
ν_{19} ring (C_α-C_β) str.	1511(−5%)	1525	1516	1519
ν_{20} ring (CCC str.) + δCH_β	1392(−6%)	1409	1386	1401
ν_{21} δCH_α	1249(+3%)	1274	1262	1215
ν_{22} δCH_β + ring (CCC str.)	1067	1074	1092	–
ν_{23} ring (δCCC)	773(+2%)	782	–	759
ν_{24} ring (δCCC)	372	350	–	–
B_{2u}				
ν_{29} CH_β str.	3089	3099	–	–
ν_{30} CH_α str.	3063	3071	–	–
ν_{31} ring (CC str.)	1534(+4%)	1526	1531	1526
ν_{32} ring (CCC str.)	1354	1349	1396	–
ν_{33} ring (CCC str.)	1271(+6%)	1195	1201	1218
ν_{34} $\delta CH_{(\beta,\alpha)}$	1162	1114	1154	–
ν_{35} $\delta CH_{(\alpha,\beta)}$ + ring(δCCC)	1084	973	1015	1023
ν_{36} ring(δCCC)	600	559	590	–
B_{3g}				
ν_{37} CH_β str.	3081	–	–	–
ν_{38} CH_α str.	3062	–	–	–
ν_{39} ring (CCC str.)	1435	–	–	–
ν_{40} ring(CCC)	1268	–	–	–
ν_{41} $\delta CH_{(\beta\&\alpha)}$ + ring(δCCC)	1144	–	–	–
ν_{42} $\delta CH_{(\alpha,\beta)}$	1142	–	–	–
ν_{43} ring (δCCC)	859	–	–	–
ν_{44} ring (δCCC)	460	–	–	–
Out of-plane				
B_{1g}				
ν_{14} $\gamma CH_{\alpha,\beta}$	985	–	–	–
ν_{15} $\gamma CH_{\beta,\alpha}$	763	–	–	–
ν_{16} $\gamma CC_\alpha + \gamma CH_\alpha$	363	–	–	–
B_{2g}				
ν_{25} γCH_β	980	–	–	–
ν_{26} $\gamma CH_{\alpha,\beta}$ + γCC	891	–	–	–
ν_{27} γ(C_9-C_{10}) + γCH_α	745	–	–	–
ν_{28} γ(C_β-C_β) + γCH_β	449	–	–	–
A_u				
ν_{10} γCH_β	981	–	–	–
ν_{11} γCH_α	877	–	–	–
ν_{12} γ(C_β-C_β) + $\gamma CH_{\alpha,\beta}$	474	–	–	–
ν_{13} γ(C_α-C_β) + γCH_α	172	–	–	–
B_{3u}				
ν_{45} γCH_α	997	979	–	–
ν_{46} γCH_β	795	754	762	
ν_{47} $\gamma CC_{(9-10),\alpha}$ + γCH_α	459	425	420	–
ν_{48} $\gamma CC_{(9,10)(\beta-\beta)}$ + γCH	163	175	–	–

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).

As we have explained in former papers [24–27], the MINDO/3-FORCES method is best described as a combination of Dewar's MINDO/3 semiempirical SCF-MO method and Pulay's gradient method for the calculation of equilibrium geometries and force constants [28]. The computer program was written to calculate the cartesian force constants F_{ij} of the molecule. The force constants were then used to calculate the molecular vibration frequencies according to the Wilson's equation

$$\sum_j L_j(F_{ij} - M_{ij}\lambda) = 0. \quad (1)$$

The equilibrium coordinates (x_i) and eigenvector coef-

Table 3. Calculated IR absorption intensities of the naphthalene radical cation.

Symmetry and description	Intensity Integ. Γ_i cm^2/mol	Absorb. A_i km/mol	abinitio [7] km/mol	abinitio [19] km/mol
In-plane				
A_g				
ν_1 CH_β str.	0.00	0.00	0.00	0.00
ν_2 CH_α str.	0.00	0.00	0.00	0.00
ν_3 ring ($CC_{(\beta-\beta),(9-10)}$) str.	0.00	0.00	0.00	0.00
ν_4 ring (CCC str.)	0.00	0.00	0.00	0.00
ν_5 ring (C_9-C_{10}) str.	0.00	0.00	0.00	0.00
ν_6 $\delta CH_{(\beta,\alpha)}$	0.00	0.00	0.00	0.00
ν_7 $\delta CH_{(\alpha\&\beta)}$	0.00	0.00	0.00	0.00
ν_8 ring(δCCC)	0.00	0.00	0.00	0.00
ν_9 ring(δCCC)	0.00	0.00	0.00	0.00
B_{1u}				
ν_{17} CH_β str.	457.20	16.08	1.00	–
ν_{18} CH_α str.	952.45	33.29	2.00	–
ν_{19} ring (C_α-C_β) str.	2548.5	40.11	147.0	82.20
ν_{20} ring (CCC str.) + δCH_β	1335.98	17.54	19.00	27.00
ν_{21} $\delta CH-\alpha$	119.00	1.40	5.00	10.70
ν_{22} δCH_β + ring (CCC str.)	576.51	6.15	22.00	3.50
ν_{23} ring (δCCC)	0.03	0.00	0.00	–
ν_{24} ring (δCCC)	6.04	0.02	0.00	–
B_{2u}				
ν_{29} CH_β str.	431.78	15.23	1.00	–
ν_{30} CH_α str.	0.82	0.03	11.00	–
ν_{31} ring (CC str.)	5081.07	81.21	180.00	30.20
ν_{32} ring (CCC str.)	2677.71	36.27	3.00	23.20
ν_{33} ring (CCC str.)	4597.98	58.42	31.00	215.60
ν_{34} $\delta CH_{(\beta,\alpha)}$	161.51	1.77	1123.00	10.20
ν_{35} $\delta CH_{(\alpha,\beta)}$ + ring (δCCC)	46.45	0.50	662.00	11.10
ν_{36} ring (δCCC)	289.78	1.61	324.00	8.30
B_{3g}				
ν_{37} CH_β str.	0.00	0.00	0.00	0.00
ν_{38} CH_α str.	0.00	0.00	0.00	0.00
ν_{39} ring (CCC str.)	0.00	0.00	0.00	0.00
ν_{40} ring (CCC)	0.00	0.00	0.00	0.00
ν_{41} $\delta CH_{(\beta\&\alpha)}$ + ring (δCCC)	0.00	0.00	0.00	0.00
ν_{42} $\delta CH_{(\alpha,\beta)}$	0.00	0.00	0.00	0.00
ν_{43} ring (δCCC)	0.00	0.00	0.00	0.00
ν_{44} ring (δCCC)	0.00	0.00	0.00	0.00
Out of-plane				
B_{1g}				
ν_{14} $\gamma CH_{\alpha,\beta}$	0.00	0.00	0.00	0.00
ν_{15} $\gamma CH_{\beta,\alpha}$	0.00	0.00	0.00	0.00
ν_{16} $\gamma CC_\alpha + \gamma CH_\alpha$	0.00	0.00	0.00	0.00
B_{2g}				
ν_{25} γCH_β	0.00	0.00	0.00	0.00
ν_{26} $\gamma CH_{\alpha,\beta}$ + γCC	0.00	0.00	0.00	0.00
ν_{27} γ(C_9-C_{10}) + γCH_α	0.00	0.00	0.00	0.00
ν_{28} γ(C_β-C_β) + γCH_β	0.00	0.00	0.00	0.00
A_u				
ν_{10} γCH_β	0.00	0.00	0.00	0.00
ν_{11} γCH_α	0.00	0.00	0.00	0.00
ν_{12} γ(C_β-C_β) + $\gamma CH_{\alpha,\beta}$	0.00	0.00	0.00	0.00
ν_{13} γ(C_α-C_β) + γCH_α	0.00	0.00	0.00	0.00
B_{3u}				
ν_{45} γCH_α	152.89	1.37	4.00	–
ν_{46} γCH_β	1049.58	7.52	162.00	78.30
ν_{47} $\gamma CC_{(9-10),\alpha}$ + γCH_α	1364.98	5.65	48.00	19.90
ν_{48} $\gamma CC_{(9,10)(\beta-\beta)}$ + γCH	432.8	0.36	5.00	–

ficients L_j were used to evaluate the atomic displacement vectors R_k^A, which when plotted, applying the DRAW.MOL routine [29], yield a pictorial description of each vibration mode. They were applied to evaluate the atomic partial participation (APP) [23].

Results and Discussion

Naphthalene Radical Ions

The geometry calculation for the naphthalene radical cation yielded a D_{2h} symmetry, similar to that of the uncharged naphthalene Figure 1. In Table 1 the equilibrium bond distances and angles are listed and compared with theoretical values calculated by other methods [7, 21].

It is seen that the total symmetry is maintained, although some of the bond distances are changed due to the positive charge, e. g. shortening of C_9-C_1 and elongation of C_1-C_2. The calculated equilibrium geometry was applied for the calculation of the vibration frequencies and IR absorption intensities. Table 2 includes the frequency values and assignments, according to the Herzberg's convention [30], of the corresponding modes of the radical cation. By the valence assignment of the calculated normal modes, their corresponding graphical representations were considered,

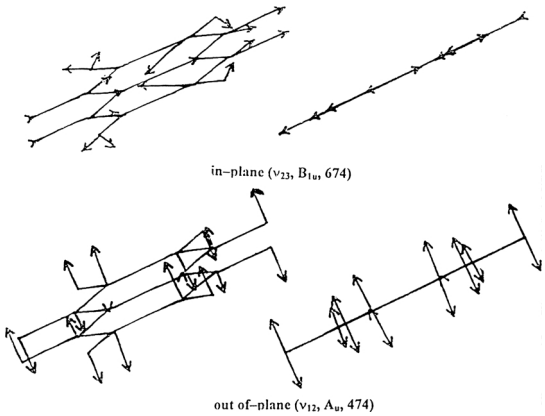

Fig. 2. DRAW.MOL plotted graphical pictures of two vibration modes of naphthalene radical cation.

as drawn with the DRAW.MOL program, as well as their APP values. Figure 2 shows such graphical pictures for two modes, in plane and out of plane. Table 3 shows the calculated IR absorption intensities of the radical cation.

A similar treatment was done for the naphthalene radical anion. Table 4 shows its calculated geometry values. Tables 5 and 6 include its calculated vibration frequencies and IR absorption intensities respectively.

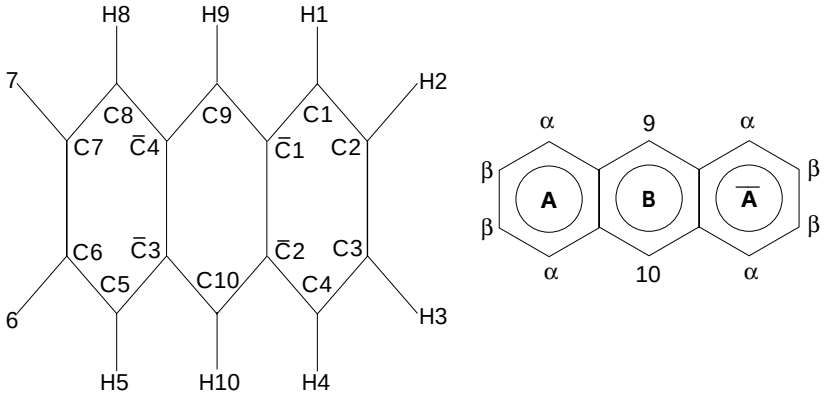

Fig. 3. Structure of the anthracene radical cation, showing, (a) the numbering of the C and H atoms and (b) the designation of the atoms in the molecule.

Table 4. Bond distances (Å) and angles (deg.) of naphthalene radical anion.

Atoms	Calculated values for the	
	Radical anion	Neutral molecule [30]
C_1'-C_2'	1.492	1.462
C_1'-C_1	1.435	1.449
C_1-C_2	1.413	1.380
C_2-C_3	1.396	1.430
C_1-H_1	1.109	1.107
C_2-H_2	1.111	1.105
$< C_1\ C_1'\ C_2$	117.500	118.000
$< C_1'\ C_1\ C_2$	122.400	122.000
$< C_1\ C_2\ C_3$	120.200	120.000
$< H_1\ C_1\ C_1'$	119.200	118.000
$< H_2\ C_2\ C_1$	119.700	120.000

Due to the similarity of their molecular symmetries, the radical ions exhibit similar symmetry modes of vibration to those of the neutral molecule. Comparison of these modes will be described in succeeding paragraphs.

The Anthracene Radical Ions

Applying the MINDO/3-FORCES method, the equilibrium geometries for the anthracene radical cation and anion were calculated. Table 6 gives the obtained bond distances and angles of the radical cation compared to those of the neutral molecule.

A study of the bond distances and angles shows that the radical cation maintains the D_{2h} symmetry (Fig. 3). The bond distances of the ion deviate from those of the neutral molecule. The found symmetry was applied to the assignment of its 66 modes of vibration (3N-6). The modes were identifed as in plane and out of plane vibrations (Fig. 4).

Tables 7 and 8 give the assigned vibration frequencies and absorption intensities of the radical cation.

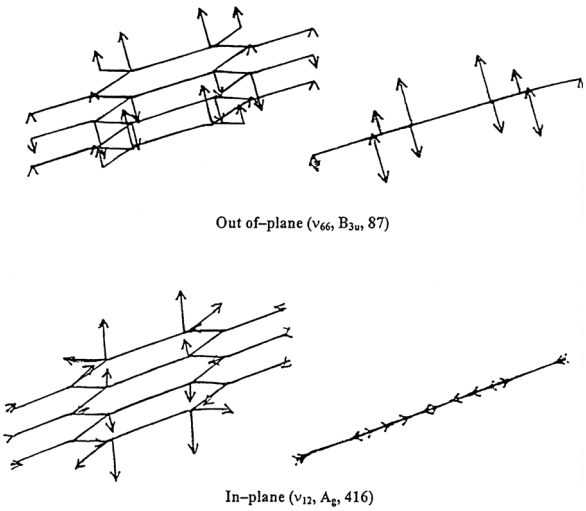

Fig. 4. DRAW,MOL plotted graphical pictures of two vibration modes of anthracene radical cation.

A similar treatment was done for the antracene anion. Table 9 shows its calculated geometry and Table 10 its vibration frequencies and IR absorption intensities respectively.

Inspecting the geometric values of Table 9, one easily finds out that the anthracene radical anion maintains the D_{2h} symmetry too.

The calculated vibration frequencies of the cation (and consequently of the neutral species) of both molecules show a remarkable agreement with those calculated by the abinitio method or measured experimentally. The biggest deviation of the calculated from the experimental frequencies in the case of the naphthalene radical cation is +6% ($\nu_{35}B_{2u}$), and that of the anthracene radical cation is +5% ($\nu_{47}B_{2u}$). The close agreement confirms the correctness of the treatment,

Table 5. Calculated vibration frequencies and IR absorption intensities of the naphthalene radical anion.

Symmetry and description		Frequency Scaled cm^{-1}	Intensity Integ. I_i cm^2/mol	Intensity absorb. A_i km/mol
In-plane				
A_g				
ν_1	$CH_{\alpha,\beta}$ str.	3022	0.00	0.00
ν_2	$CH_{\beta,\alpha}$ str.	2992	0.00	0.00
ν_3	ring (C_β-C_β) str.	1582	0.00	0.00
ν_4	ring (C_α-C_β) str.	1452	0.00	0.00
ν_5	ring (C_9-C_{10}) str.	1333	0.00	0.00
ν_6	δCH_β	1182	0.00	0.00
ν_7	$\delta CH_{\alpha,\beta}$	1163	0.00	0.00
ν_8	ring (δCCC)	918	0.00	0.00
ν_9	ring (δCCC)	520	0.00	0.00
B_{1u}				
ν_{17}	CH_α str.	3005	11050.3	379.11
ν_{18}	CH_β str.	2976	743.7	25.3
ν_{19}	ring (C_α-C_β) str.	1536	2226.2	35.6
ν_{20}	ring (CCC str.) + δCH_β	1404	53.9	0.71
ν_{21}	δCH_α	1191	8.17	0.10
ν_{22}	δCH_β + ring (δCCC)	1073	3.58	0.04
ν_{23}	ring (δCCC)	783	12.87	0.09
ν_{24}	ring (δCCC)	385	185.89	0.66
B_{2u}				
ν_{29}	$CH_{\alpha\&\beta}$ str.	3010	7204.95	247.5
ν_{30}	$CH_{\beta\&\alpha}$ str.	2988	7295.8	248.85
ν_{31}	ring (CC str.)	1527	6476.2	102.98
ν_{32}	ring (CCC str.)	1350	2020.5	27.28
ν_{33}	ring (CCC str.)	1299	3590.1	46.62
ν_{34}	δCH_β	1177	173.24	1.92
ν_{35}	δCH_α	1162	99.04	1.09
ν_{36}	ring (δCCC)	607	487.9	2.74
B_{3g}				
ν_{37}	CH_α str.	3000	0.00	0.00
ν_{38}	CH_β str.	2972	0.00	0.00
ν_{39}	ring (CCC str.)	1467	0.00	0.00
ν_{40}	δCH_α + ring (CCC)	1202	0.00	0.00
ν_{41}	δCH_β + ring(δC_9-C_{10}	1151	0.00	0.00
ν_{42}	$\delta CH_{\alpha,\beta}$ + ring (δCCC)	1060	0.00	0.00
ν_{43}	ring (δCCC)	799	0.00	0.00
ν_{44}	ring (δCCC)	505	0.00	0.00
Out of-plane				
B_{1g}				
ν_{14}	γCH_β	829	0.00	0.00
ν_{15}	γCH_α	728	0.00	0.00
ν_{16}	γCC + γCH_α	342	0.00	0.00
B_{2g}				
ν_{25}	γCH_β	924	0.00	0.00
ν_{26}	$\gamma(C_9$-$C_{10})$	729	0.00	0.00
ν_{27}	γCH_α + $\gamma(C_9$-$C_{10})$	702	0.00	0.00
ν_{28}	$\gamma(C_\alpha$-$C_\beta)$ + γCH_β	496	0.00	0.00
A_u				
ν_{10}	γCH_β	916	0.00	0.00
ν_{11}	γCH_α	719	0.00	0.00
ν_{12}	γCC + γCH_β	545	0.00	0.00
ν_{13}	$\gamma(C_\alpha$-$C_\beta)$ + $\gamma CH_{\alpha,\beta}$		0.00	0.00
B_{3u}				
ν_{45}	γCH_β + $\gamma(C_\beta$-$C_\beta)$	776	697.7	5.26
ν_{46}	γCH_α + γCC	694	1466.08	9.88
ν_{47}	$\gamma(C_9$-$C_{10})$ + γCH_α	504	781.06	3.55
ν_{48}	$\gamma CC_{(9-10)(\beta-\beta)}$ + γCH_β	191	35.18	0.06

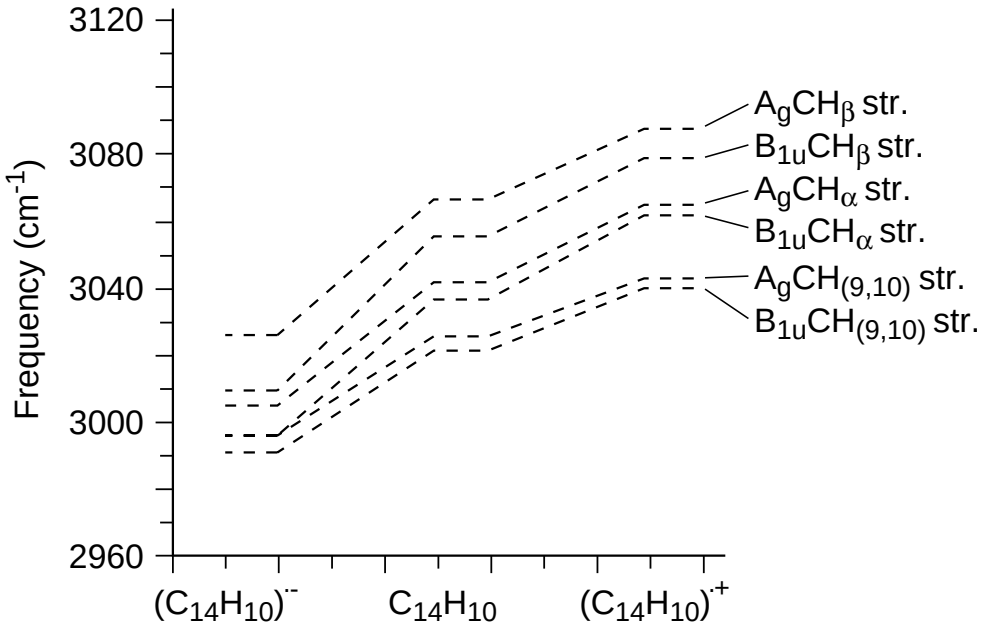

Fig. 5. Graphical representation for νCH str. of anthracene, radical anion, neutral molecule and radical cation.

which allowed a detailed analysis of the valence form of these modes too. No valence assignment was reported in former theoretical works. A comparison with the experimental frequencies could not be done for the

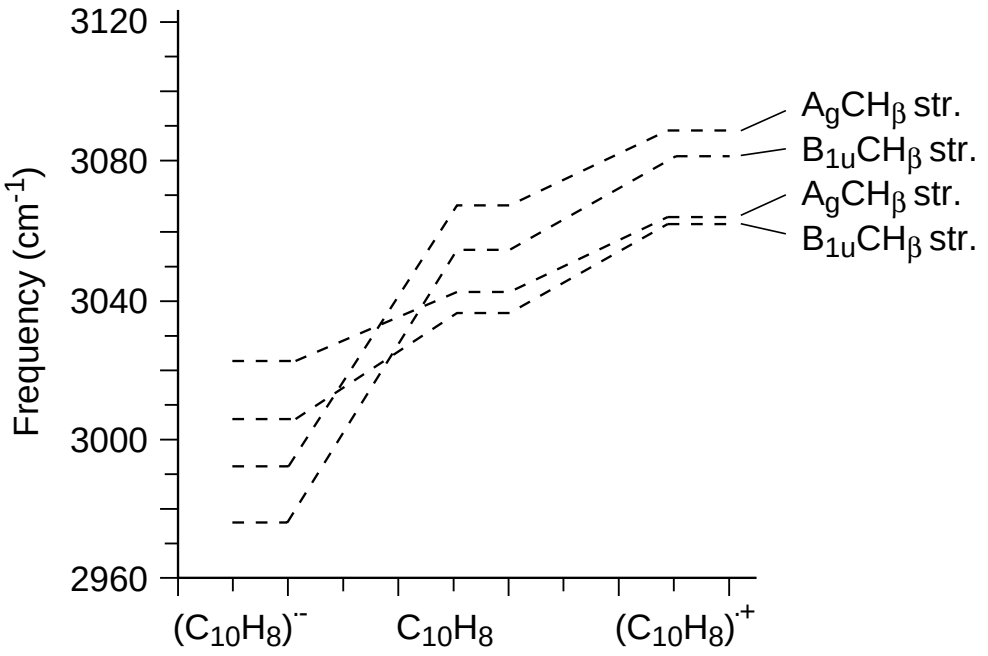

Fig. 6. Graphical representation for νCH str. of naphthalene, radical anion, neutral molecule and radical cation.

Table 6. Bond distances (Å) and angles (deg.) of the anthracene radical cation.

Atoms	This work calcd.	abinitio.[7]	DF.[21]	neutral molecule[19]
C_1-C_2	1.400	1.376	1.393	1.370
C_1-C_1'	1.439	1.403	1.417	1.463
C_1'-C_9	1.431	1.404	1.412	1.419
C_1-C_2'	1.484	1.423	1.442	1.473
C_2-C_3	1.414	1.397	1.408	1.442
C_1-H_1	1.105	1.072	–	1.107
C_2-H_2	1.104	1.071	–	1.105
C_9-H_9	1.108	1.073	–	1.109
$< C_1' C_1 C_2$	122.100	120.200	–	122.600
$< C_1 C_1' C_9$	124.700	121.700	–	124.700
$< C_1 C_1' C_2'$	117.700	119.200	–	117.300
$< C_2 C_1' C_9$	117.600	119.100	–	118.000
$< C_1 C_2 C_3$	120.200	120.500	–	120.000
$< C_1' C_9 C_4'$	124.800	121.800	–	124.700
$< H_1 C_1 C_1'$	118.600	119.500	–	118.000
$< H_2 C_2 C_1$	119.800	119.900	–	121.300
$< H_9 C_9 C_1'$	117.600	119.100	–	118.000

radical anion since no experimental values are known for it.

The valence assignment of the vibration frequencies for all three species of each molecule reveals interesting relations between their values:

The CH_β stretching frequency of the radical cations is always higher than that of the CH_α bonds. For naphthalene the following comparative relation holds:

$$\nu_{sym}(CH_\beta)^{\cdot+} \text{ str.} > \nu_{asym}(CH_\beta)^{\cdot+} \text{ str.} > \nu_{sym}(CH_\alpha)^{\cdot+} \text{ str.} > \nu_{asym}\ (CH_\alpha)^{\cdot+} \text{ str.}$$

And for the anion:

$$\nu_{sym}(CH_\alpha)^{\cdot-} \text{ str.} > \nu_{asym}(CH_\alpha)^{\cdot-} \text{ str.} > \nu_{sym}(CH_\beta)^{\cdot-} \text{ str.} > \nu_{asym}(CH_\beta)^{\cdot+} \text{ str.}$$

For the two anthracene radical ions:

$$\nu_{sym}(CH_\beta) \text{ str.} > \nu_{asym}(CH_\beta) \text{ str.} > \nu_{sym}(CH_\alpha) \text{ str.} > \nu_{asym}(CH_\alpha) \text{ str.}$$

For the C-C streching vibrations, the sequence for the naphthalene radical cation und anion is found as

$$\nu_{sym} \text{ ring}(C_\beta\text{-}C_\beta) \text{ str.} > \nu_{asym} \text{ ring}(C_\alpha\text{-}C_\beta) \text{ str.} > \nu_{sym} \text{ ring}(C_\alpha\text{-}C_\beta) \text{ str.} > \nu_{sym} \text{ ring}(C_9\text{-}C_{10}) \text{ str.}$$

In the case of the anthracene ions, however, the highest frequency belongs to that of the C_α-C_β bond:

$$\nu_{asym} \text{ ring}(C_\alpha\text{-}C_\beta) \text{ str.} > \nu_{asym} \text{ ring}(C_\beta\text{-}C_\beta) \text{ str.} > \nu_{asym} \text{ ring } (CC_{m.b.}).$$

The in plane CH deformation frequencies of the naphthalene cation and anion follow the order

Table 7. Calculated vibration frequencies and normal modes of anthracene radical anion.

Symmetry and description	This work scaled	Frequency cm^{-1} Others calcd.[5]	Others scaled[9]	Others exptl.[5b,17]
In-plane				
A_g				
ν_1 CH_β str.	3087	3083	–	–
ν_2 CH_α str.	3064	3059	–	–
ν_3 $CH_{(9,10)}$ str.	3042	3049	–	–
ν_4 Ring (CC str.)$_{(\beta-\beta),(m.bs.)}$	1538	1584	–	–
ν_5 Ring (CCC str.)	1543	1537	–	–
ν_6 Ring (CC str.)	1327	1331	–	–
ν_7 Ring (CCC str.)+δCH_α	1421	1247	–	–
ν_8 δCH_β	1161	1211	–	–
ν_9 $\delta CH_{\alpha,\beta}$ + ring (C_β-C_β) str.	1094	1033	–	–
ν_{10} Ring (δCCC)	886	758	–	–
ν_{11} Ring (δCCC)	614	622	–	–
ν_{12} Ring (δCCC)	416	381	–	–
B_{1u}				
ν_{22} CH_β str.	3078	3071	3085	–
ν_{23} CH_α str.	3061	3055	3069	–
ν_{24} $CH_{(9,10)}$ str.	3039	3033	3059	–
ν_{25} Ring (CC str.)	1573(−1%)	1585	1581	1586
ν_{26} Ring (CCC str.)	1483(+2%)	1495	1492	1457
ν_{27} Ring (CCC str.)	1267(−2%)	1334	1331	1291
ν_{28} $\delta CH_{\alpha,\beta}$	1241(−4%)	1265	1234	1290
ν_{29} $\delta CH_{\beta,\alpha}$	1155	1148	1121	–
ν_{30} Ring (δCCCC)	841	907	894	–
ν_{31} Ring (δCCCC)	656	643	634	–
ν_{32} Ring (δCCCC)	246	224	221	–
B_{2u}				
ν_{39} CH_β str.	3087	3038	3097	–
ν_{40} CH_α str.	3063	3058	3071	–
ν_{41} Ring (CC str.)	1527(+1%)	1559	1556	1540
ν_{42} Ring (CCC str.)	1415(−1%)	1511	1508	1418
ν_{43} Ring (CC str.)	1323	1354	1322	1341
ν_{44} Ring (CC str.) + $\delta CH_{(9,10)}$	1284	1237	1207	–
ν_{45} $\delta CH_{(9,10)}$ + ring (CCC str.)	1168(−2%)	1189	1161	1188
ν_{46} $\delta CH_{\beta,\alpha}$	1160(−2%)	1144	1142	1183
ν_{47} $\delta CH_{\alpha,\beta}$ + ring (CC str.)	1090(+5%)	1034	1031	1034
ν_{48} Ring (δCCC) + $\delta CH_{(9,10)}$	930	818	861	–
ν_{49} Ring (δCCC)	593	612	603	–
B_{3g}				
ν_{50} CH_β str.	3087	3071	–	–
ν_{51} CH_α str.	3061	3055	–	–
ν_{52} Ring (C_α-C_β str.)	1548	1576	–	–
ν_{53} Ring (δCCC)	1344	1452	–	–
ν_{54} Ring (CCC str.) + $\delta CH_{(9,10)}$	1411	1437	–	–
ν_{55} $\delta CH_{(9,10,\alpha)}$	1267	1294	–	–
ν_{56} $\delta CH_{(9,10,\alpha)}$ + ring (δCCC)	1129	1203	–	–
ν_{57} δCH_β	1148	1105	–	–
ν_{58} Ring (δCCC)	857	919	–	–
ν_{59} Ring (δCCC)	508	515	–	–
ν_{60} Ring (δCCC)	385	382	–	–
Out of-plane				
B_{1g}				
ν_{18} $\gamma CH_{\alpha,\beta}$	977	987	–	–
ν_{19} $\gamma CH_{\beta,\alpha}$	800	759	–	–
ν_{20} $\gamma CC_{(m.bs.)} + \gamma CH_\alpha$	480	468	–	–
ν_{21} $\gamma CC_{(m.bs.)} + \gamma CH_\beta$	226	220	–	–
B_{2g}				
ν_{33} γCH_β	982	1029	–	–
ν_{34} $\gamma CH_{(9,10)} + \gamma CC_{(m.bs.)}$	896	947	–	–
ν_{35} $\gamma CH_{(9,10,\alpha)} + \gamma CC$	823	858	–	–
ν_{36} $\gamma CH_{(m.bs.)} + \gamma CH_{(9,10)}$	760	737	–	–
ν_{37} $\gamma CC_\beta + \gamma CH_\beta$)	525	568	–	–
ν_{38} γ(C_9-C_{10})+$\gamma CH_{(9,10)}$	254	274	–	–
A_u				
ν_{13} γCH_β	980	1028	–	–
ν_{14} γCH_α	930	887	–	–
ν_{15} $\gamma CC + \gamma CH_\alpha$	742	759	–	–
ν_{16} γ(C_β-C_β) + γCH_β	495	493	–	–
ν_{17} $\gamma CC_\alpha + \gamma CH_\alpha$	115	120	–	–
B_{3u}				
ν_{61} $\delta CH_{(\alpha,9,10,\beta)}$	987	995	979	–
ν_{62} $\gamma CH_{(9,10,\beta)}$	941(+3%)	920	905	912
ν_{63} $\gamma CH_{(\beta,\alpha)}$	782(+5%)	748	736	748
ν_{64} $\gamma CH_{(9,10)} + \gamma CC_{(m.bs.)}$	442(+2%)	443	435	432
ν_{65} $\gamma CC_{(9,10,\alpha)} + \gamma CH_{(9,10,\alpha)}$	370	383	376	–
ν_{66} $\gamma CC_{(\beta-\beta),(9-10)} + \gamma CH_\beta$	87	90	83	–
B_{3g}				
ν_{50} CH_β str.	3087	3071	–	–
ν_{51} CH_α str.	3061	3055	–	–
ν_{52} Ring (C_α-C_β str.)	1548	1576	–	–
ν_{53} Ring (δCCC)	1344	1452	–	–
ν_{54} Ring (CCC str.) + $\delta CH_{(9,10)}$	1411	1437	–	–
ν_{55} $\delta CH_{(9,10,\alpha)}$	1267	1294	–	–
ν_{56} $\delta CH_{(9,10,\alpha)}$ + ring (δCCC)	1129	1203	–	–
ν_{57} δCH_β	1148	1105	–	–
ν_{58} Ring (δCCC)	857	919	–	–
ν_{59} Ring (δCCC)	505	515	–	–
Out of-plane				
B_{1g}				
ν_{18} $\gamma CH_{\alpha,\beta}$	977	987	–	–
ν_{19} $\gamma CH_{\beta,\alpha}$	800	759	–	–
ν_{20} $\gamma CC_{(m.bs.)} + \gamma CH_\alpha$	480	468	–	–
ν_{21} $\gamma CC_{(m.bs.)} + \gamma CH_\beta$	226	220	–	–
B_{2g}				
ν_{33} γCH_β	982	1029	–	–
ν_{34} $\gamma CH_{(9,10)} + \gamma CC_{(m.bs.)}$	896	947	–	–
ν_{35} $\gamma CH_{(9,10,\alpha)} + \gamma CC$	823	858	–	–
ν_{36} $\gamma CC_{(m.bs.)} + \gamma CH_{(9,10)}$	760	737	–	–
ν_{37} $\gamma CC_\beta + \gamma CH_\beta$	525	568	–	–
ν_{38} γ(C_9-C_{10})+$\gamma CH_{(9,10)}$	254	274	–	–
A_u				
ν_{13} γCH_β	980	1028	–	–
ν_{14} γCH_α	930	887	–	–
ν_{15} γCC+γCH_α	742	759	–	–
ν_{16} γ(C_β-C_β) + γCH_β	495	493	–	–
ν_{17} $\gamma CC_\alpha + \gamma CH_\alpha$	115	120	–	–
B_{3u}				
ν_{61} $\delta CH_{(\alpha,9,10,\beta)}$	987	995	979	–
ν_{62} $\gamma CH_{(9,10,\beta)}$	941(+3%)	920	905	912
ν_{63} $\gamma CH_{(\beta,\alpha)}$	782(+5%)	748	736	748
ν_{64} $\gamma CH_{(9,10)} + \gamma CC_{(m.bs.)}$	442(+2%)	443	435	432
ν_{65} $\gamma CC_{(9,10,\alpha)} + \gamma CH_{(9,10,\alpha)}$	370	383	376	–
ν_{66} $\gamma CC_{(\beta-\beta),(9-10)} + \gamma CH_\beta$	87	90	83	–

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).

$$\nu_{\text{asym}}(\delta CH_\alpha) > \nu_{\text{sym}}(\delta CH_\beta) \quad \nu_{\text{asym}}(\delta CH_\beta) > \nu_{\text{sym}}(\delta CH_\alpha),$$

and the anthracene radical ions

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

Table 8. Calculated IR absorption intensities for the anthracene radical cation.

Symmetry and description	Intensity Integ. $I_i^{\cdot}$ cm^2/mol	Absorb. A_i calcd. [7, 17] km/mol	calcd. [21] km/mol		Symmetry and description	Intensity Integ. $I_i^{\cdot}$ cm^2/mol	Absorb. A_i calcd. [7, 17] km/mol	calcd. [21] km/mol	
In-plane					B_{3g}				
A_g					ν_{50} CH_β str.	0.00	0.00	0.00	0.00
ν_1 CH_β str.	0.00	0.00	0.00	0.00	ν_{51} CH_α str.	0.01	0.00	0.00	0.00
ν_2 CH_α str.	0.00	0.00	0.00	0.00	ν_{52} Ring (C_α-C_β str.)	0.00	0.00	0.00	0.00
ν_3 $CH_{(9,10)}$ str.	0.08	0.00	0.00	0.00	ν_{53} Ring (δCCC)	0.00	0.00	0.00	0.00
ν_4 Ring (CC str.)$_{(\beta-\beta),(\text{m.bs.})}$	0.00	0.00	0.00	0.00	ν_{54} Ring (CCC str.) + $\delta CH_{(9,10)}$	0.01	0.00	0.00	0.00
ν_5 Ring (CCC str.)	0.00	0.00	0.00	0.00	ν_{55} $\delta CH_{(9,10,\alpha)}$	0.00	0.00	0.00	0.00
ν_6 Ring (CC str.)	0.00	0.00	0.00	0.00	ν_{56} $\delta CH_{(9,10,\alpha)}$ + ring (δCCC)	0.00	0.00	0.00	0.00
ν_7 Ring (CCC str.)+δCH_α	0.00	0.00	0.00	0.00	ν_{57} δCH_β	0.00	0.00	0.00	0.00
ν_8 δCH_β	0.00	0.00	0.00	0.00	ν_{58} Ring (δCCC)	0.00	0.00	0.00	0.00
ν_9 $\delta CH_{\alpha,\beta}$ + ring(C_β-C_β) str.	0.01	0.00	0.00	0.00	ν_{59} Ring (δCCC)	0.00	0.00	0.00	0.00
ν_{10} Ring (δCCC)	0.00	0.00	0.00	0.00	ν_{60} Ring (δCCC)	0.00	0.00	0.00	0.00
ν_{11} Ring (δCCC)	0.00	0.00	0.00	0.00	**Out of-plane**				
ν_{12} Ring (δCCC)	0.00	0.00	0.00	0.00	B_{1g}				
B_{1u}					ν_{18} $\gamma CH_{\alpha,\beta}$	0.00	0.00	0.00	0.00
ν_{22} CH_β str.	942.57	33.12	0.00	–	ν_{19} $\gamma CH_{\beta,\alpha}$	0.00	0.00	0.00	0.00
ν_{23} CH_α str.	995.57	34.79	2.00	–	ν_{20} $\gamma CC_{(\text{m.bs.})} + \gamma CH_\alpha$	0.00	0.00	0.00	0.00
ν_{24} $CH_{(9,10)}$ str.	900.09	31.23	4.0	–	ν_{21} $\gamma CC_{(\text{m.bs.})} + \gamma CH_\beta$	0.00	0.00	0.00	0.00
ν_{25} Ring (CC str.)	2386.09	39.11	55.0	54.50	B_{2g}				
ν_{26} Ring (CCC str.)	22.41	0.33	21.0	21.00	ν_{33} γCH_β	0.00	0.00	0.00	0.00
ν_{27} Ring (CCC str.)	1413.56	17.91	11.0	16.40	ν_{34} $\gamma CH_{(9,10)} + \gamma CC_{(\text{m.bs.})}$	0.00	0.00	0.00	0.00
ν_{28} $\delta CH_{\alpha,\beta}$	128.86	1.51	11.0	12.10	ν_{35} $\gamma CH_{(9,10,\alpha)} + \gamma CC$	0.00	0.00	0.00	0.00
ν_{29} $\delta CH_{\beta,\alpha}$	312.89	3.41	0.00	–	ν_{36} γCC_β-$C_{(\text{m.bs.})} + \gamma CH_{(9,10)}$	0.00	0.00	0.00	0.00
ν_{30} Ring (δCCC)	19.27	0.15	2.00	–	ν_{37} $\gamma CC_\beta + \gamma CC_\beta$	0.00	0.00	0.00	0.00
ν_{31} Ring (δCCC)	2.09	0.01	2.00	–	ν_{38} γ(C_9-C_{10})+$\gamma CH_{(9,10)}$	0.00	0.00	0.00	0.00
ν_{32} Ring (δCCC)	21.85	0.05	1.00	–	A_u				
B_{2u}					ν_{13} γCH_β	0.00	0.00	0.00	0.00
ν_{39} CH_β str.	1076.97	37.95	4.00	–	ν_{14} γCH_α	0.00	0.00	0.00	0.00
ν_{40} CH_α str.	6.28	0.22	4.00	–	ν_{15} $\gamma CC + \gamma CH_\alpha$	0.00	0.00	0.00	0.00
ν_{41} Ring (CC str.)	12670.48	201.57	37.00	91.80	ν_{16} γ(C_β-C_β) + γCH_β	0.00	0.00	0.00	0.00
ν_{42} Ring (CCC str.)	15578.97	220.48	49.00	196.80	ν_{17} $\gamma CC_\alpha + \gamma CH_\alpha$	0.00	0.00	0.00	0.00
ν_{43} Ring (CC str.)	21244.30	292.8	56.00	267.40	B_{3u}				
ν_{44} Ring (CC str.) + $\delta CH_{(9,10)}$	2559.58	32.87	834.00	–	ν_{61} $\delta CH_{(\alpha,9,10,\beta)}$	38.18	0.34	10.00	4.70
ν_{45} $\delta CH_{(9,10)}$ + ring (CCC str.)	948.98	11.09	1196.00	156.10	ν_{62} $\gamma CH_{(9,10,\beta)}$	26.81	0.23	41.00	20.90
ν_{46} $\delta CH_{\beta,\alpha}$	65.47	0.72	2.00	0.04	ν_{63} $\gamma CH_{(\beta,\alpha)}$	928.93	6.54	147.00	68.40
ν_{47} $\delta CH_{\alpha,\beta}$ + ring (CC str.)	9.61	0.10	6.00	3.60	ν_{64} $\gamma CH_{(9,10)} + \gamma CC_{(\text{m.bs.})}$	1076.00	4.62	61.00	27.20
ν_{48} Ring (δCCC)+$\delta CH_{(9,10)}$	1107.26	10.30	1.00	2.50	ν_{65} $\gamma CC_{(9,10,\alpha)} + \gamma CH_{(9,10,\alpha)}$	110.06	0.37	4.00	–
ν_{49} Ring (δCCC)	257.19	1.41	0.00	–	ν_{66} $\gamma CC_{(\beta-\beta),(9-10)} + \gamma CH_\beta$	421.13	0.33	2.00	–

Table 9. Bond distances (Å) and angles (deg.) of anthracene radical anion.

Atoms	Calculated values for the Radical anion	Neutral molecule [30]
C_1-C_2	1.398	1.370
C_1-C_1	1.439	1.463
C_1-C_9	1.430	1.419
C_1-C_2	1.486	1.473
C_2-C_3	1.412	1.442
C_1-H_1	1.110	1.107
C_2-H_2	1.110	1.105
C_9-H_9	1.110	1.109
$< C_1\ C_1\ C_2$	122.800	122.600
$< C_1\ C_1\ C_9$	125.200	124.700
$< C_1\ C_1\ C_2$	117.300	117.300
$< C_2\ C_1\ C_9$	117.500	118.000
$< C_1\ C_2\ C_3$	119.900	120.000
$< C_1\ C_9\ C_4$	125.000	124.700
$< H_1\ C_1\ C_1$	118.900	118.000
$< H_2\ C_2\ C_1$	120.300	121.300
$< H_9\ C_9\ C_1$	117.500	118.000

The out of plane vibration frequencies of the naphthalene radical ions show $\gamma(CH_\beta)^{\cdot+} > \gamma(CH_\alpha)^{\cdot+}$.

Interionic Correlation

Of higher interest is the comparison of the frequencies of the three species radical cation, neutral molecule and radical anion. It is seen that generally the frequencies of the radical anions are nearer to those of the neutral molecules than those of the radical cations. This might be explained in terms of the following facts:

- The energy required for the formation of the radical cation is much higher than that for the radical anion. The calculated magnitude of $E_{\text{HOMO}} = -8.2$ eV of naphthalene is bigger than that of $E_{\text{LUMO}} = +0.47$ eV;
- The formed anion is expected to be the thermodynamically more stable than the corresponding radical cation. For this reason, the change in the valence binding energies of the bonds of the anion, relative to

Table 10. Calculated vibration frequencies and IR absorption intensities of anthracene radical anion.

Symmetry and description		Frequency Scaled cm^{-1}	Intensity Integ. Γ_i cm^2/mol	Intensity absorb. A_i km/mol
In-plane				
A_g				
ν_1	$CH_{(\beta,\alpha)}$ str.	3026	0.01	0.00
ν_2	$CH_{(9,10),\alpha\&\beta}$ str.	3005	0.00	0.00
ν_3	$CH_{(9,10),\alpha}$ str.	2996	0.00	0.00
ν_4	Ring (CCC str.)	1601	0.00	0.00
ν_5	Ring (CC str.)	1485	0.00	0.00
ν_6	Ring (CC str.)	1328	0.00	0.00
ν_7	Ring (CC str.)$_{(m.bs.),(\beta-\beta)}$	1293	0.00	0.00
ν_8	δCH_β	1173	0.00	0.00
ν_9	δCH_α	1169	0.00	0.00
ν_{10}	Ring (δCCC)	884	0.00	0.00
ν_{11}	Ring (δCCC)	620	0.00	0.00
ν_{12}	Ring (δCCC)	420	0.00	0.00
B_{1u}				
ν_{22}	$CH_{(\alpha,\beta)}$ str.	3009	12887.7	442.68
ν_{23}	$CH_{(9,10)}$ str.	2996	1057.2	36.20
ν_{24}	$CH_{(\beta,\alpha)}$ str.	2991	12.14	0.41
ν_{25}	Ring (C_α-C_β) str.	1589	1826.7	30.24
ν_{26}	Ring (CCC str.)	1497	0.12	0.00
ν_{27}	Ring (CCC str.) + δCH_β	1348	4.24	0.05
ν_{28}	δCH_α	1251	25.08	0.30
ν_{29}	$\delta CH_{(\beta,\alpha)}$	1162	127.1	1.39
ν_{30}	Ring (δCCC)	842	13.91	0.11
ν_{31}	Ring (δCCC)	661	9.84	0.06
ν_{32}	Ring (δCCC)	250	246.25	0.57
B_{2u}				
ν_{39}	CH_β str.	3022	11490.0	396.4
ν_{40}	$CH_{(\alpha,\beta)}$ str.	2999	3067.40	105.01
ν_{41}	Ring (CC str.)	1519	14282.2	225.94
ν_{42}	Ring (CCC str.)	1438	16877.7	242.7
ν_{43}	Ring ($CC_{(m.br.)}$ str.)+$\delta CH_{(9,10)}$	1379	23475.7	323.65
ν_{44}	Ring (C_α-C_β) str. + $\delta CH_{(9,10)}$	1277	1861.9	23.78
ν_{45}	$\delta CH_{(9,10)}$ + ring (CC str.)	1177	34.93	0.41
ν_{46}	$\delta CH_{(\beta,\alpha)}$	1172	105.1	1.16
ν_{47}	$\delta CH_{(\alpha,\beta)}$	1166	156.76	1.72
ν_{48}	Ring (δCCC) + $\delta CH_{(9,10)}$	932	2884.1	26.87
ν_{49}	Ring (δCCC)	599	67.05	0.37
B_{3g}				
ν_{50}	$CH_{(\alpha,\beta)}$ str.	3008	0.00	0.00
ν_{51}	$CH_{(\beta,\alpha)}$ str.	2990	0.00	0.00
ν_{52}	Ring (C_α-C_β) str.	1561	0.01	0.00
ν_{53}	Ring (δCCC)	1461	0.00	0.01
ν_{54}	Ring (CCC str.) + $\delta CH_{(9,10)}$	1344	0.02	0.00
ν_{55}	$\delta CH_{(9,10,\alpha)}$	1278	0.00	0.00
ν_{56}	$\delta CH_{(9,10,\alpha)}$ + ring (δCCC)	1121	0.00	0.00
ν_{57}	$\delta CH_{(\beta,\alpha)}$	1157	0.00	0.00
ν_{58}	Ring (δCCC)	836	0.00	0.00
ν_{59}	Ring (δCCC)	530	0.00	0.00
ν_{60}	Ring (δCCC)	398	0.00	0.00
Out of-plane				
B_{1g}				
ν_{18}	$\gamma CH_{(\alpha,\beta)}$	885	0.00	0.00
ν_{19}	$\gamma CH_{(\beta\&\alpha)}$	782	0.00	0.00
ν_{20}	$\gamma CC_{(m.bs.)} + \gamma CH_\alpha$	497	0.00	0.00
ν_{21}	$\gamma CC_{(m.bs.)} + \gamma CH_\beta$	257	0.00	0.00
B_{2g}				
ν_{33}	$\gamma CH_{(\beta,\alpha)} + \gamma CC$	867	0.00	0.00
ν_{34}	$\gamma CH_{(\alpha,\beta)} + \gamma CC_{(m.bs.)}$	778	0.00	0.00
ν_{35}	$\gamma CC + \gamma CH_{(9,10,\alpha)}$	790	0.00	0.00
ν_{36}	$\gamma CH_{(9,10)} + \gamma CC$	704	0.00	0.00
ν_{37}	γ(C_α-C_β) + γCH_β	541	0.00	0.00
ν_{38}	γ(C_9-C_{10}) + $\gamma CH_{(9,10)}$	256	0.00	0.00
A_u				
ν_{13}	γCH_β	935	0.00	0.00
ν_{14}	γCH_α	838	0.00	0.00
ν_{15}	$\gamma CC_{(m.bs.)}$	701	0.00	0.00
ν_{16}	γ(C_β-C_β) + γCH_β	522	0.00	0.00
ν_{17}	γ(C_α-C_β) + $\gamma CH_{(\alpha,\beta)}$	117	0.00	0.00
B_{3u}				
ν_{61}	$\gamma CH_{(\alpha\&\beta)} + \gamma CC$	821	387.77	3.09
ν_{62}	$\gamma CH_{(9,10,\beta,\alpha)}$	793	1152.37	8.23
ν_{63}	$\gamma CH_{(9,10,\alpha,\beta)} + \gamma CC$	694	455.40	3.07
ν_{64}	$\gamma CC_{(m.bs.)} + \gamma CH_{(9,10,\alpha)}$	503	751.76	3.41
ν_{65}	$\gamma CC_{(9,10,\alpha)} + \gamma CH_{(9,10,\alpha)}$	352	113.17	0.36
ν_{66}	$\gamma CC_{(\beta-\beta),(9-10)}$	95	33.12	0.03

the neutral molecule, is smaller than that of the radical cation.

Comparing the calculated frequencies for the three species of each molecule, the following relations are detected:

In-plane Vibrations

The CH stretching frequencies decrease on going from the radical cation to the radical anion. For naphthalene:

$\nu_{sym}(CH_\alpha)^{\cdot+}$ str. $> \nu_{sym}(CH_\alpha)$ str. $> \nu_{sym}(CH_\alpha)^{\cdot-}$ str.
$\nu_{sym}(CH_\beta)^{\cdot+}$ str. $> \nu_{sym}(CH_\beta)$ str. $> \nu_{sym}(CH_\beta)^{\cdot-}$ str.,

and similarly for anthracene:

$\nu_{sym}(CH_\alpha)^{\cdot+}$ str. $> \nu_{sym}(CH_\alpha)$ str. $> \nu_{sym}(CH_\alpha)^{\cdot-}$ str.
$\nu_{asym}(CH_\alpha)^{\cdot+}$ str. $> \nu_{asym}(CH_\alpha)$ str.
$> \nu_{sym}(CH_\alpha)^{\cdot-}$ str.
$\nu_{sym}(CH_\beta)^{\cdot+}$ str.$> \nu_{sym}(CH_\beta)$ str.
$> \nu_{sym}(CH_\beta)^{\cdot-}$ str.
$\nu_{asym}(CH_\beta)^{\cdot+}$ str. $> \nu_{asym}(CH_\beta)$ str.
$> \nu_{asym}\ (CH_\beta)^{\cdot-}$ str.
$\nu(CH_{(9,10)})^{\cdot+}$ str. $> \nu\ (CH_{(9,10)})$ str.
$> \nu\ (CH_{(9,10)})^{\cdot-}$ str.

The reason for this change is obviously the change in the C-H force constants for the bonds, caused by the change of the electric charge of the molecules. Figures 5 and 6 show schematically these changes in the vibration frequencies of the C-H bonds.

No uniformed change in the C-C stretching vibrations could be detected for the ions of both molecules. The succession order of the C-C stretching frequencies differs from than that of the C-H stretching vibrations, the neutral molecule showing in most cases the highest

C-C vibration frequency. The reason for that is the different bond orders of the different C-C bonds and thus the different changes in these bond orders, and consequently their force constants, on reduction or oxidation of the molecules. The change for the naphthalene molecule is viewed in the following scheme:

ν_{sym} (C_β-C_β)> ν_{sym}(C_β-C_β)$^{\cdot-}$ > ν_{sym}(C_β-C_β)$^{\cdot+}$
ν_{asym} (C_β-C_β)$^{\cdot+}$ > ν_{asym}(C_β-C_β)$^{\cdot-}$ > ν_{asym}(C_β-C_β)
ν_{sym} (C_9-C_{10})$^{\cdot+}$ > ν_{sym}(C_9-C_{10})$^{\cdot-}$ > ν_{sym}(C_9-C_{10})
ν_{asym} (C_α-C_β)> ν_{asym}(C_α-C_β)$^{\cdot-}$ > ν_{asym}(C_α-C_β)$^{\cdot+}$

as well as

ν_{sym} (CCC str.)> ν_{sym}(CCC str.)$^{\cdot-}$> ν_{sym}(CCC str.)$^{\cdot+}$
ν_{asym}(CCC str.) > ν_{asym}(CCC str.)$^{\cdot+}$
> ν_{asym}(CCC str.)$^{\cdot-}$,

and for the anthracene molecule

$\nu_{sym}CC_{m.b.} > \nu_{sym}\ CC^{\cdot+}_{m.b.} > \nu_{sym}CC^{\cdot-}_{m.b.}$
$\nu_{asym}(C_\alpha$-$C_\beta) > \nu_{asym}\ C_\alpha$-$C^{\cdot-}_\beta > \nu_{asym}\ C_\alpha$-$C^{\cdot+}_\beta$

Out-of-Plane Vibrations

For these vibrations, the sequence of change in frequencies depends on the position of the CH bond too. Different types of vibration frequency changes are found for both naphthalene and anthracene molecules. For naphthalene

$\gamma(CH_\alpha)> \gamma(CH_\alpha)^{\cdot+} > \gamma(CH_\alpha)^{\cdot-}$
$\gamma(CH_\beta)^{\cdot+} > \gamma(CH_\beta)> \gamma(CH_\beta)^{\cdot-}$,

and for the anthracene molecule and ions

$\gamma(CH_\alpha)^{\cdot+} > \gamma(CH_\alpha)> \gamma(CH_\alpha)^{\cdot-}$
and $\gamma(CH_\beta)^{\cdot+} > \gamma(CH_\beta)> \gamma(CH_\beta)^{\cdot-}$.

Finally, for the γCC vibrations the changes in the frequencies are found to be for naphthalene:

$\gamma(C_\beta$-$C_\beta)^{\cdot-} > \gamma\,(C_\beta$-$C_\beta)> \gamma(C_\beta$-$C_\beta)^{\cdot+}$,

and for anthracene:

$\gamma(C_9$-$C_{10})^{\cdot-} > \gamma\,(C_9$-$C_{10})> \gamma(C_9$-$C_{10})^{\cdot+}$,
$\gamma CC_{m.b.} > \gamma CC^{\cdot-}_{m.b.} > \gamma CC^{\cdot+}_{m.b.}$
$\gamma(C_\alpha$-$C_\beta)> \gamma(C_\alpha$-$C_\beta)^{\cdot-} > \gamma(C_\alpha$-$C_\beta)^{\cdot+}$
$\gamma(C_\beta$-$C_\beta)^{\cdot-} > \gamma(C_\beta$-$C_\beta)> \gamma(C_\beta$-$C_\beta)^{\cdot+}$.

Conclusion

Application of the semiempirical MINDO/3-FORCES SCF-MO method to the calculation of the vibration frequencies of the naphthalene and anthracene radical cations yield frequency values that are close to those of the corresponding experimental and abinitio frequencies. The so calculated frequencies for the radical cations are expected to be of similar "quality". For the cations the maximal percent deviation of the calculated from the experimental frequencies is +6%. The treatment allows a complete valence and symmetry assignment of all frequencies to their corresponding modes. The normal corrdinate analysis is greatly helped by the application of the DRAW.MOL program and the evaluation of the corresponding APP values. The treatment allows the estimation of the frequency changes in the molecules due to the change of the molecular charge. The C-H and C-C vibrations change in different manners on changing the molecular charge.

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