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Quantum Chemical Description of the Vibration Motion of Chrysene, Comparison Results of the MINDO/3-FORCES Method , ab initio and Density Functional (B3LYP)

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Abstract

Vibration frequencies and IR absorption intensities for the chrysene molecule in its calculated equilibrium structure were calculated quantum mechanically applying both the semiempirical MINDO/3-FORCES, the ab initio and density functional (B3LYP 6-311G) methods. The MINDO/3-FORCES frequency values were scaled applying scaling factors that had been evaluated formerly for naphthalene, anthracene and pyrene. Similarly the ab initio frequencies were scaled, and both treatments gave vibration motions of correct symmetries and sequence in frequency values. The calculated frequencies of MINDO/3-FORCES and scaled and ab initio methods, were close to the literature experimental frequencies. The (B3LYP 6-311G) treatment yielded frequency values that were very close to the experimental and MINDO/3-FORCES forces frequencies. Comparison of the results for different vibration modes showed a dependence of the vibration frequencies on the atomic site of the vibration. Thus the following relations were detected:

$\nu_{sym}(\text{CH str.})\beta\ (\uparrow\uparrow\ \downarrow\downarrow) > \nu_{asym}(\text{CH str.})\beta\ (\uparrow\uparrow\ \uparrow\uparrow) >$
$\nu_{asym}(\text{CH str.})\beta(\uparrow\downarrow\ \downarrow\uparrow) > \nu_{sym}(\text{CH str.})\beta(\uparrow\downarrow\ \uparrow\downarrow) >$
$\nu_{sym}(\text{CH str.})\ \overline{\alpha}\ , \overline{\overline{\alpha}}\ (\uparrow\uparrow\ \downarrow\downarrow) > \nu_{asym}(\text{CH str.})\ \overline{\alpha}\ , \overline{\overline{\alpha}}\ (\uparrow\uparrow\ \uparrow\uparrow) >$

$\nu_{asym}(\text{CH str.})\alpha > \nu_{sym}(\text{CH str.})\alpha > \nu_{asym}(\text{CH str.})\ \overset{\equiv}{\alpha} > \nu_{sym}(\text{CH str.})\overset{\equiv}{\alpha} >$
$\nu_{sym}(\text{CH str.})\ \overline{\alpha}\ , \overline{\overline{\alpha}}\ (\uparrow\downarrow\ \uparrow\downarrow) > \nu_{asym}(\text{CH str.})\ \overline{\alpha}\ , \overline{\overline{\alpha}}\ (\uparrow\downarrow\ \downarrow\uparrow)$
Generally the following relations hold;
$\nu\ (\text{CH str.})\beta > \nu\ (\text{CH str.})\alpha$ and

$\nu\ (\text{CH str.})\beta > \nu\ (\text{CH str.})\ \overline{\alpha}, \overline{\overline{\alpha}} > \nu\ (\text{CH str.})\alpha > \nu(\text{CH str.})\overset{\equiv}{\alpha}$

Similar relations were detected for other valance vibrations.

الخلاصة

أجريت حسابات ميكانيك الكم لترددات الاهتزاز وشدد امتصاص الاشعة تحت الحمراء لجزيئة الكرايسين العطرية عند شكلها الهندسي المتوازن والمحسوب وفق أسلوب MINDO/3-FORCES شبه التجريبي و أسلوب ab initio حيث اجريت المقايسة لقيم الترددات المحسوبة باستعمال ثوابت قيمت سابقاً للعديد من الجزيئات ألعطرية متعددة الحلقات المتعادلة منها و ذات الشحن الموجبة و السالبة ووفق أسلوب دوال الكثافة (B3LYP).
اعطت المعالجة ترددات صحيحة من حيث التماثل وتسلسل القيم وقريبة من القيم التجريبية المعروفة في الادبيات و متقاربة لكلتي الطريقتين، كما أعطت حسابات دوال الكثافة (B3LYP/ 6-311G) قيم ترددات اهتزاز قريبة جدا من القيم التجريبية وقيم MINDO/3-FORCES المقيسة. كما و بينت مقارنة قيم ترددات الاهتزاز للاواصر C-H و C-C المختلفة في الجريئة وجود علاقات مقارنة ثابتة بينها تظهر اعتماد القيم على الموقع التاصري للذرات في الجريئة كالعلاقة بين ترددات المط للاواصر C-H ذات المواقع المختلفة:

$\nu_{sym}(\text{CH str.})\beta\,(\uparrow\uparrow\ \downarrow\downarrow) > \nu_{asym}(\text{CH str.})\beta\,(\uparrow\uparrow\ \uparrow\uparrow) >$
$\nu_{asym}(\text{CH str.})\beta(\uparrow\downarrow\ \ \downarrow\uparrow) > \nu_{sym}(\text{CH str.})\beta(\uparrow\downarrow\ \ \uparrow\downarrow) >$
$\nu_{sym}(\text{CH str.})\ \overline{\alpha}\,,\ \overline{\overline{\alpha}}\,(\uparrow\uparrow\ \ \downarrow\downarrow) > \nu_{asym}(\text{CH str.})\ \overline{\alpha}\,,\ \overline{\overline{\alpha}}\,(\uparrow\uparrow\ \ \uparrow\uparrow) >$

$\nu_{asym}(\text{CH str.})\alpha > \nu_{sym}(\text{CH str.})\alpha > \nu_{asym}(\text{CH str.})\ \overset{\equiv}{\alpha} > \nu_{sym}(\text{CH str.})\ \overset{\equiv}{\alpha} >$
$\nu_{sym}(\text{CH str.})\ \overline{\alpha}\,,\ \overline{\overline{\alpha}}\ (\uparrow\downarrow\ \ \uparrow\downarrow) > \nu_{asym}(\text{CH str.})\ \overline{\alpha}\,,\ \overline{\overline{\alpha}}\,(\uparrow\downarrow\ \ \downarrow\uparrow)$

و تنطبق العلاقات الاتية عموما على نتائج الحساب :

$\nu\,(\text{CH str.})\beta > \nu\,(\text{CH str.})\alpha$

.

$\nu\,(\text{CH str.})\beta > \nu\,(\text{CH str.})\ \overline{\alpha}\,,\overline{\overline{\alpha}} > \nu\,(\text{CH str.})\alpha > \nu(\text{CH str.})\ \overset{\equiv}{\alpha}$

وكذلك الحال بالنسبة لباقي الحركات الاهتزازية

Introduction

Increasing interest in the vibration spectra of polyaromatic hydrocarbons (PAH's) was noticed in the recent years [1-4]. The studies were caused mainly by the assumed presence of these molecules in the interstellar spaces [1-4] as well as their properties as hazardous carcinogenic pollutants [5]. Chrysene is a prominent member of the PAH family. Its vibration spectrum was subject of study for many research groups [6-9]. An attempt to study its detailed IR spectrum was done by Garrigoulagrange et al. [6]. Later, Schrader et al. [7] studied its Raman spectrum, followed by the FT-IR study of Mamantov et al. [8]. In all these studies no detailed analysis of its vibrational motion could be obtained. In some of them the efforts were concentrated at the IR bands with the highest absorption intensity. The complete valance type normal coordinates analysis of chrysene was attempted firstly by Cyvin et al. [9], who applied both Raman and IR spectroscopic measurements as well as the valance force field calculation for this purpose. As much as we could find in the literature, no complete valane type normal coordinate analysis based on quantum mechanical treatment had been done for chrycene molecule before [10], and consequently no comparative study for the different C-H or C-C exsist. For this reason we found it necessary to study the problem applying a quantum mechanical method. Our method of choice in treating such problems had been the MINDO/3-FORCES method [11-14]. It was applied successfully for the vibration analysis of various polyaromatic hydrocarbon (PAH) molecules [15]. In these treatments the Wilson's secular equation (1) for the vibration frequencies was applied [16];

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

Where Fij is the element of the cartesian force constant matrix.
Mij is the reduced mass matrix element.
λ is the vibration eigenvalue of the secular equation (1).

The eigenvector coefficients L_j are used in our treatment to calculate the "atomic displacement vectors", R_k according to the following equation;

$$R_k^A = \sqrt{(L_{ik})_x^2\, X_i^2 + (L_{ik})_y^2\, Y_i^2 + (L_{ik})_z^2\, Z_i^2} \quad .(2)$$

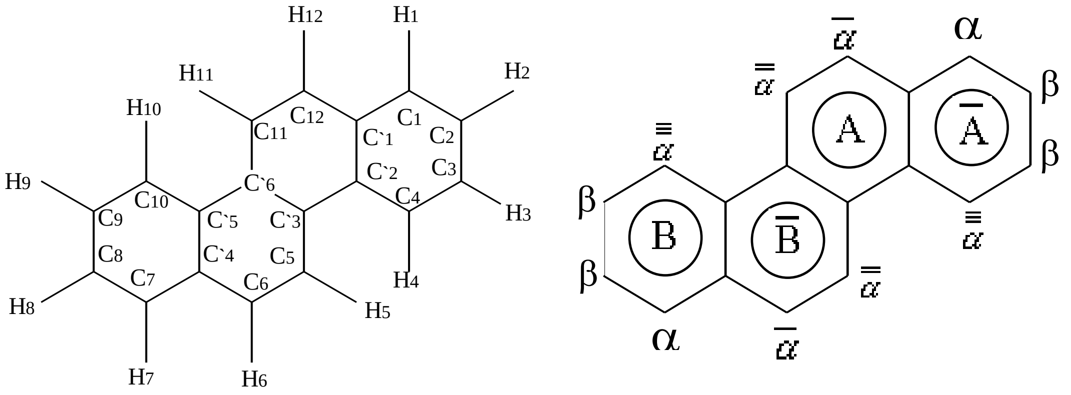
Where R_k^A is the atomic displacement vector and X_i, Y_i, and Z_i are the cartesian unit vectors of atom i. These vectors are drawn graphically then, applying the DRAW.MOL routine [13b] for all atoms and all vibration modes.

Useful for the assignment of the vibration modes has been the definition of the partial participation value ($PPA_{i,k}$) for the atom i at the vibration mode k, which defines the participation of each atom in any of the vibration modes [13,14].

The other method that was applied in this study is the ab initio method [17], for which we utilized the Gaussian computer program [18] of Pople et al. In the present calculations the 6-311G basis was chosen for the treatment.

Results and discussion.

Chrysene is a planar molecule of C_{2h} symmetry, Fig.1. It has (3N-6=84) modes of vibration. According to the group theoretical treatment, these modes are classified in to the following irreducible representations; in-plane ($29A_g$ and $28B_u$) and out of plane ($14A_u$ and $13B_g$). According to the same character table, the modes A_g and B_g should be IR inactive (Raman active), while A_u and B_u should be IR active (Raman inactive). The structure of chrysene molecule is shown in fig. 1.



(a) (b)

Fig. 1. Structure of chrysene molecule showing; a- the numbering of the atoms according to the IUPAC convention; b- the different designations of the C and H atoms as applied in the present study.

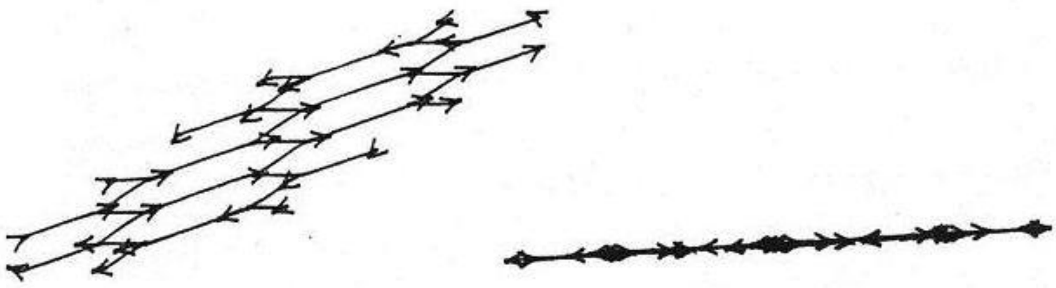
The vibration frequencies were calculated for chrysene at its equilibrium geometry, which resulted from the MINDO/3-FORCES and ab initio treatment, varying all its 3N cartesian coordinates, Table 1.

Table (1): Calculated geometry for chrysene molecule.

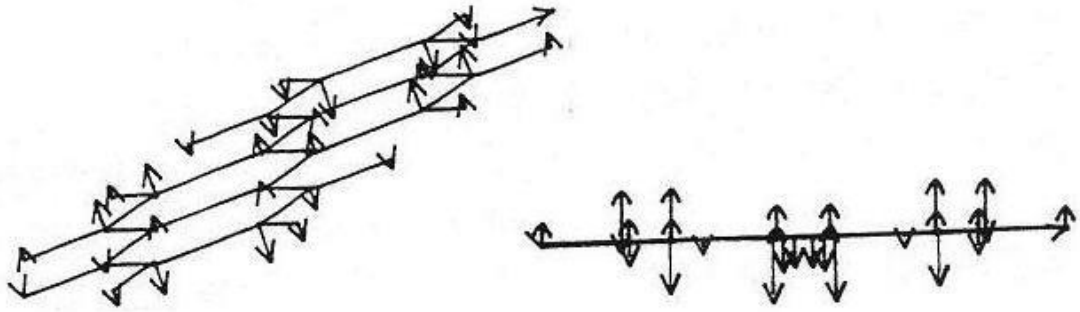
Bond/Angle Å/ deg.	**Mindo/3-FORCES calcd.**	**ab initio calcd.**	**B3LYP**	**Force Field calcd.** [8]	**(9) expt.**
$C_1 C_2$	1.384	1.401	1.366	1.379	1.379
$C_1 C`_1$	1.442	1.401	1.413	1.422	1.427
$C_2 C_3$	1.422	1.401	1.406	1.412	1.392
$C_3 C_4$	1.385	1.401	1.368	1.383	1.379
$C_4 C`_2$	1.446	1.401	1.416	1.425	1.405
$C_{11} C`_6$	1.459	1.401	1.433	1.439	1.423
$C_{11} C_{12}$	1.366	1.401	1.347	1.366	1.365
$C`_1 C`_2$	1.456	1.401	1.408	1.411	1.406
$C_1 C_{12}$	1.454	1.401	1.348	1.434	1.418
$C`_2 C`_3$	1.486	1.401	1.452	1.455	1.465
$C`_3 C`_6$	1.442	1.401	1.396	1.406	1.397
$H_1 C_1$	1.107	1.107	1.074	-------	-------
$H_2 C_2$	1.105	1.107	1.073	-------	-------
$H_3 C_3$	1.105	1.107	1.073	-------	-------
$H_4 C_4$	1.107	1.107	1.070	-------	-------
$H_{11} C_{11}$	1.107	1.107	1.070	-------	-------
$H_{12} C_{12}$	1.107	1.107	1.074	-------	-------
$< C_1 C_2 C_3$	119.340	120	119.481	-------	-------
$< C_2 C_3 C_4$	120.000	120	120.510	-------	-------
$< C_3 C_4 C`_2$	123.367	120	121.384	-------	-------
$< C`_6 C_{11} C_{12}$	123.367	120	121.601	-------	-------
$< C_{11} C_{12} C`_1$	122.000	120	121.029	-------	-------
$< C_1 C`_1 C_{12}$	123.367	120	120.826	-------	-------
$< C_{12} C`_1 C`_2$	117.400	120	119.147	-------	-------
$< C`_1 C`_2 C_4$	116.104	120	117.660	-------	-------
$< C_4 C`_2 C`_3$	124.750	120	123.090	-------	-------
$< C`_3 C`_6 C_{11}$	116.743	120	118.776	-------	-------
$< C`_5 C`_6 C_{11}$	122.683	120	121.208	-------	-------
$< H_1 C_1 C_2$	118.000	120	120.412	-------	-------
$< H_1 C_1 C`_1$	119.340	120	118.649	-------	-------
$< H_2 C_2 C_3$	120.664	120	119.974	-------	-------
$< H_6 C_6 C_5$	119.340	120	120.257	-------	-------
$< H_3 C_3 C_2$	119.340	120	119.696	-------	-------
$< H_4 C_4 C_3$	117.400	120	118.326	-------	-------
$< H_{11} C_{11} C_6$	118.685	120	119.721	-------	-------
$< H_{12} C_{12} C_{11}$	119.340	120	120.257	-------	-------

Inspecting the calculated values for both methods, one finds that in both cases, and almost equally, good agreements with the experimental data detected for the majority of the geometric parameters. However apparent deviations are detected for other, but different geometric parameters. As for the MINDO/3-FORCES treatment the deviations from the experiment are obvious for the following C-C bonds; $C_1 – C_2$, $C_4 – C_{2}^{\backprime}$, $C_{1}^{\backprime}$- $C_{2}^{\backprime}$ and $C_{4}^{\backprime}$- $C_{6}^{\backprime}$; where as for the ab initio calculation the deviations are noticed for the following bonds; C_1- C_2, C_1- $C_{1}^{\backprime}$, C_3-C_4, C_{11}-$C_{6}^{\backprime}$, C_{11}-C_{12}.

The MINDO/3-FORCES energy calculation was stopped after reaching a minimal gradiant value of 10^{-5} au/au. Having evaluated the (3Nx3N) cartesian force constant matrix, it was introduced to the Wilson's equation (1). The solution of the equation yield the vibration frequency values and eigenvector coefficients L_{ik} for all atoms. Fig. 2 shows the picture of two such vibration modes, in-plane and out of plane, as plotted by the DRAW. MOL routine.



In–plane



Out of–plane

Fig 2. DRAW. MOL graphical picture for two vibration modes of chrysene, at different projection angles. The figure shows clearly the planarity of the molecule.

Table 2 includes the calculated (3N-6) vibration frequencies for the molecule, Table 3 includes the corresponding IR absorption intensities.

Table (2): Calculated vibration frequencies for chrysene molecule.

Symmetry And discription		Frequency cm^{-1}				
		ab initio	Mindo/3- Forces	Gaussian 6-311G	Force field	exptl. [9] IR & Raman
		scaled	scaled	B3LYP	calc. [9]	
	In-plane					
$A_g{}^*$						
v_1	CHβ str.	3052	3065	3070	3040	3061
v_2	CHα str.	3026	3053	3055	3037	3045
v_3	CH $\overline{\beta}$, $\overline{\overline{\alpha}}$ str.	3011	3046	3045	3035	3038
v_4	CHα str.	2993	3038	3028	3032	3025
v_5	CH str. $\overset{\equiv}{\alpha}$	2988	3033	3025	3031	3025
v_6	CH $\overline{\beta}$, $\overline{\overline{\alpha}}$ str.	2982	3029	3017	3030	2997
v_7	ring (CC str.) $\overset{\equiv}{\alpha}$ $\overline{\beta}$ -	1642	1653	1619	1685	1627
v_8	ring (CC str.) β, $\overset{\equiv}{\alpha}$	1613	1640	1615	1639	1619
v_9	ring (CCC str.)	1614	1616	1565	1596	1603
v_{10}	ring (CCC str.)	1552	1577	1543	1566	1576
v_{11}	ring (CCC str.)	1487	1486	1498	1550	1560
v_{12}	ring (CCC str.)	1466	1445	1479	1471	1454
v_{13}	ring (CCC str.)	1400	1401	1371	1465	1434
v_{14}	ring (CCC str.)	1373	1331	1348	1445	1382
v_{15}	ring (CCC str.)	1325	1290	1323	1348	1364
v_{16}	δCH $\overset{\equiv}{\alpha}$	1268	1271	1285	1238	1254
v_{17}	δCH α, $\overset{\equiv}{\alpha}$	1208	1247	1235	1178	1230
v_{18}	δCH $\overline{\beta}$, $\overline{\overline{\alpha}}$	1200	1196	1218	1151	1143
v_{19}	δCH $\overline{\beta}$, $\overline{\overline{\alpha}}$	1175	1184	1213	1098	1136
v_{20}	δCH α, $\overset{\equiv}{\alpha}$	1144	1166	1167	1064	1087
v_{21}	δCH α, β + ring (CCC str.)	1045	1097	1055	999	1043
v_{22}	ring (δCCC) + δCH	1010	1037	1017	902	1019
v_{23}	ring (δCCC)	878	864	890	838	880
v_{24}	ring (δCCC)	770	828	780	737	770
v_{25}	ring (δCCC) (ring elongation A & $\overline{A}$)	591	708	693	667	680
v_{26}	ring (δCCC) (ring elongation A & $\overline{A}$)	570	584	581	563	570
v_{27}	ring (δCCC) (anticlock.bend., ring B & $\overline{B}$)	481	486	489	445	481
v_{28}	ring (δCCC) (clock. bend. ring A & $\overline{A}$)	378	394	395	353	382
v_{29}	ring (δCCC) (anticlock bend. ring A & $\overline{A}$)	288	301	293	254	293

Table (2): (contd.1) chrysene molecule.

B_u^{**}						
v_{57}	CHβ str.	3052	3065	3069.6	3040	3063
v_{58}	CHβ str.	3026	3053	3056	3037	3053
v_{59}	CH $\overline{\text{ꭓo}}$, $\overline{\overline{\alpha}}$ str.	3011	3045	3044	4036	3067
v_{60}	CHα str.	2994	3038	3030	3032	3054
v_{61}	CH $\overline{\overline{\alpha}}$, $\overset{\equiv}{\alpha}$ str.	2987	3033	3024	3031	3014
v_{62}	CH $\overline{\text{ꭓo}}$, $\overline{\overline{\alpha}}$ str.	2982	3028	3017	3030	2996
v_{63}	ring (CC str.) β- $\overset{\equiv}{\alpha}$	1614	1645	1620	1649	1625
v_{64}	ring (CC str.) $\overline{\overline{\alpha}}$ $\overline{\text{ꭓo}}$ -	1605	1624	1604	1616	1618
v_{65}	ring (CC str.)	1517	1532	1540	1605	1514
v_{66}	ring (CC str.) ring B, $\overline{\mathrm{B}}$	1480	1478	1512	1535	1485
v_{67}	ring (CCC str.)	1466	1435	1474	1513	1434
v_{68}	ring (CCC str.)	1454	1401	1455	1489	1405
v_{69}	ring (CCC str.)	1351	1376	1335	1468	1360
v_{70}	ring (CCC str.) + δCH $\overline{\text{ꭓo}}$	1310	1303	1329	1323	1344
v_{71}	δCH $\overline{\text{ꭓo}}$	1267	1259	1281	1250	1299
v_{72}	δCH $\overline{\text{ꭓo}}$	1240	1257	1254	1182	1264
v_{73}	ring (CCC str.) + δCH	1207	1207	1234	1153	1259
v_{74}	δCH $\overline{\text{ꭓo}}$	1169	1183	1192	1131	1232
v_{75}	δCHβ, α	1118	1166	1157	1054	1143
v_{76}	δCH + ring (CC str.)	1068	1093	1087	1030	1080
v_{77}	δCH + ring (CC str.)	1017	1067	1036	903	1019
v_{78}	ring (δCCC)	1067	989	887	857	869
v_{79}	ring (δCCC)	852	828	861	815	813
v_{80}	ring (δCCC)	685	706	699	687	760
v_{81}	ring (δCCC)	492	570	582	547	532
v_{82}	ring (δCCC) (clock. bend. ring B, anticlock. bend. ring $\overline{\mathrm{B}}$)	422	544	550	469	476
v_{83}	ring (δCCC)	479	495	500	466	422
v_{84}	ring (δCCC) (clock. bend. ring A, anticlock. bend. ring $\overline{\mathrm{A}}$)	184	183	206	139	189
Out of–plane						
A_u^{**}						
v_{30}	γCHβ	1003	969	1062	999	1150
v_{31}	γCH $\overline{\text{ꭓo}}$	980	965	1033	990	------
v_{32}	γCHα, $\overset{\equiv}{\alpha}$, β	961	952	1025	966	943
v_{33}	γCHα, $\overline{\overline{\alpha}}$	871	916	940	894	884
v_{34}	γCH $\overline{\text{ꭓo}}$	810	878	897	863	852
v_{35}	γCH + γCC	757	757	845	780	771
v_{36}	γCC (puck.) + γCH	723	726	779	715	744
v_{37}	γCC (puck.) + γCH	561	614	626	558	554

Table (2): (contd.2) chrysene molecule.

ν_{38}	γCC (puck.) + γCH	542	549	596	524	532
ν_{39}	γCCC (puck.) + γCH	410	448	475	412	415
ν_{40}	γCCC (puck.)	279	295	324	306	292
ν_{41}	γCC (puck.) + γCH	260	244	280	252	246
ν_{42}	γCC (puck.) + γCH	73	77	138	123	135
ν_{43}	γCC (puck.) + γCH	47	48	92	70	60
B_g^*						
ν_{44}	γCH	1003	969	1061	999	989
ν_{45}	γCH	989	964	1044	987	965
ν_{46}	γCH	959	950	1018	968	948
ν_{47}	γCH	876	915	945	888	861
ν_{48}	γCH	837	840	893	868	831
ν_{49}	γCC (puck.) + γCH	774	823	837	788	805
ν_{50}	γCH	732	793	826	763	746
ν_{51}	γCC (puck.) + γCH	660	675	709	661	712
ν_{52}	γCC (puck.) + γCH	500	537	560	509	513
ν_{53}	γCC (puck.) + γCH	464	501	518	452	408
ν_{54}	γCC (puck.) + γCH	373	393	424	399	390
ν_{55}	γCC (puck.) + γCH	167	180	217	219	197
ν_{56}	γCC (puck.) + γCH	129	138	181	188	179

γ: out of plane bending vibration.
δ in- plane bending vibration.
*: IR inactive (Raman active).
**: IR active (Raman inactive).

Scaling factors for MINDO/3-F [19, 21]: 0.876 (CH str.); 0.96 (ring (CC) str.); 1.06 (δCH); 1.08 (ring (δCCC); 1.11 (γCH) or (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).

Scaling factors for ab initio: 0.89 (CH str.) or (ring (CC) str.); 0.91 ring (CCC) str.; 0.9 (δCH) or (ring (δCCC); 1.11 (γCH); 0.85 (γCCC) or (γCC).

No scaling factors for B3LYP calculations.

Table 3 includes the ranges of calculated frequencies of chrysene calculated with the three prominent methods, and classified according to the valance modes of vibrations. Remarkable is that for all three different methods the calculated frequencies are close to the experimental values. It should be noticed however that, for the ab initio results scaled frequencies are considered rather than the unscaled, which on their turn show large deviations from the experiment, as might be viewed from the frequency values of Table 2.

Table 3. Ranges of calculated frequencies of vibration of chrysene calculated with the MINDO/3-FORCES, abinitio and Force Field methods.

Description	Calculated frequency cm^{-1}		Experimental frequency cm^{-1}	
	MINDO/3-FORCES	ab initio	Force Field (8)	IR&Raman (9)
C-H str.	3065– 3028	3052– 2982	3040 – 3030	3061 – 2996
C-C str.	1653 – 1478	1662– 1480	1685 – 1485	1627 – 1434
CCC str.	1616 – 1290	1614 – 1325	1596 – 1348	1603 – 1364
δCH	1271 – 1067	1268– 1017	1238 – 977	1254 – 1019
δCCC	1037 – 183	1010– 184	902 – 139	1019 – 189
γCH	969 – 757	1003 – 757	999 – 780	1050 – 771
γCC	726 – 48	723 – 47	715 – 70	744 – 60

The close values of the three methods might be viewed in the list of their percent deviations from the corresponding experimental frequencies. For all the three methods close percent deviation values are noticed. For all three methods the smallest percent deviations are calculated for the $C\text{-}H_{str.}$ Vibrations (0.11 – 1.13%), the biggest for the out of plane γCC vibration (2.42 – 21.00%). Percent deviation values for other vibration modes fall within similar range for all three methods.

Table 4. percent deviations of the calculated vibration frequencies applying the three different methods from the corresponding experimental frequencies.

Description	**Percent deviation**		
	MINDO/3-FORCES (scaled)	**ab initio (scaled)**	**Force Field**
C-H str.	0.130 – 0.106	0.294 – 0.467	0.686 – 1.134
C-C str.	1.598 – 3.068	2.150 – 3.200	2.335 – 3.419
CCC str.	0.810 – 5.425	0.686 – 2.800	0.436 – 2.943
δCH	1.355 – 4.715	1.116 – 0.196	1.276 – 2.355
δCCC	1.766 – 3.714	0.883 – 2.640	1.668 – 3.597
γCH	2.020 – 1.815	1.415 – 1.815	1.011 – 6.355
γCC	2.420 – 20.00	2.822 – 21.00	3.897 – 16.00

Fig (3) shows the graphical pictures of some vibration modes as drawn through the DRAW. MOL. routine.

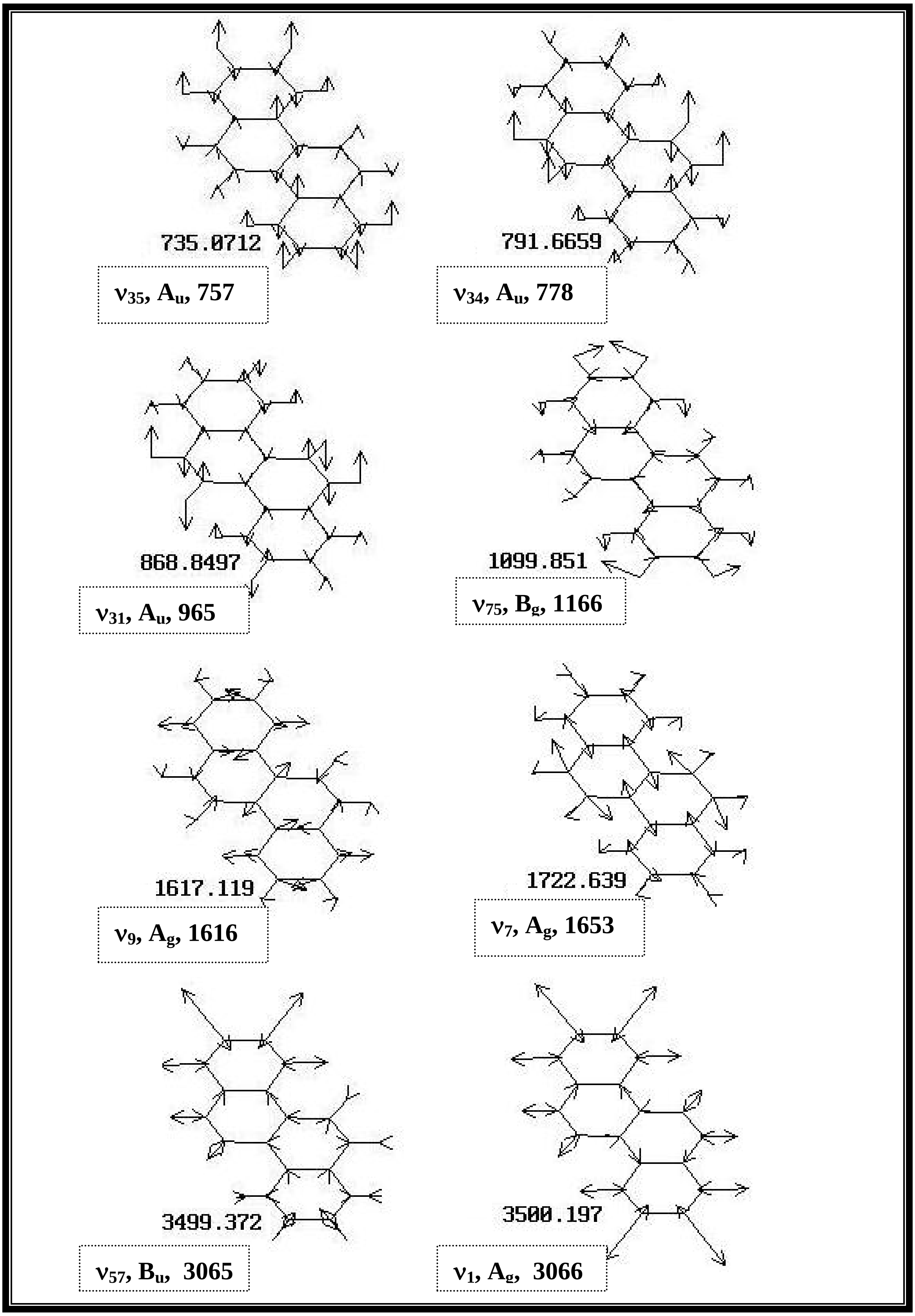


Fig.3 Graphical pictures of some vibration modes of chrysene as drawn through the DRAW. MOL. routine.

Table (5): Calculated IR absorption intensities for chrysene molecule.

Symmetry and description		intensity			
		this work			exptl.
		integd. Γ_i	absorb. A_i	calcd.[8]	Relative [9]
In–plane		cm^2/mol	km/mol	cm^2/mol	intensity
A_g^*					
v_1	CH s. str.	0.00	0.00	0.00	w
v_2	CH s. str.	0.00	0.00	0.00	m
v_3	CH s. str.	0.00	0.00	0.00	w
v_4	CH s. str.	0.00	0.00	0.00	w
v_5	CH s. str.	0.00	0.00	0.00	-------
v_6	CH s. str.	0.00	0.00	0.00	w, bd
v_7	ring (CC str.)	0.00	0.00	0.00	m
v_8	ring (CC str.)	0.00	0.00	0.00	m
v_9	ring (CCC str.)	0.00	0.00	0.00	s
v_{10}	ring (CCC str.)	0.00	0.00	0.00	vs
v_{11}	ring (CCC str.)	0.00	0.00	0.00	w
v_{12}	ring (CCC str.)	0.00	0.00	0.00	w, sh
v_{13}	ring (CCC str.)	0.00	0.00	0.00	vs
v_{14}	ring (CCC str.)	0.00	0.00	0.00	vs
v_{15}	ring (CCC str.)	0.00	0.00	0.00	vs
v_{16}	δCH	0.00	0.00	0.00	w
v_{17}	δCH	0.00	0.00	0.00	w
v_{18}	δCH	0.00	0.00	0.00	m
v_{19}	δCH	0.00	0.00	0.00	w
v_{20}	δCH	0.00	0.00	0.00	vw
v_{21}	δCH + ring (CCC str.)	0.00	0.00	0.00	w
v_{22}	ring (δCCC) + δCH	0.00	0.00	0.00	vs
v_{23}	ring (δCCC)	0.00	0.00	0.00	m
v_{24}	ring (δCCC)	0.00	0.00	0.00	s
v_{25}	ring (δCCC) (ring elongation A & $\overline{A}$)	0.00	0.00	0.00	s
v_{26}	ring (δCCC) (ring elongation A & $\overline{A}$)	0.00	0.00	0.00	s
v_{27}	ring (δCCC) (anticlock bend. ring B & $\overline{B}$)	0.00	0.00	0.00	w
v_{28}	ring (δCCC) (clock. bend. ring A & $\overline{A}$)	0.00	0.00	0.00	m
v_{29}	ring (δCCC) (anticlock bend. ring A & $\overline{A}$)	0.00	0.00	0.00	vs
B_u^{**}					
v_{57}	CH str.	5304.39	185.62	s	0.00
v_{58}	CH str.	4256.20	148.38	s	0.00
v_{59}	CH str.	3856.77	134.11	s	0.00

Table (5): (contd.1) chrysene molecule.

ν_{60}	CH str.	169.25	5.87	vs	0.00
ν_{61}	CH str.	1020.35	35.34	s	0.00
ν_{62}	CH str.	548.26	18.96	m	0.00
ν_{63}	ring (CC str.)	1.27	0.02	w	0.00
ν_{64}	ring (CC str.)	20.50	0.35	s	0.00
ν_{65}	ring (CC str.)	9.48	0.15	w	0.00
ν_{66}	ring (CC str.)	44.44	0.68	m	0.00
ν_{67}	ring (CCC str.)	33.95	0.49	vs	0.00
ν_{68}	ring (CCC str.)	2.04	0.03	w	0.00
ν_{69}	ring (CCC str.)	0.73	0.01	m	0.00
ν_{70}	ring (CCC str.) + δCH	24.57	0.30	w	0.00
ν_{71}	δCH	171.90	2.04	vs	0.00
ν_{72}	δCH	294.94	3.50	vs	0.00
ν_{73}	ring (CCC str.) + δCH	328.66	3.75	s	0.00
ν_{74}	δCH	213.07	2.38	m, sh	0.00
ν_{75}	δCH	25.30	0.28	m	0.00
ν_{76}	δCH + ring (CC str.)	617.22	6.75	w	0.00
ν_{77}	δCH + ring (CC str.)	344.96	3.68	m	0.00
ν_{78}	ring (δCCC)	95.84	0.88	vs	0.00
ν_{79}	ring (δCCC)	133.93	1.03	vs	0.00
ν_{80}	ring (δCCC)	350.58	2.29	vs	0.00
ν_{81}	ring (δCCC)	43.33	0.23	w	0.00
ν_{82}	ring (δCCC) (clockwise bend. ring B, anticlock bend. ring $\overline{B}$)	13.19	0.07	m	0.00
ν_{83}	ring (δCCC)	93.69	0.43	s	0.00
ν_{84}	ring (δCCC) (clockwise bend. ring A, anticlock bend. ring $\overline{A}$)	31.37	0.05	w	0.00
Out of–plane					
A_u^{**}					
ν_{30}	γCH	1.20	0.01	w	0.00
ν_{31}	γCH	2.21	0.02	------	0.00
ν_{32}	γCH	0.57	0.00	s	0.00
ν_{33}	γCH	19.78	0.16	w	0.00
ν_{34}	γCH	167.43	1.33	m	0.00
ν_{35}	γCH + γCC	227.32	1.67	vs	0.00
ν_{36}	γCC (puck.) + γCH	0.16	0.00	vs	0.00
ν_{37}	γCC (puck.) + γCH	12.34	0.07	m	0.00
ν_{38}	γCC (puck.) + γCH	1.32	0.01	w	0.00
ν_{39}	γCCC (puck.) + γCH	9.10	0.04	ws	0.00
ν_{40}	γCCC (puck.)	0.18	0.00	m	0.00
ν_{41}	γCC (puck.) + γCH	24.56	0.05	ws	0.00
ν_{42}	γCC (puck.) + γCH	4.00	0.00	w	0.00
ν_{43}	γCC (puck.) + γCH	11.40	0.00	vw	0.00

Table (5): (contd.2) chrysene molecule

B_g^*					
ν_{44}	γCH	0.00	0.00	0.00	vw
ν_{45}	γCH	0.00	0.00	0.00	vw
ν_{46}	γCH	0.00	0.00	0.00	vw
ν_{47}	γCH	0.00	0.00	0.00	vw
ν_{48}	γCH	0.00	0.00	0.00	vw
ν_{49}	γCC (puck.) + γCH	0.00	0.00	0.00	vw
ν_{50}	γCH	0.00	0.00	0.00	w
ν_{51}	γCC (puck.) + γCH	0.00	0.00	0.00	vw
ν_{52}	γCC (puck.) + γCH	0.00	0.00	0.00	vw
ν_{53}	γCC (puck.) + γCH	0.00	0.00	0.00	vw
ν_{54}	γCC (puck.) + γCH	0.00	0.00	0.00	w
ν_{55}	γCC (puck.) + γCH	0.00	0.00	0.00	vw
ν_{56}	γCC (puck.) + γCH	0.00	0.00	0.00	w

γ: out of plane bending vibration.
δ in- plane bending vibration.
*: IR inactive (Raman active).

**: IR active (Raman inactive).

In-plane vibration frequencies:

Twelve CH stretching vibrations ν_1-ν_6 (A_g) and ν_{57}-ν_{62} (Bu) result from the calculation. Their frequencies range (3066-3029) cm^{-1} for MINDO/3-FORCES and (3052-2982) cm^{-1} for the ab initio method. In all these modes the largest APP values fall at the H atoms, with very small values $\overset{\equiv}{\alpha}$ for the attached C atoms. Both methods yield that the C_2 symmetric modes have higher frequencies than the antisymmetric modes. Table 2 includes all of these different vibration frequencies. The successive order of frequencies for the different C-H stretching modes as classified according to the type of bond (α, ,, $\overline{\varkappa}$, $\overline{\overline{\alpha}}$ and β) may be summarized in the following scheme.

ν_{sym}(CH str.)β (↑↑ ↓↓) > ν_{asym}(CH str.)β (↑↑ ↑↑) >
ν_1 ν_{57}
ν_{asym}(CH str.)β(↑↓ ↓↑) > ν_{sym}(CH str.)β (↑↓ ↑↓)
ν_{58} ν_2

ν_{sym}(CH str.) $\overline{\varkappa}$, $\overline{\overline{\alpha}}$ (↑↑ ↓↓) > ν_{asym}(CH str.) $\overline{\varkappa}$, $\overline{\overline{\alpha}}$ (↑↑ ↑↑) >
ν_3 ν_{59}
ν_{asym}(CH str.)α > ν_{sym}(CH str.)α >
ν_{60} ν_4
ν_{asym}(CH str.) $\overset{\equiv}{\alpha}$ > ν_{sym}(CH str.) $\overset{\equiv}{\alpha}$ >
ν_{61} ν_5
ν_{sym}(CH str.) $\overline{\varkappa}$, $\overline{\overline{\alpha}}$ (↑↑ ↓↓) > ν_{asym}(CH str.) $\overline{\varkappa}$, $\overline{\overline{\alpha}}$
ν_6 ν_{62}

Generally the following relation holds;

$\nu(\text{CH str.})\beta > \nu(\text{CH str.})\alpha$

and

$\nu\,(\text{CH str.})\beta > \nu\,(\text{CH str.})_{\overline{\alpha},\,\overline{\overline{\alpha}}} > \nu\,(\text{CH str.})\alpha > \nu(\text{CH str.})\overset{\equiv}{\alpha}$.

The calculated IR absorption intensities (Table 5) for all these modes are high and range from (6.00-185.6) km/mol. The highest intensity belongs to the ν_{57}(Bu) mode of 3065 cm^{-1}.

Seventeen C-C stretching frequencies resulted from the calculation. Their vibration frequencies range is (1645-1479) cm^{-1} for MINDO/3-FORCES and (1662-1480) cm^{-1} for the ab initio method. The vibration of highest frequency belongs to $\nu_7(A_g)$, which is localized at the C$\overline{\alpha}$-C$\overline{\overline{\alpha}}$ bond of the B and $\overline{\text{B}}$ rings. The next higher frequency is that of ν_{63} (B_u) then $\nu_8(A_g)$, falling at the C -C$_\beta$ bonds. The order of frequency values may be summarized in the following relation.

$\nu_{sym}(\text{CC str.})\ \overline{\alpha} - \overline{\overline{\alpha}} > \nu_{asym}(\text{CC str.})\ \overline{\alpha} - \overline{\overline{\alpha}} > \nu_{asym}(\text{CC str.})\beta - \overset{\equiv}{\alpha} >$

$\nu_{sym}(\text{CC str.})\ \beta - \overset{\equiv}{\alpha} > \nu_{sym}(\text{CC str.})_{\text{middle bonds}} > \nu_{asym}(\text{CC str.})_{\text{middle bonds}}$

Other calculated in-plane ring stretching vibrations are the eleven CCC stretching vibrations with frequency values (1617-1290)cm^{-1} for the MINDO/3-FORCES and (1614-1325) cm^{-1} for the ab initio method.. The highest frequency among them belongs to the symmetric ν_9(Ag) mode.

As for the δCH deformation modes, twelve are calculated with various frequency values ranging from (1271-1067) cm^{-1} for the MINDO/3-FORCES and (1268-1017) cm^{-1} for the abinitio method . The APP values and graphical analysis show that the vibration motion of all these modes is mainly localized at the corresponding H atoms. Vibrations of different CH bonds show different frequencies, indicating different deformation force constants. Thus different δCH frequencies are found for the α, $\overline{\alpha}$, $\overline{\overline{\alpha}}$, and β (C-H) bonds. The sequence of these values is summarized in the following scheme;

$(\delta\text{CH}\overset{\equiv}{\alpha})\ \text{sym}\ \overset{\equiv}{\alpha} > \text{asym}\,(\delta\text{CH})\ \overset{\equiv}{\alpha} > \text{asym}\,(\delta\text{CH})_{\alpha,}\ \overset{\equiv}{\alpha} > \text{sym}\,(\delta\text{CH})_{\alpha,}\ \overset{\equiv}{\alpha} >$

$\text{sym}\,(\delta\text{CH})_{\overline{\alpha}}\,,\ \overline{\overline{\alpha}} > \text{asym}\,(\delta\text{CH})_{\overline{\alpha}}\,,\ \overline{\overline{\alpha}} > \text{asym}\,(\delta\text{CH})_{\overline{\alpha}}\,,\beta > \text{sym}\,(\delta\text{CH})\beta$

Generally the following relations hold;

$$(\delta\text{CH})_{\alpha} > (\delta\text{CH})\,\beta$$

and

$$(\delta\text{CH})\ \overset{\equiv}{\alpha} > (\delta\text{CH})_{\alpha} > (\delta\text{CH})\ \overline{\alpha}\,,\overline{\overline{\alpha}} > (\delta\text{CH})\beta$$

Beside these deformations the sixteen (δCCC) ring deformations appear in the table at frequencies (1037-183) cm^{-1} for the MINDO/3-FORCES and (1010-184) cm^{-1} for the **ab initio** method . Among these is the clock-anticlockwise deformation frequency ν_{84} (B_u).

Out of plane vibrations;

These include the thirteen IR inactive out of plane deformations of B_g representation and fourteen A_u vibrations (IR active). All of these modes could be identified on inspecting their APP values and studying their graphical pictures. The frequencies of the twelve γCH vibrations range from (969–757) cm^{-1} for the MINDO/3-FORCES and (1003-757) cm^{-1} for the ab initio method. Different frequencies are calculated for γCH vibrations localized at different CH bonds. The highest frequency belongs to the ν_{30}(A_u) mode, localized at the four $(C\text{-}H)_\beta$ bonds of the rings A and $\overline{A}$. The lowest frequency belongs to ν_{50}(B_g). The frequencies for the deformation of other CH bonds belonging to the rings A and $\overline{A}$ fall between these two in their values. Generally one may order the frequencies according to the following scheme;

$$(\gamma CH)_\beta > (\gamma CH)_{\overline{\omega}\ \&\ \overline{\overline{\alpha}}} > (\gamma CH)_{\text{middle bonds}} > (\gamma CH)_{\beta,\ ,\ \alpha} > (\gamma CH)_\alpha$$

In all these modes the symmetric vibrations show higher frequencies than their asymmetric modes.

As for the 15 ring out of plane vibration modes, the participation of the H atoms in them are very small. They represent puckering motions of the molecular plane. The frequencies of the fifteen γCC vibrations range from (762-48) cm^{-1} for the MINDO/3-FORCES and (723-47) cm^{-1} for the ab initio method. The calculated IR absorption intensities are very small (0.00-0.07) km/mol. The highest intensity belongs to ν_{37}(A_u) of 614 cm^{-1} (MINDO/3-FORCES). The order of their frequencies exhibits the following scheme;

$$(\gamma ring)_{\text{middle bonds}} > (\gamma ring)\beta\ (\uparrow\downarrow)A_g > (\gamma ring)_{\overline{\omega}} > (\gamma ring)_{\alpha,\ \overline{\overline{\alpha}}} > (\gamma ring)_\beta\ (\uparrow\uparrow)B_g$$

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