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Semi-empirical and vibrational studies of flavone and some deuterated analogues

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Abstract—The infrared solid state, Raman solid state and tetrachloride solution spectra of flavone have been obtained. Assignments of most of the vibrational data have been performed by comparison between the spectra of flavone and three isotopic species, deuterated on the A, B and C rings, respectively. The vibrational frequencies for all the investigated compounds have been calculated from the conformational analysis of flavone using the semi-empirical AM1 method and compared with experimental values. The correlation is more or less satisfactory; however, for some vibrational modes, the calculated isotopic shifts agree better with experiment than do the frequencies themselves. Specific vibrational modes which retain a benzene ring mono-substituted and ortho-distributed character have been recognized in the spectra, according to literature data, isotopic frequency shifts and graphic representation of the atomic displacements.

INTRODUCTION

FLAVONE (2-phenyl-4H-1-benzopyran-4-one) is the basic molecule of the group of flavonoid compounds which are widely distributed in the plant kingdom. These natural products exhibit various interesting biological activities [1, 2]. Flavone consists of two rings (A and B) joined together by a three-carbon link which is formed into a γ-pyrone ring, also called the C ring (Fig. 1). Apart from several studies on the infrared (IR) absorption behaviour of the carbonyl group [3–7], no attempt has been made before to assign precisely the vibrational spectral data of the flavone molecule. In a previous paper discussing the physical structure of the flavone molecule, the aromatic nature of the A and B ring systems was clearly suggested [8]. Because of this, we may expect to notice in the IR and Raman spectra of flavone, some bands which can be described as vibrational modes of individual rings.

In the present investigation, we intend to ascribe most of the experimental frequencies by combined use of (i) some vibrational results [7, 9–12] on mono-substituted and ortho-di-substituted benzene derivatives which characterize the aromatic properties of A and B rings; (ii) the isotopic shifts observed for three deuterated flavones: flavone 3-d, flavone 5, 6, 7, 8-d4 and flavone 2′, 3′, 4′, 5′, 6′-d5; and (iii) the harmonic vibrational frequencies and the potential energy distribution (P.E.D.) obtained from semi-empirical calculations.

EXPERIMENTAL

Compounds

The flavone studied was an Extrasynthèse product, used without further purification.

Flavones selectively deuterated on each ring have already been synthesized and studied by NMR and mass spectrometry [13–15]. The authors used two different methods to obtain the species

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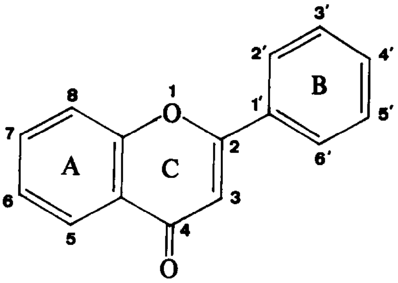

Fig. 1. Chemical structure and skeletal numbering of the flavone molecule.

labelled on benzene [16] or pyran [15] rings. We have chosen the first pathway [16] for the three isotopomers but ortho-benzoyloxyacetophenone was converted into (2-hydroxybenzoyl)-benzoylmethane by means of NaH in DMSO [17] instead of KOH in pyridine. The deuterated starting materials were obtained in the following manner.

(a) *Flavone* 2', 3', 4', 5', 6'-d5. The required benzoyl-d5 chloride was prepared by carbonation of Grignard reagents of bromobenzene-d5 [18] followed by reaction of the deuterated benzoic acid with $SOCl_2$.

(b) *Flavone* 5, 6, 7, 8-d4. The required ortho-hydroxyacetophenone-d4 was obtained from phenol. In a dry box, 0.5 g of sodium was carefully added to 12 cm^3 of heavy water followed by 0.7 g of aluminium–nickel catalyst. When gas evolution had ceased, 7 g of purified phenol was dissolved and the well-stirred mixture was heated at 100°C for 55 h with exclusion of atmospheric moisture. After cooling, the catalyst was filtered and washed with ether. The aqueous solution was acidified by 6 N HCl and extracted several times with ether. After drying the ethereal solution on Na_2SO_4, the solvent was evaporated. After four exchanges, deuterated phenol was acetylated by Schotten–Baumann reaction with acetic anhydride [19]. The pentadeuterophenylacetate (97% D) was subjected to Fries rearrangement [20]: 3.8 g of AcO (Ph-d5) was added to 3.6 g $AlCl_3$ dissolved in 17 ml of dried 1,2-dichloroethane. The mixture was magnetically stirred at 95°C for 24 h. After the usual work-up, ortho-hydroxyacetophenone-d4 containing some starting material was obtained and benzoylated, as described by Wheeler [16]. The overall yield for transposition and benzoylation was 40%.

(c) *Flavone* 3-d. Guidugli *et al.* [15] obtained 3-deuteroflavone by oxidation of 3,3'-dideuteroflavanone. We prefered to use the modified method of Wheeler [16, 17]. After exchange of acidic hydrogen in (2-hydroxybenzoyl)-benzoylmethane with ethanol-OD, cyclization in acetic-d with deuterated sulfuric acid yielded flavone 3-d.

Isotopic purity of the deuterated flavones was determined by NMR spectroscopy more than 97% D was found in all the compounds.

Instrumental

The IR spectra were recorded on a Brucker FT-IR IFS113 spectrophotometer in the 1700–500 cm^{-1} range with a spectral resolution of 2 cm^{-1}. Flavones were studied in potassium bromide matrix (2%).

The FT-Raman spectra of investigated compounds in solid state and in carbon tetrachloride solution were recorded in the 3500–500 cm^{-1} range with a spectral resolution of 4 cm^{-1}. They were obtained with the FRA106 accessory of the Brucker FT-IR IFS88 spectrophotometer. Sample excitation was achieved with 1.06 μm radiation from a YAG laser with about 400 mW power.

The Raman spectra were also recorded with an XY instrument (Dilor, France). This instrument has an excitation at 514.5 nm, allowing performance of polarization measurements.

Calculations

First of all, the geometry of the flavone molecule was model-built from standard geometrical parameters and optimized with PC Model program (version 3.2) using the SCF method. This PCM version used the MMX force field method developed by J. J. Gajewski and K. E. Gilbert which is based on Allinger's MM2 mechanic program with some extensions [21, 22]. Secondly,the optimized geometry (bond lengths, bond angles and dihedral angles) obtained by MMX calculation was set as the input data for an AM1 semi-empirical treatment. The semi-empirical optimized energy minimization and the vibrational frequencies were computed with a MOPAC (version 5.01) program package and were carried out on an IBM 3090 (CIRCE CNRS, Orsay). For the three isotopic products, the force field calculations were performed from the AM1 output data of flavone. The graphic representations of the atom displacements were obtained with a self-made program. They allowed us on the one hand, to recognize some specific modes that imply only one of the three rings and to localize them in the experimental spectra; and on the other hand, to stress the fact that many couplings occur between the different ring systems which essentially explain the great complexity of the spectra.

Results and Discussion

For the four flavones mentioned above, semi-empirical AM1 calculations were performed and harmonic vibrational frequencies were computed from the optimized geometries. It should be noted that the semi-empirical methods are well suited to reproducing geometrical conformations of isolated molecules since no intermolecular interaction is taken into account (molecules are assumed to be in the gas phase). In the crystal packing, bond lengths are systematically smaller. It is also well known, in solid state, that the intermolecular forces can strongly reduce dihedral angles [23] such as the torsion angle C3–C2–C1′–C6′ (~28°) of flavone. That is the reason why it appeared reasonable to use the calculated data only for the treatment of the spectra of flavones in solution. The force constants obtained from the geometry optimization are generally overestimated and give calculated frequencies higher than the expected values, and it is essential to make some scaling. Some studies of analogous molecules clearly suggest that the calculated frequencies must be multiplied by an empirical factor 0.89 to approximately correct the combined errors due to neglect of electron correlation and anharmonicity, both of which tend to lower the frequencies [24, 25].

The FT-IR and FT-Raman spectra in solid state, FT-Raman spectra in CCl_4 solution of flavone and investigated deuterated analogues are shown on Figs 2–4, respectively, in the range 1700–500 cm^{-1}. The FT-Raman spectra are similar in wavenumbers to those obtained with the conventional instrument. The low depolarization ratio ($0.25 < \rho < 0.5$) obtained for all the observed lines is consistent with a C_1 symmetry for the molecule and only A modes are observed. Table 1 presents the experimental and scaled calculated frequencies together with their tentative assignment for the four investigated molecules. Wilson's notation [26] is used for the modes which involve only one ring and retain their benzene mode character. However, as the substitution of the aromatic ring produces mode changes, this nomenclature, adapted from Wilson's notation, is used only for description purposes.

For some vibrations, deuteration implies a more or less important frequency shift of the absorption and diffusion bands of the unsubstituted flavone molecule. As a result, when only one ring system is involved, it is easy to ascribe a band to a specific chromophore unequivocally even if the mode that occurs is not a well-known characteristic mode of substituted aromatic rings. Moreover, the P.E.D. allows us to confirm this assignment and to localize other vibrational modes. The examination of Table 1 shows a rather good correlation between theoretical and experimental values for some wavenumbers. A better correlation could perhaps be obtained by using a specific scaling factor for stretching, in-plane bending and out-of-plane bending vibrations [27] but the use of different factors should not be suitable for mixed modes which involve more than one motion type. However, for the modes which exhibit a significant discrepancy in frequencies, the calculated and observed isotopic shifts are in good agreement. From these considerations, some characteristic modes can be discussed. The vibrations arising below 500 cm^{-1} have not been investigated.

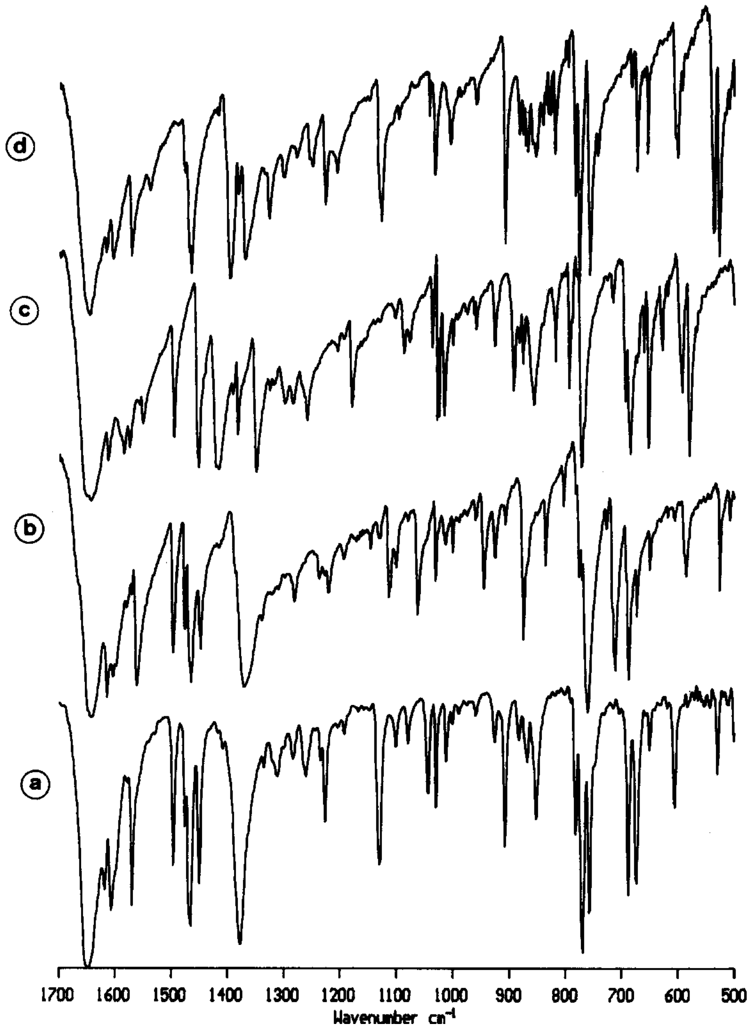

Fig. 2. Solid state FT-IR spectra of flavone (a), flavone-3d (b), flavone-d4 (c) and flavone-d5 (d).

The carbonyl stretching mode

The carbonyl stretching frequency ν(C=O) is located at 1652 cm^{-1} in the solution Raman spectrum [3–7] even if the calculated value is overestimated; it appears as a large and strong band. By taking into account the experimental spectral resolution, the different isotopic substitutions do not bring about very sensitive frequency shifts, as was expected. A shift towards the higher frequencies is noticed in the Raman spectrum (1652 cm^{-1}) of flavone in solution in comparison with the corresponding solid state one (1634 cm^{-1}). This may be explained by an increase in the π conjugation between the B phenyl ring and the pyrone part through the inter-ring bond. Indeed, as has been previously shown [8], the torsion angle between the side phenyl group and the rest of the molecule strongly influences the π electrons' distribution. In solid state, the dihedral angle (~0°) is smaller than in solution (~28°) because of constraints induced by effective intermolecular interactions in the crystal, which results in a stronger π electron delocalization. The frequency shift of 16 cm^{-1} between the IR and the Raman bands obtained from the solid state may come from the interaction with potassium bromide, often observed using the pellet technique [3, 28].

Ring systems vibrational modes

In-plane skeletal vibrations: ν(C–C). In the solid state Raman spectrum, the band observed at 1619 cm^{-1} can be associated with the C2–C3 stretching vibration that occurs

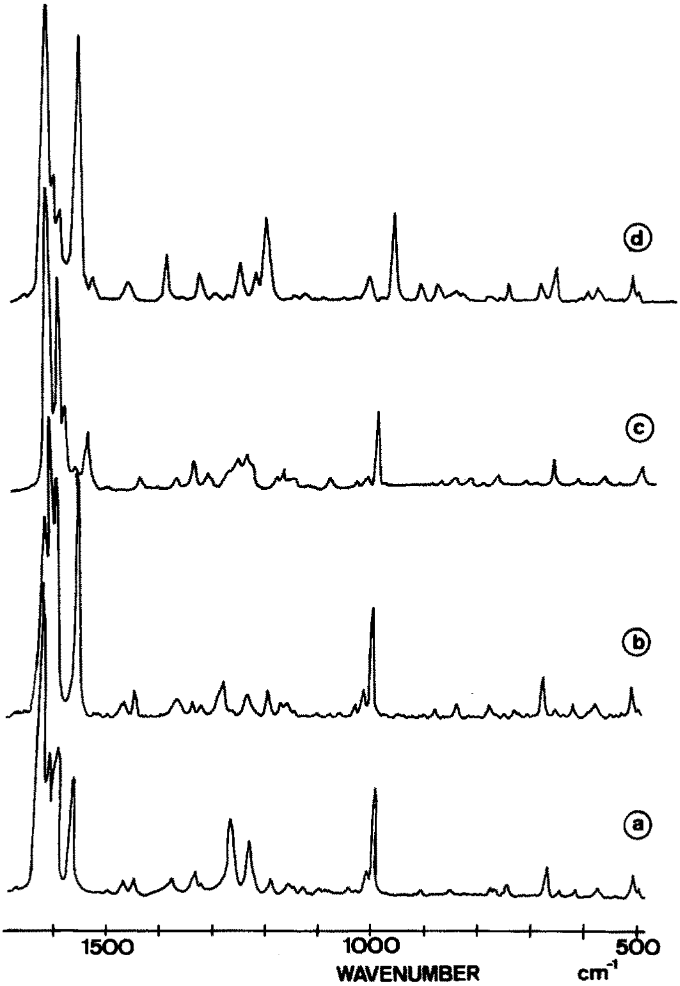

Fig. 3. Solid state FT-Raman spectra of flavone (a), flavone-3d (b), flavone-d4 (c) and flavone-d5 (d); excitation: 1.06 μm.

as a shoulder on the IR spectrum. In the CCl_4 Raman spectrum, this line appears at 1624 cm^{-1}. This assignment (in relative accordance with the calculation) is strengthened by the fact that no sensitive shift is detected with isotopic substitutions as for the carbonyl stretching mode. The corresponding Raman frequency in solution is observed to be a little higher than in the solid state. This fact enhances the hypothesis of a stronger conjugation between the B and C rings through the C2–C1′ linkage in solid state. Then, the decreased double bond character of the C2–C1′ linkage in solid state. Then, the decreased double bond character of the C2–C1′ bond normally involves a decrease in the corresponding stretching vibration. The frequency calculations and the graphic representation of the atom displacements shown on Fig. 5a tend to confirm this assignment. The 8a and the 8b modes of the A and B ring systems occur between 1610 and 1570 cm^{-1} [9–12]. The deuteration affects the respective frequencies only slightly since only skeletal vibrations are involved. Nevertheless, it appears very difficult to locate precisely the 8b mode of the A ring and 8a mode of the B ring in the flavone and in the flavones-d4 and -d5 spectra. Because of this, we assume there exists either a mechanical coupling between both A and B ring systems or the two vibrations mentioned above are too close to be distinguished from each other. The 19a and 19b modes of the A and B ring systems are observed in the 1500–1445 cm^{-1} range [9–12]. As far as the A ring is concerned, for the flavone-d4 molecule, it appears difficult to estimate precisely the spectral shifts from the calculated values but we suggest including the corresponding mode in the 1349 cm^{-1} band which is relatively broad. As far as the B ring is concerned, the 1395 cm^{-1}

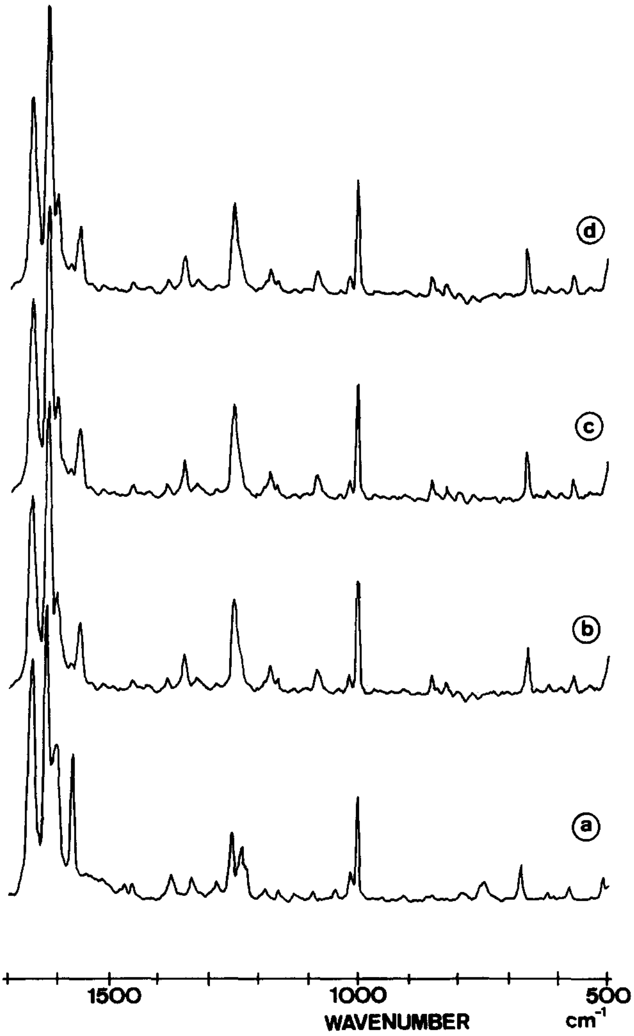

Fig. 4. FT-Raman spectra of flavone (a), flavone-3d (b), flavone-d4 (c) and flavone-d5 (d) in carbon tetrachloride solution (the solvent line has been subtracted).

frequency is presumably due to the 19a vibration in the flavone-d5 spectra, but the 19b mode cannot be obviously recognized. The 14 mode of the A ring appears near 1336 cm^{-1} [9, 11]. The 14 mode of the B ring could not be picked out from the substituted flavone-d5 spectra. In fact, either one may be implied in some mechanical couplings, or the IR and Raman intensities are too small to make it clearly appear in the 1330–1200 cm^{-1} range. We also expect to find in the 1400–1200 cm^{-1} range the C–O–C stretching modes of the chromone moiety. These bands are usually very strong [7]. In flavone, the only bands of appreciable strength in this region are located at 1378 and 1260 cm^{-1} in the IR spectrum [3]. In the solid state Raman spectrum, we notice two appreciable lines at 1377 and 1267 cm^{-1} whereas in carbon tetrachloride, they appear at 1374 and 1253 cm^{-1}, respectively. As will be mentioned later, the band near 1260 cm^{-1} mostly involves the inter-ring bond stretching vibration. So, the band close to 1378 cm^{-1} should result from the asymmetric stretching mode of the pyrone oxide function, especially since it does not seem to depend on the flavone physical state and does not present a significant shift with isotopic substitutions.

For this spectra range analysis, it is clear that the use of the nearest calculated wavenumber band of flavone is not convenient for a correct assignment. As the isotopic shifts are not significant, the use of the mode type performed by P.E.D. is more adapted.

Inter-ring stretching vibration: ν(C2–C1′). Several observed bands should involve the C2–C1′ inter-ring stretching mode. Coupling effects with deformations lead to a rather bad correlation with calculated wavenumbers. However, we suggest from the P.E.D. that the band which rises near 1260 cm^{-1} in the solid state IR and Raman spectra involves the main participation of the inter-ring bond stretching mode coupled nevertheless with all parts of the molecule (Fig. 5b). This assignment is partly confirmed by the frequency shift of $-14\,cm^{-1}$ in the Raman spectrum obtained from CCl_4 solution. Indeed, this band seems to be sensitive to the conformational structure of flavone which is different dependng on whether the molecule lies in solution (with a twisted structure) or in solid state (with a planar structure) [8].

Radial skeletal vibrations: Δ(C–C). The band at 1000 cm^{-1} which appears in the Raman spectra of the flavone molecule is typically characteristic of the linear combination of the 1 and 12 'breathing' modes of the B ring. The spectra of flavone-3d and flavone-d4 still contain this band while the spectra of the derivative -d5 show the corresponding shifted components at 959 cm^{-1}. The frequencies pertaining to the 6b and 6a vibrations of the A and B rings lie in the 630–500 cm^{-1} region [9–12]. The 6b mode of the B ring appears in the IR and Raman spectra at 619 cm^{-1} even if the IR absorption band is very weak. It may be expected at 592 cm^{-1} in the flavone-d5 spectra. The 6a and 6b modes of the A ring have been respectively recognized at 577 and 511 cm^{-1} in the solid state Raman spectra of the flavone molecule (at 577 and 509 cm^{-1} in CCl_4 solution). Indeed, the disappearance of these two bands in the flavone-d4 Raman spectra tends to assume that they imply only one ring system. Although no corresponding frequencies could be found for the analogue -d4, they are probably located below 500 cm^{-1}. As for other vibrational modes in the 1200–1300 cm^{-1} spectral range, it is difficult to find the corresponding mode in the spectra of deuterated analogues. Indeed, the deuteration can entirely modify the normal modes.

Out-of-plane skeletal vibration: Γ(C–C). The strong IR band at 688 cm^{-1} is ascribed to the 4 mode of the B ring [9, 11, 12]. This mode is not observed in the Raman spectra maybe because of the weakness of its intensity. The 4 mode of the A ring is expected near 700 cm^{-1} [9–11] but in spite of the deuterated products spectra, no assignment has been tempted.

C–H *vibrational modes*

C–H *stretching modes*: ν(C–H). The corresponding components appear at 3071 cm^{-1} as a rather large spectral band in the Raman spectra of flavone. We simultaneously note the presence of two bands close to 3070 and 2295 cm^{-1} in each spectrum of the deuterated analogues. Frequency calculations and graphic outputs show that C–H stretching vibrations are specific of each ring (no coupling is expected—Fig. 5c) and occur in a small frequency range. Such information could explain the appearance of both experimental bands noted above which are in a ratio of about 1.34, i.e. not very far from $\sqrt{2}$.

C–H *in-plane bending vibrations*: δ(C–H). For this kind of vibration, it is well known that the use of a scaling factor of 0.89 is not suitable, and it is evident that a bad correlation between observed and calculated wavenumbers is obtained. However, the relative observed isotopic shifts are in quite good agreement with the calculated ones. The 15 modes of the B and A rings (or 9a with Varsanyi's notation) are observed at 1159 and 1148 cm^{-1}, respectively in the Raman spectrum (Fig. 5d) [9–12]. We assume that the first one shifts close to 840 cm^{-1} in the flavone-d5 spectra and the other near 850 cm^{-1} in the flavone-d4 spectra. The 9a mode of the B ring (Fig. 5e) that lies near 1193 cm^{-1} in the solid state IR and Raman spectra of flavone is observed at 876 cm^{-1} for flavone-d5 [9, 11]. The 1132 cm^{-1} Raman band and the 1129 cm^{-1} IR component are believed to pertain to the 9b mode of the A ring [9, 11]. This apparent frequency shift may be partly

Table 1. Calculated (Cal.), experimental frequencies (1700–500 cm^{-1}) for solid (sol.) and solution (CCl$_4$), and tentative assignments for flavone and deuterated analogues

Flavone				Flavone-3d				Flavone-d4				Flavone-d5					
	Raman		IR		Raman		IR		Raman		IR		Raman		IR	Tentative assignment	
Cal.	CCl$_4$	sol.	sol.	Cal.	CCl$_4$	sol.	sol.	Cal.	CCl$_4$	sol.	sol.	Cal.	CCl$_4$	sol.	sol.		
1812	1652	1634	1650	1811	1648	1628	1642	1811	1652	1631	1644	1812	1651	1634	1645		ν(C=O)
			1627				1629				1629				1629		
1657	1624	1619	1619	1651	1618	1616	1614	1656	1619	1615	1612	1656	1621	1617	1616		ν(C2–C3)
1584	1607	1603	1607	1584	1610	1604	1604	1584	1602			1580	1609	1604	1604	8b (A)	
																+	ν(C–C)
1581	1603	1603	1598	1580		1604	1604	1580		1600	1590	1584	1574	1571	1571	8a (B)	
1566	1572	1570	1579	1566	1565	1562	1579	1566	1575	1575	1574	1559		1539	1538	8b (B)	ν(C–C)
1575		1570	1570	1575	1565	1562	1570	1570	1557	1553	1551	1573		1571	1571	8a (A)	ν(C–C)
1452			1496	1452			1497	1438			1495	1444		1396	1395	19a (B)	ν(C–C)
1471	1475	1474	1475	1471	1478	1475	1476	1465	1347	1349	1349	1467		1475	1475	19b (A)	ν(C–C)
1435	1466	1469	1465	1435	1465	1468	1469	1423	1347	1349	1349	1423	1467	1468	1469	19a (A)	ν(C–C)
1396	1451	1451	1448	1396	1449	1449	1447	1395		1453	1451	1352		1325	1326	19b (B)	ν(C–C)
1349	1374	1377	1378	1346	1364	1370	1370	1344	1385	1383	1382	1333	1395	1396	1381		ν(C–O–C)
1230	1331	1336	1336	1234	1335	1340	1339	1218		1325	1325	1232		1335	1334	14 (A)	ν(C–C)
1227		1325		1227		1322		1227	1322	1325		1210				14 (B)	ν(C–C)
1173	1282	1280	1283	1173	1291	1290	1282	1173	1282	1280	1285	914		1007	1004	3 (B)	δ(C–H)
1151			1283	1151		1283	1282	916			1015	1151		1279	1278	3 (A)	δ(C–H)
1302	1253	1267	1260	1302				1290	1248	1265		1281	1250	1257			ν(inter-ring)
	1234	1236	1235		1235	1237				1235						(B)	
	1224	1228	1225		1223	1225	1227		1225				1224	1227	1227		
			1204								1204				1205	(C)	

1101	1185	1193	1192	1099	1189	1195	1193	1100	1188	1193	1193	789		876	876	9a (B)	δ(C–H)
1066	1159	1159		1066	1160	1161		1066	1160	1159		772		842		15 (B)	δ(C–H)
1070	1148	1148		1070		1146	1146	764	852	851	856	1070		1150	1148	15 (A)	δ(C–H)
1055	1127	1132	1129	1053			1128	802	852	851	856	1053		1131	1126	9b (A)	δ(C–H)
	1089	1092	1101							1090				1096			
1046		1080	1079	1044		1080	1080	1046	1082	1080	1076	761		830	830	18b (B)	δ(C–H)
			1044				1031				1028				1042		
983		1030	1028	986	1030	1031	1031	985			1028	765		842	840	18a (B)	δ(C–H)
	1014	1013	1011		1018	1016	1013		1018	1018	1015						
885	1001	1000	1001	888	1001	1000	1000	872	1001	1000	1000	870	960	959	959	1 + 12 (B)	Δ(C–C)
899		975	973	899		977	974	899		977	974	797			801	5 (B)	γ(C–H)
882		960	959	882			960	882			959	742			757	17a (B)	γ(C–H)
857			924	857			925	857			926	733		744	743	17b (B)	γ(C–H)
874	908	908	909	874	909	908	906	735				874		908	907	17b (A)	γ(C–H)
830	850	852	853	759		803	803	830	852	851	852	832		852	856		γ(C3–H)
	835	838	844		832	836											
			781				775								775	(A)	
725		771	769	722		767	771	725		771	771	614		538	536	11 (B)	γ(C–H)
732	744	748	760	728		744	760	572			580	730		744	757	11 (A)	γ(C–H)
			688				688				685				601	4 (B)	Γ(C–C)
	673	674	673		673	674	672								672		
	650	650	652			652	650			655	653			655	654		
585	619	619	620	585	620	618	618	585	620	619	618	562		593	592	6b (B)	Δ(C–C)
	608	606	608				606								601		
	577	577			577	577								575		6a (A)	Δ(C–C)
555	509	511		557		509		546				552		511		6b (A)	Δ(C–C)

The notation ν, δ, Δ, γ and Γ refer respectively to stretching, C–H in-plane bending, radial skeletal vibrations, C–H out-of-plane bending and skeletal out-of-plane bending modes. The description of modes are only indicative; they correspond to the main character of the vibration. Only calculated frequencies which correspond to observed vibrational lines are tabulated.

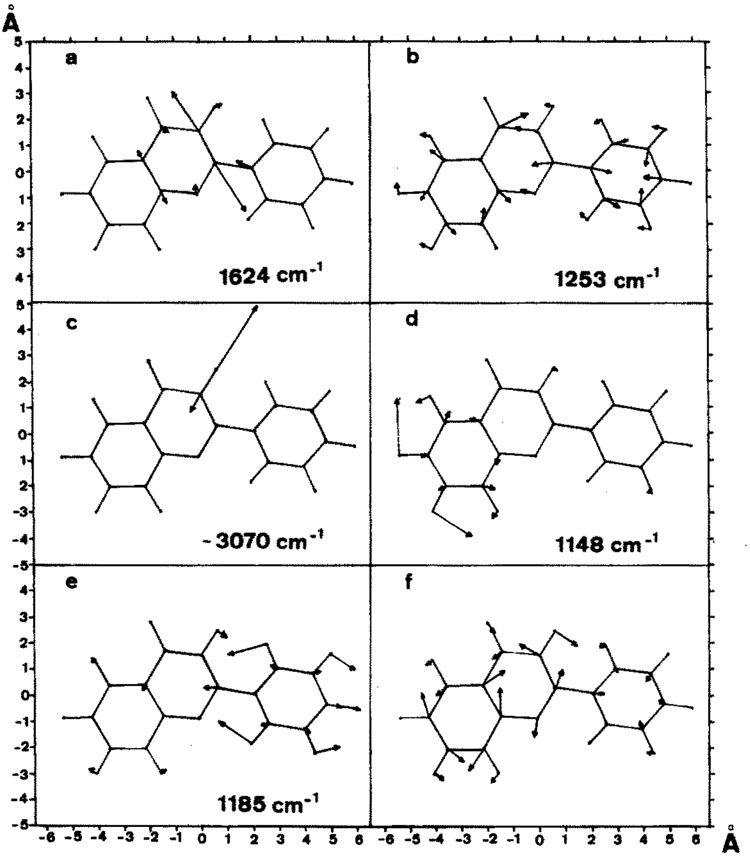

Fig. 5. Some graphic representations of calculated atomic displacements (multiplied by a factor of 3 for a better visualization): (a) the C2–C3 linkage stretching mode; (b) the C2–C1′ inter-ring stretching mode coupled with a vibration of the γ-pyrone part; (c) the C3–H stretching mode; (d) a typical δ(C–H) mode localized on the A ring: the 15 mode; (e) a typical δ(C–H) mode localized on the B ring: the 9a mode; (f) a typical vibrational mode which involves the whole molecule, not assigned in this study. The observed frequency in the Raman spectrum of flavone in CCl_4 solution is given for a, b, c, d and e illustrations.

explained by the KBr matrix effect as previously noted for the carbonyl stretching vibration. This mode may shift towards lower frequencies in the flavone-d4 spectra near 850 cm^{-1} and thus may be superposed with the C–H out-of-plane deformation of the pyrone group, which will be discussed later. The 3 modes of the A and B ring systems respectively appear near 1280 cm^{-1} in the solid state IR spectrum of the flavone molecule [9–12]. For the deuterated molecule -d5, the 3 mode of the A ring does not move, whereas that of the B ring shifts to 1004 cm^{-1}. For the flavone-d4, the isotopic substitution involves a frequency shift of the band corresponding to the 3 mode of the A ring (1015 cm^{-1}). This shift, less important than expected, is probably due to a mechanical coupling with vibrational modes of the rest of the molecule. The 18a and 18b vibrations of the B ring system presumably appear in the solid state IR spectrum at 1028 and 1079 cm^{-1}, respectively [9, 11, 12]. We suggest that they shift towards 840 and 830 cm^{-1} in the flavone-d5 spectra [9] which present many weak and thin bands in this spectral range.

C–H *out-of-plane bending vibrations*: λ(C–H). As previously mentioned for in-plane bending modes, these vibrations are assigned mainly with the help of P.E.D. and isotopic shifts.

The 973 cm^{-1} weak IR band possibly corresponds to the 5 mode of the B ring system [9, 11], since such a vibration normally occurs in this spectral range and because it appears in all the deuterated spectra apart from the flavone-d5 spectrum, where it possibly corresponds to the very weak line at 801 cm^{-1} [9]. The spectral IR components at 955 and 924 cm^{-1} may respectively belong to the 17a and 17b modes of the B phenyl ring [9, 11, 12]. Such assignment is supported by the fact that they appear for both flavone-3d and flavone-d4 whereas they disappear for flavone-d5. These bands possibly shift near 750 cm^{-1}. A medium IR band and a very weak Raman component at 908 cm^{-1} may be ascribed to the 17b mode of the A ring [9, 11] since they both disappear in the flavone-d4 spectra, but the attempt made to recognize these bands was not decisive. The bands near 770 cm^{-1} in the Raman and IR spectra come from the 11 vibrations of the B ring [9, 11, 12]. If the corresponding spectral component is strong and rather broad for the IR absorption, it appears as a weak band in the Raman spectra. The 536 cm^{-1} band in the spectra of flavone-d5 may be characteristic of the substitution pattern on the B ring [9]. The band at 760 cm^{-1} in the IR absorption is supposed to represent the 11 mode of the A ring system whose frequency shifts to 580 cm^{-1} in the flavone-d4 spectrum [9, 11]. In a previous study [3], it has been shown that many chromone and flavone derivatives present a strong band near 850 cm^{-1} in IR spectra which may be ascribed to the C–H pyrone out-of-plane deformation mode. In flavone, the 853 cm^{-1} band, which is strong in IR absorption but very weak in Raman diffusion, may be assigned to this vibration. In addition, this frequency occurs in the flavone-d5 and flavone-d4 spectra and has a lower value (803 cm^{-1}) for the flavone-3d molecule.

Note

A relevant assignment has not been made for a certain number of infrared bands because they probably involve more than one ring of the flavone molecule. However, if we exclude the fact that some of them are native mechanical couplings, we can imagine that a majority results in overtones which could explain the apparent complexity of the infrared spectra.

CONCLUSION

The aim of this work was to obtain a better understanding of the structure of flavone. Even if some discrepancies are observed, the structural parameters obtained with the AM1 method give a satisfactory agreement with the vibrational spectra.

(i) The calculated wavenumbers are located in the same spectra range and almost in the same order as those observed in the experimental data.

(ii) For stretching modes, a good correlation between experimental and calculated values are obtained.

(iii) For bending modes for which the calculated wavenumber is far from the experimental ones, the calculated isotopic shifts are of the same order of magnitude as those observed in the spectra.

Analysis of the atomic displacement confirms that some vibrational modes retain their benzene ring character and we could assign some specific modes for rings A, B and C:

(i) ν(C–C) vibrations that gather the characteristic modes of substituted benzene 8a, 8b, 19a, 19b and 14 are located on the range 1600–1400 cm^{-1}.

(ii) The inter-ring stretching vibration is strongly coupled with all parts of the molecule even if it mainly contributes to a specific vibrational mode. It is interesting to notice the frequency shift from the solid state to solution which stresses the conformational difference of the flavone molecule depending on its physical state.

(iii) Γ(C–C) vibrations imply the modes number 4 and 16 of Wilson's notation. However, only the 4 mode of the B ring could have been located in the 700–500 cm^{-1} range.

(iv) As far as δ(C–C) vibrations are concerned, we found several bands characteristic of the 6 modes. We also noticed a Raman component at 1000 cm^{-1} which is rather weak and sharp in the IR spectrum of flavone and which corresponds to a linear combination of 1 and 12 modes of mono-substituted aromatic systems.

(v) ν(C–H) vibrations which appear in the Raman spectra near 3070 cm^{-1} as a large non-resolved band seem, to imply individual rings according to calculations and deuterated products spectra.

(vi) γ(C–H) vibrations which occur in the 900–700 cm^{-1} range are generally specific of only one ring system.

(vii) δ(C–H) vibrations are also well-recognized at typical frequencies of mono- and ortho-di-substituted benzene derivatives of the 1200–1000 cm^{-1} range.

We also assigned experimental bands to vibrators of the γ-pyrone part of the molecule such as the stretching vibrations of the groups C=O, C2–C3 and the out-of-plane bending vibration of the group C3–H. But we also had some difficulties in analysing the spectral region 1300–1200 cm^{-1} which is very complex and entirely modified with the deuteration (Fig. 5f). Thus, we assume it involves many mechanical couplings between C–H bending and C–C stretching vibrations.

The knowledge of the spectroscopic properties of flavone, which is the simplest structure of the flavonoids group, will be useful as a basis for the study of the vibrational spectra of flavonoid parent compounds.

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