RESEARCH ARTICLE

European Journal of Advanced Chemistry Research
www.ej-chem.org

Comparative Studies of Experimental and Simulated IR Spectra of Some Selected Flavonoid Compounds

Kishor Arora, Anil Kumar Sharma, and Anu Parmar

ABSTRACT

Flavonoid compounds are a class of poly-phenolic secondary metabolites usually found in various plants. These compounds were of interest in the study of various workers in the past because of their utility as medicinal compounds. These compounds can be extracted from plants and workers have tried to synthesize them also. A lot of references related to the studies of these compounds are available in the literature to explore their structural and other related properties. This communication reports the studies on experimental and simulated IR spectra of some selected Flavonoid compounds based on quantum-chemical semi-empirical methods using different AM1 and PM3 approaches. Other related geometrical parameters obtained after optimizations are also reported. It has also been tried to study and include parameters related to the FMO approach theoretically for these compounds.

Keywords: HOMO-LUMO, Semi-Empirical Methods, Spectral Studies, Simulation of Spectra.

ISSN: 2684-4478

DOI: 10.24018/ejchem.2022.3.3.113

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I. INTRODUCTION

Flavonoid compounds are the part of poly-phenol part of phytonutrients. These compounds are a class of poly-phenolic secondary metabolites usually found in various plants. Therefore, these compounds are thus commonly consumed in diets. There are several important groups of flavonoids, such as anthocyanidins, flavanols, flavones, flavonols, flavonones and iso-flavones [1].

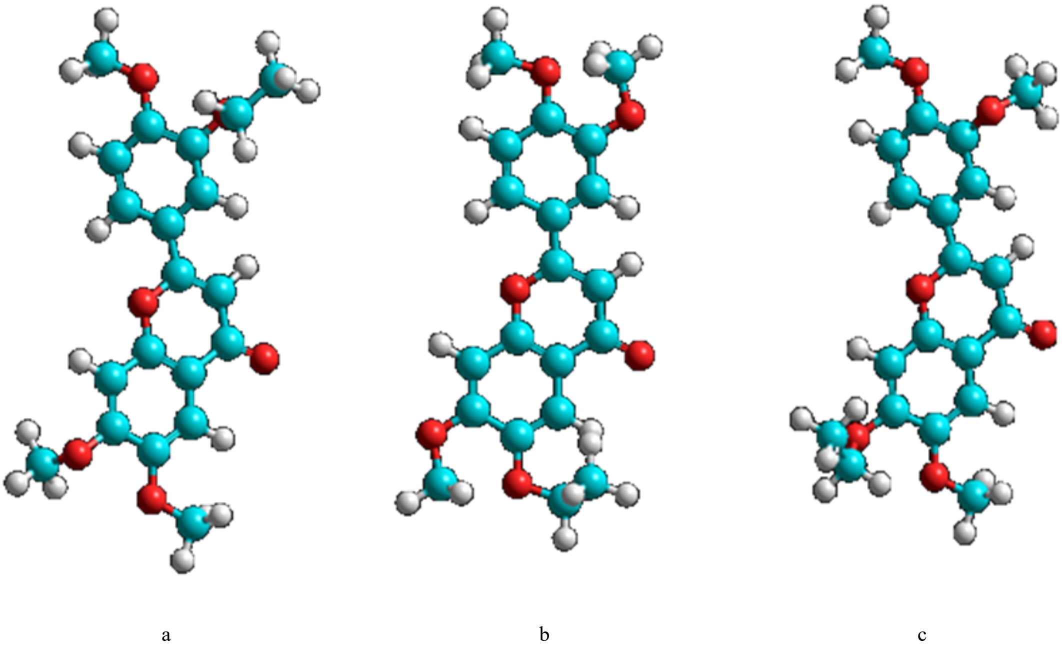
Flavones include the compounds like luteolin and apigenin. Various herbs and hot peppers are good sources of flavones. Flavones are associated with antioxidant benefits and with the metabolizing of drugs [2]. Flavonoid compounds have utility because of their medicinal values even in Ayurvedas. Though these compounds can be extracted and obtained from plants, but workers have tried to explore properties along with their laboratory synthesis via different synthetic routes. A lot of work has been done in this regard i.e. in the studies of these compounds using different approaches, different techniques, etc. [3]-[7].

A spectral study of any Organic compound for the purpose of its structural establishment is one of the major tools or techniques in use in this regard. In the modern era, researchers are also studying the simulation of spectra of Organic compounds using computational methods. These methods are becoming popular among researchers nowadays. Quantum chemical viz. ab initio or semi-empirical based studies of simulation of spectra are now prevailing among researchers/scientists pursuing their studies in theoretical chemistry. So far as these studies are concerned, these studies provide better insight into the compounds so far as the studies of their structural, spectral or other parameters are concerned [8]-[14].

Though a lot of work has been done in the studies of Flavonoid compounds [15]-[17], but there is still a possibility left to explore them using a theoretical chemistry approach i.e. studying their simulated spectra and its comparison with the experimental one. Keeping this in mind we wish to report the studies on experimental and simulated IR spectra of some selected Flavonoid compounds which are and its comparison with the experimental one. Keeping this in mind we wish to report the studies on experimental and simulated IR spectra of some selected Flavonoid compounds which are

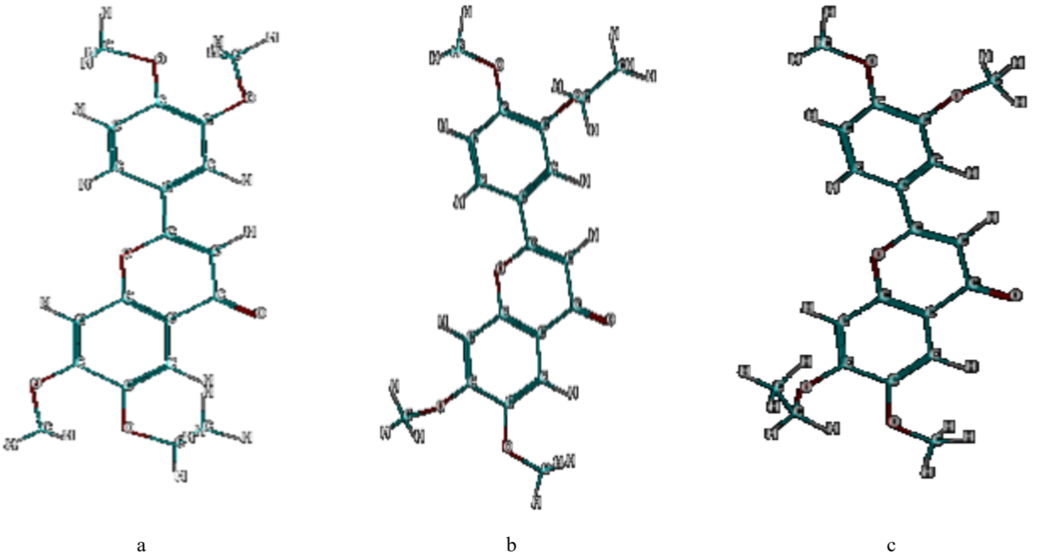
Fal 1: 6,7,4'-Trimethoxy-3'-ethoxy flavones [m. pt. 179-1800 c]
Fal2: 7, 3'4'-Trimethoxy-6-ethoxy flavones [m. pt. 211-2120 c]
Fal3: 6, 3'4'-Trimethoxy-7-ethoxy flavones [m.pt.215-160c]

Structures of the compounds under study are given in Fig. 1 and in Fig. 2.



a b c

Fig. 1. Flavonoid compounds under study (Ball and stick Fig.); a) FAL 1, 6,7,4'-Trimethoxy-3'-ethoxy flavones; b) FAL 2, 7, 3'4'-Trimethoxy-6-ethoxy flavones; c) FAL3, 6, 3'4'-Trimethoxy-7-ethoxy flavones.



a b c

Fig. 2. Flavonoid compounds under study, a) FAL1, 6,7,4'-Trimethoxy-3'-ethoxy flavones; b) FAL2, 7, 3'4'-Trimethoxy-6-ethoxy flavones; c) FAL3, 6, 3'4'-Trimethoxy-7-ethoxy flavones.

II. EXPERIMENTAL

The Flavonoid compounds for which studies are reported in this communication were obtained/ procured as reported earlier 10. Melting Point of each and every compound was obtained using Metler's melting point determination apparatus and are reported along with the name of the compounds under study, in introduction section of this communication.

The FTIR spectra of these flavonoid compounds under study were recorded on a Perkin Elmer Model Spectrum -2 Infrared Spectrophotometer in the range of 4000 to 400 cm-1 at SAIF University of Delhi, Delhi.

III. DETAILS FOR COMPUTATIONAL STUDIES

The computational studies were carried out on Intel based Pentium core-2 Duo machine with configuration Intel (R) core TM 2 Duo CPU, T5450@1.66 GHZ, 2 GB RAM, 250 GB HDD. All computations were carried out on it.

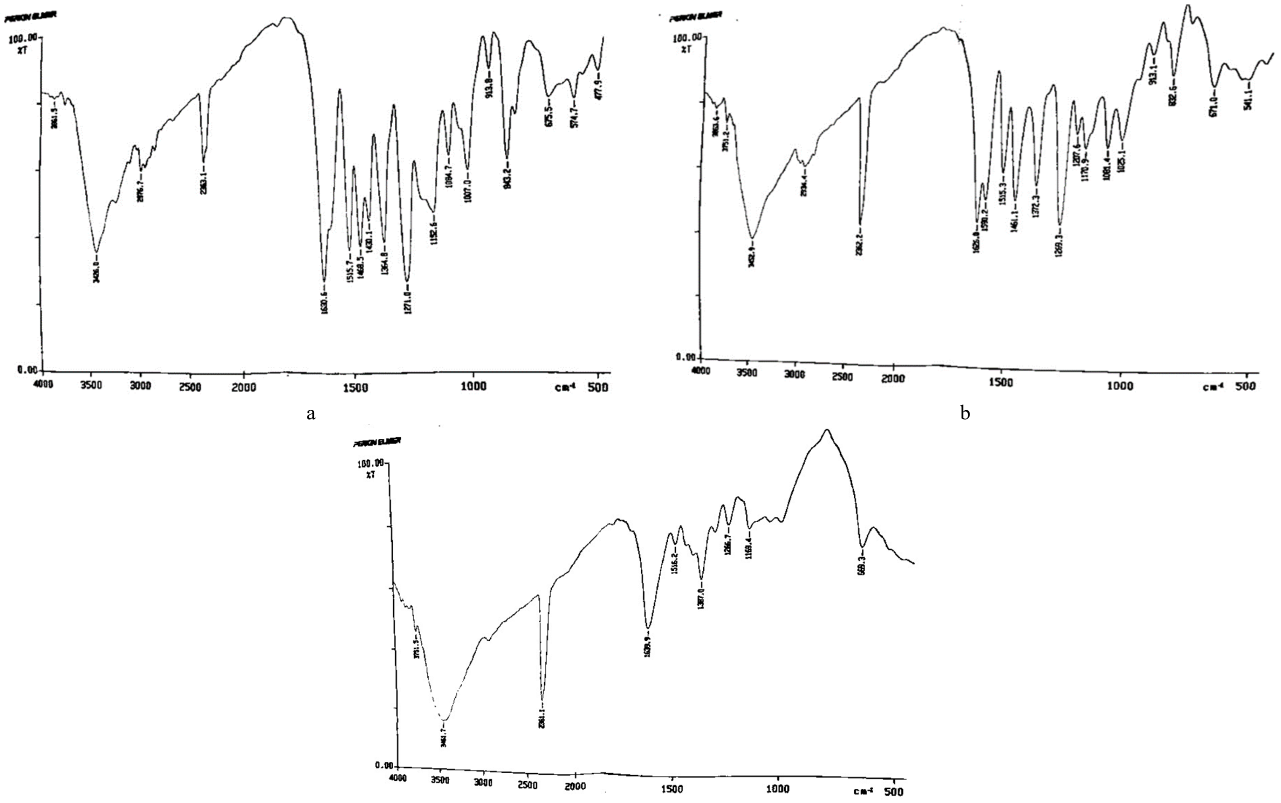
Semi-empirical methods viz. AM1, PM3, MNDO and ZINDO1 were employed for various quantum chemical calculations. These computations were carried out by the computer software HYPERCHEM 8.0 professional version. The computed parameters such as normal modes or vibration frequencies were also obtained on the same platform. The methods viz. AM1 and PM3 were employed. These have their usual meanings, and these may be considered Hamiltonians or keywords for the methods understudies. The correlation diagrams, modeling equations, and all other statistical calculations were carried out on MS Excel as usually carried out by other workers [3]-[9].

IV. RESULTS AND DISCUSSION

A. *IR Spectral Studies*

The FTIR spectra of these synthesized flavonoid compounds were recorded on a Perkin Elmer Model Spectrum -2 Infrared Spectrophotometer in the range of 4000 to 400 cm-1 at SAIF University of Delhi, Delhi. These spectra are given in Fig. 3.

The vibration modes for the compounds under study were also computed on the software HYPERCHEM 8.0 professional version. These were computed using semi-empirical AM1 and PM3 methods. These computed vibration frequencies are given in Table I, Table II and Table III, along with the experimentally observed vibration modes and with assignments to these modes.



a

b

c

Fig. 3. Experimental spectra of the flavonoid compounds under study (FAL 1 – FAL 3); a) FAL-1 compound, 6,7,4'-Trimethoxy-3'-ethoxy flavones; b) FAL-2 compound, 7, 3'4'-Trimethoxy-6-ethoxy flavones; c) FAL-3 compound, 6, 3'4'-Trimethoxy-7-ethoxy flavones.

TABLE I: EXPERIMENTALLY OBSERVED AND COMPUTED VIBRATION FREQUENCIES FOR THE COMPOUND FAL 1

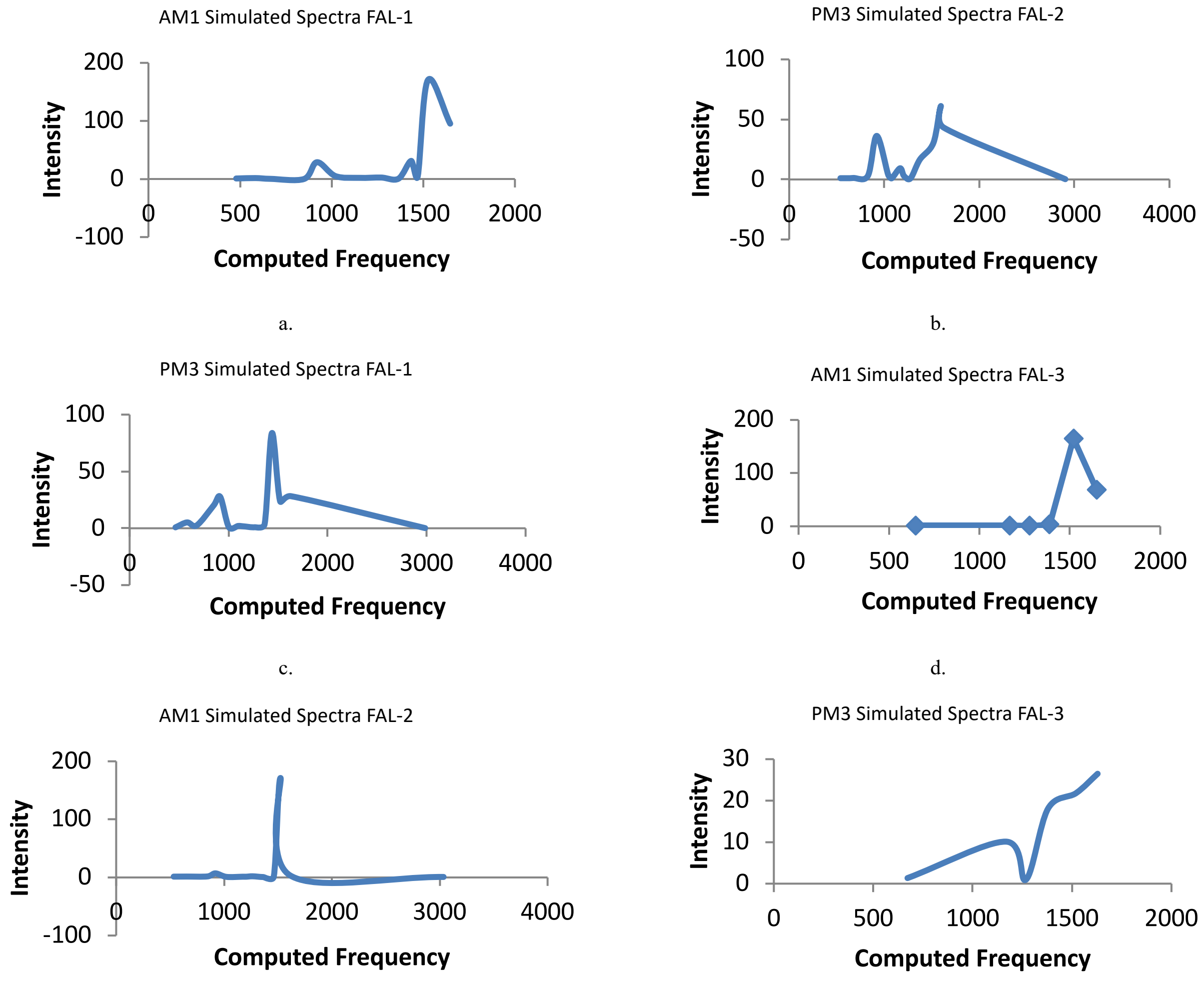
Experimental observed vibration frequency (cm-1)	AM1 (computed vibration frequency)	PM3 (computed vibration frequency)	Assignment
477.9	478.88	463.28	δ(CCC)
574.7	583.9	580.6	δ(CCC)
675.5	667.2	677.66	δ(CCC)
843.2	849.7	848.81	(CCC)rb
913.8	919.83	914.98	δ(C-H)
1007	1020.73	1002.65	(CCC)Tri
1152.6	1152.64	1152.75	δ(C-H)
1271	1269.8	1265.24	υ(C-H)
1364.8	1364.7	1363.58	υ(C-O)
1430.1	1434.08	1437.43	$\upsilon_{as}(C-CH_3)$
1515.7	1524.72	1520.92	υ(C=C)
1630.6	1646.74	1629.11	υ(C=O)

TABLE II: Experimentally Observed and Computed Vibration Frequencies for the Compound FAL2

Experimental observed vibration frequency (cm-1)	AM1 (computed vibration frequency)	PM 3 (computed vibration frequency)	Assignment
541.1	533.2	538.36	δ(CCC)
671	654.25	672.18	δ(CCC)
832.6	846.68	827.63	(CCC)
913.1	919.56	920.2	δ(C-H)
1025.1	1021.78	1040.7	δ(C-O)
1170.9	1172.67	1166.05	δ(C-H)
1207.6	1206.14	1207.42	δ(C-H)
1269.3	1265.61	1275.73	υ(C-H)
1372.3	1363.81	1372.71	υ(C-O)
1461.1	1461.14	1516.97	υ(C=C)
1515.3	1523.4	1595.48	υ(C=C)
1626	1612.5	1626.22	υ(C=O)
2934.4	3035.9	2904.77	υ(C-H)

TABLE III: Experimentally Observed And Computed VIBRATION FREQUENCIES For The Compound FAL 3

Experimental observed vibration frequency (cm-1)	Am1 (computed vibration frequency)	Pm3 (computed vibration frequency)	Assignment
669.3	648.8	672.3	δ(CCC)
1169.4	1168.7	1166.44	δ(C-H)
1266.7	1278.53	1268.14	υ(C-H)
1387	1387.8	1379.2	υ(C-O)
1516.2	1520.8	1520.73	υ(C=C)
1639.9	1649.2	1628.63	υ(C=O)



a.

b.

c.

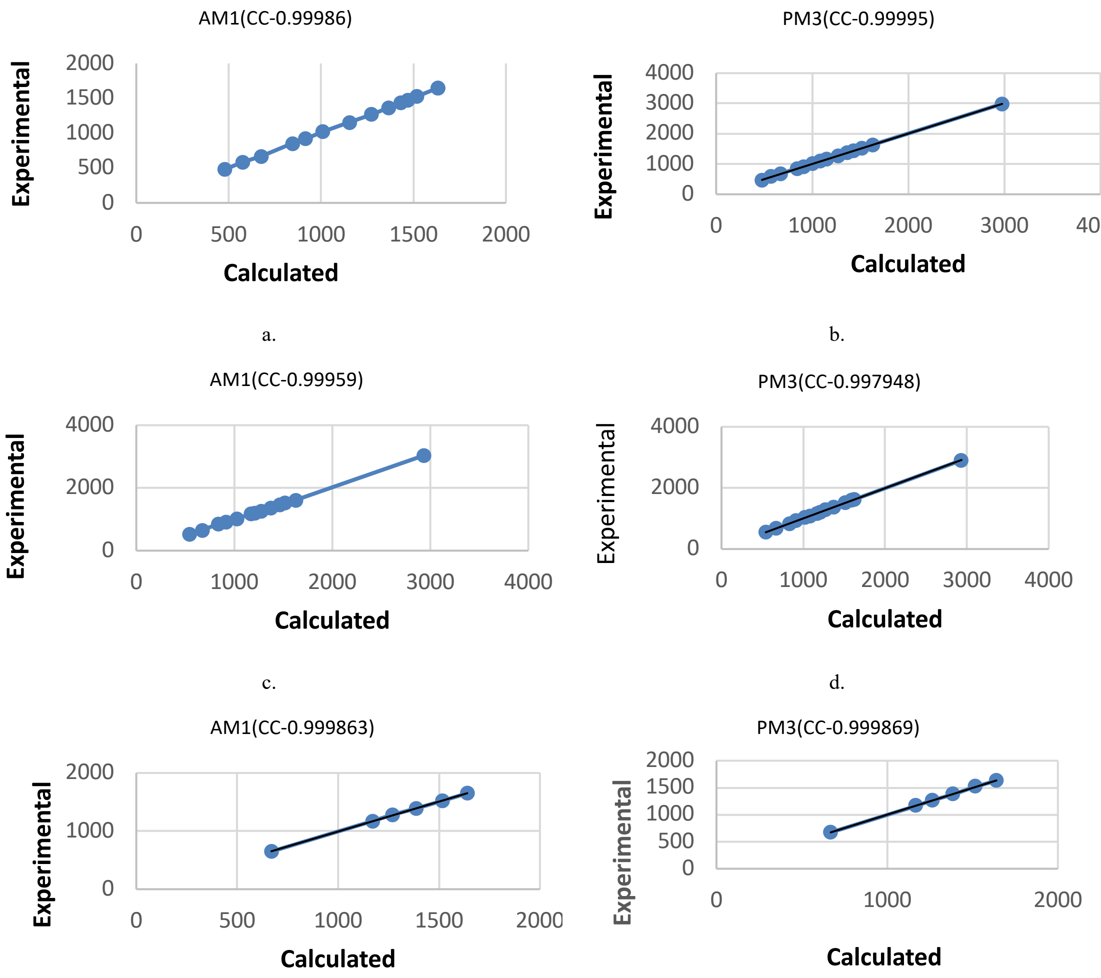
d.

e.

f.

Fig. 4. Simulated spectra on the basis of AM1 and PM3 computations for the Flavonoid compounds; a) Simulated Spectra of FAL1 on the basis of AM1, b) Simulated Spectra of FAL2 on the basis of PM3, c) Simulated Spectra of FAL1 on the basis of PM3, d) Simulated Spectra of FAL3 on the basis of AM1, e) Simulated Spectra of FAL2 on the basis of AM1, f) Simulated Spectra of FAL3 on the basis of PM3.

Table I, Table II and Table III show that the notable peaks in the case of these compounds are:1645-1625 cm $^{-1}$ υ(C=O); 1525-1510 cm^{-1} υ(C=C); 1380-1360 cm^{-1} υ(C-O); 1280-1260 cm-1 υ(C-H) and 1175-1155 cm^{-1} δ(C-H) which are also observed within a permissible error on computations done using these AM1 and PM3 methods. All other peaks are also listed in Table I, Table II, and Table III. The simulated spectra of these compounds designed on the basis of these methods are shown in Fig. 4.



a. b.

c. d.

e. f.

Fig. 5. Correlation between observed and AM1 and PM3 computed vibration frequencies for the Flavonoid Compounds, a) Correlation diagram for FAL 1 compound using AM1 method; b) Correlation diagram for FAL 1 compound using PM 3 method; c) Correlation diagram for FAL 2 compound using AM1 method; d) Correlation diagram for FAL 2 compound using PM3 method; e) Correlation diagram for FAL 3 compound using AM1 method; f) Correlation diagram for FAL 3 compound using PM 3 method.

The correlation between the experimental and computed vibration frequencies is perfect and in the range 0.99975 - 0.99995. The correlation diagrams are also designed for these observations which are shown in Fig 5. This indicates that these methods are appropriate for studying simulated spectra of such compounds. These computed results are in good agreement with the experimental one as observed [11]-[12].

B. *Other Computed Structural Parameters*

All other structural parameters of interest viz. heat of formation (HF); core-core interaction (CC), Total energy (TE), zero-point energy (ZPE) and electronic energy (EE) which are also computed on the basis of these methods are given in Table IV, Table V, and Table VI.

TABLE IV: COMPUTED STRUCTURAL PARAMETERS FOR THE FLAVONOID COMPOUNDS UNDER STUDY FLAVONOID COMPOUND – FAL 1

Computed Parameters	AM1	PM3
Total Energy (Kcal/Mol)	-108622.74	-102326.41
Binding Energy (Kcal/Mol)	-3906.43	-4960.28
Electronic Energy (Kcal/Mol)	-775757.37	-757018.60
Core Core Interaction (Kcal/Mol)	667134.62	654692.19
Heat of Formation (Kcal/Mol)	910.756	-143.09
Point Group	C1	C1
Zero Point Energy (Kcal/Mol)	236.185	227.146

TABLE V: Computed structural parameters for the Flavonoid compounds under study
Flavonoid compound – Fal 2

Computed Parameters	AM1	PM3
Total Energy (Kcal/Mol)	-109555.68	-102326.83
Binding Energy (Kcal/Mol)	-4839.37	-4960.71
Electronic Energy (Kcal/Mol)	-788190.78	-762102.02
Core Core Interaction (Kcal/Mol)	678635.1	659775.19
Heat of Formation (Kcal/Mol)	-22.177	-143.51
Point Group	C1	C1
Zero Point Energy (Kcal/Mol)	236.124	227.502

TABLE VI: Computed structural parameters for the Flavonoid compounds under study
Flavonoid compound – Fal 3

Computed Parameters	AM1	PM3
Total Energy (Kcal/Mol)	-102329.13	-109497.644
Binding Energy (Kcal/Mol)	-4963	-4781.33
Electronic Energy (Kcal/Mol)	-773522.13	-761747.77
Core Core Interaction (Kcal/Mol)	659418.63	679983.84
Heat of Formation (Kcal/Mol)	-145.813	38.860
Point Group	C1	C1
Zero Point Energy (Kcal/Mol)	227.46	236.158

C. *FMO Approach*

The HOMO, LUMO, and their energy gap i.e. energy gap between HOMO-LUMO have also been computed for the flavonoid compounds using semi-empirical AM1 and PM3 methods [13]-[14]. Associated with these parameters viz. HOMO and LUMO, within the framework of HF-SCF MO theory the ionization energy (IE) and electron affinity (EA), can be expressed utilizing HOMO and LUMO orbital energies [13]-[14] as

IE = -EHOMO and
EA= -ELUMO.

Similarly, the hardness that corresponds to the gap between the HOMO and LUMO orbital energies can also be computed. The larger the HOMO-LUMO energy gap implies the harder molecule. According to Koopmans's theorem for global reactivity, the reactivity trends depend upon a prediction of Chemical potential (μ), global hardness (η), electronegativity (χ), global softness (S), and electrophilicity index (ω). These are highly successful global reactivity descriptors and these global reactivity descriptors may be calculated from the energies of frontier molecular orbitals εHOMO, εLUMO [13]-[14] as per the following formulae: -

$S = 1/2\eta$
$\omega= \mu2/2\eta$
$\eta= 1/2(\varepsilon HOMO-\varepsilon LUMO)$
$\chi = -1/2(\varepsilon HOMO+\varepsilon LUMO)$
$\mu = -\chi = 1/2(\varepsilon HOMO+\varepsilon LUMO)$

All these parameters are also computed for flavonoid compounds under study in this communication and are presented in Table VII and Table VIII.

TABLE VII: AM1 Computed Homo, Lumo, Energy Gap, And Other Related Parameters For Flavonoid Compounds

	HOMO	LUMO	Energy gap	η	S	χ	μ	HOMO-1	LUMO+1
FAL1	-0.24773	0.063021	0.310751	0.184709	0.092355	0.155376	-0.15538	-0.74332	0.126826
FAL2	-0.25443	0.081886	0.336316	0.172544	0.086272	0.168158	-0.16816	-0.71393	0.108163
FAL3	-0.35402	0.0142	0.36822	0.16991	0.084955	0.18411	-0.18411	-0.79093	0.108741

TABLE VIII: PM3 Computed Homo, Lumo, Energy Gap And Other Related Parameters For Flavonoid Compounds

	HOMO	LUMO	Energy gap	η	S	χ	μ	HOMO-1	LUMO+1
FAL1	-0.030601	0.481879	0.512471	0.225639	0.11282	0.256236	-0.25624	-0.10755	0.481879
FAL2	-0.060571	0.429658	0.490229	0.184544	0.092272	0.245115	-0.24512	-0.1145	1.498726
FAL3	-0.003749	0.502973	0.506721	0.249613	0.124806	0.253361	-0.25336	-0.10504	1.514351

V. CONCLUSION

The AM1 and PM3 semi-empirical studies were carried out with the help of computer software HYPERCHEM 8.0 professional version to calculate the vibration frequency modes and to draw theoretically simulated spectra of these Flavonoid Compounds. The results thus obtained are discussed in the results and discussion section. It is clear from this part of the communication that the computed normal modes frequency of vibrations is in good agreement with experimental values as computed on the basis of these methods viz. AM1, PM3, with appreciable Correlation coefficient values. Among these methods, the AM1 method is very good as compared to the second one. The molecular geometry of the flavonoid compounds was also best with the AM1 method. The HOMO-LUMO energy gap and other related molecular properties are also discussed and reported in the present communication. The studies incorporated in the present paper are less time-consuming. These may be considered alternative methods of Studies/Teaching in the related field.

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