Density functional theory study of FTIR and FT-Raman spectra of 7-acetoxy-4-methyl coumarin

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The solid phase FTIR and FT-Raman spectra of 7-acetoxy-4-methyl coumarin have been recorded in the regions 4000-50 cm^{-1} and 3500-100 cm^{-1}, respectively. The spectra were interpreted with the aid of normal coordinate analysis following full structure optimization and force field calculation based on density functional theory using standard B3LYP/6-311+G** method and basis set. All the normal modes of vibrations are assigned and calculations of total energy distribution (TED) are also performed.

1 Introduction

Coumarin has powerful anesthetic action and has been recommended for use in laboratory experiments on animals, as it has little effect upon the circulation. It readily excites vomiting in man, which renders it unsuitable as a hypbotic. Coumarin is used perfumery, not only on account of its own fragrance, but also for its property of fixing other odours. It is employed in pharmacy to disguise disagreeable odours, especially that of iodoform, for which purpose one part of coumarin is used to fifty parts of iodoform. It is also used in cigarette manufacture, in flavoring and to produce synthetic vanilla. It is also a normal constituent of lavender oil[1]. Owing to this applications of coumarin, an attempt has been made in this study to interpret the vibrational spectra of 7-acetoxy-4-methyl coumarin (7A4MC).

The assignments of band in the vibrational spectra of molecule are an essential step in application of vibrational spectroscopy for solving various structural chemical problems. In the present study, the detailed vibrational analysis of the title compound was performed by combining the experimental and theoretical information using Pulay's density functional theory[2] (DFT).

2 Experimental Details

The pure sample of 7A4MC obtained from Lancaster chemical company, UK and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of the title compound were recorded in the region 4000-50 cm^{-1}, at a resolution of ±1 cm^{-1} using a BRUKER IFS-66 V FTIR spectrometer equipped with dual detection: a cooled MCT detector for the mid-IR and a room temperature pyroelectric detector for the far-IR range using KBr and polyethylene pellets, respectively. Boxcar apodization was used for the 250 averaged interferograms collected for both the sample and background.

The FT-Raman spectra were recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA-106 FT-Raman accessory in the 3500-100 cm^{-1} stokes region. For that, Nd: YAG laser operating at 200mw power with 1064nm excitation was used as source. The reported wave numbers are accurate with ±1 cm^{-1}.

2.1 Computational details

Density functional calculations were carried out for 7A4MC with the 1998 version (G98-DFT) of the GAUSSIAN suite programs[3] at the Becke-3-Lee-Yang-Parr (B3LYP) functional[4,5] implemented with the standard 6-311+G** large basis set. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at

the fully optimized geometry by assuming the molecule belongs to C_s point group symmetry. The transformation of force field from Cartesian to internal local symmetry coordinates, the scaling, the subsequent normal coordinate analysis (NCA), calculation of total energy distribution(TED) were done on a PC with the version V7.0-G77 of the MOLVIB program written by Sundius[6,7].

3 Results and Discussion

3.1 Molecular geometry

The molecular structure of 7A4MC having C_s symmetry is shown in Fig.1. The global minimum energy obtained by DFT structure optimization for 7A4MC is calculated as-763.8140 Hartrees. The calculated optimized geometrical parameters obtained in this study for the title compound is presented in Table 1.

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 94 standard internal coordinates (containing 22 redundancies) for the title compound are presented in Table 2. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Pulay and Fogarasi[2,8] are summarized in Table 3. The theoretically calculated DFT force fields were transformed to this set of vibrational coordinates and used in all subsequent calculations.

3.2 Vibrational spectra

The title compound consists of 26 atoms and its 72 normal modes are distributed amongst the symmetry species as:

$$\Gamma_{3N-6} = 49\ a'\ \text{(in-plane)} + 23\ a''\ \text{(out-of-plane)}$$

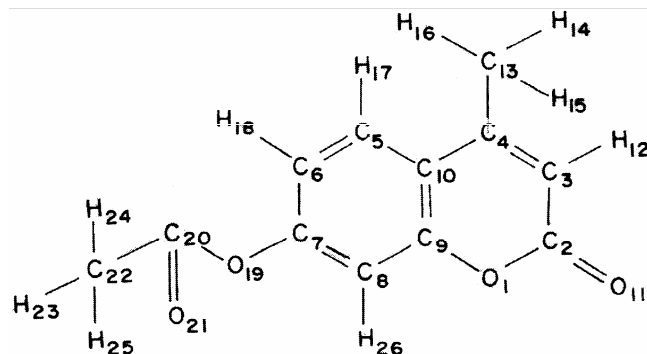All the vibrations are active both in the Raman scattering and infrared absorption. The detailed

Fig. 1 — Molecular structure of 7-acetoxy-4-methyl coumarin

vibrational assignment of fundamental modes of 7A4MC along with the calculated IR and Raman frequencies and normal mode descriptions (Characterized by TED) are presented in Table 4. The FTIR and FT-Raman spectra of the title compound are shown in Figs 2 and 3, respectively.

C-H *vibrations* — The title compound is fused with an aromatic and a heteroaromatic ring systems in which one of the ring is benzene. Hence, the molecular structure of the title compound shows the C-H stretching vibrations. The C-H stretching vibrations of benzene derivatives, generally, appear in the region 3000-3100 cm^{-1} which is the characteristic region for ready identification of C-H stretching vibrations[9,10]. In this region, the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation, the C-H vibrations have

Table 1 — Optimized geometrical parameters of 7-acetoxy-4-methyl coumarin obtained by B3LYP/6-311+G** density functional calculations

Bond length	Value (Å)	Bond angle	Value(°)
O_1-C_2	1.31	O_1-C_2-C_3	120.82
C_2-C_3	1.41	C_2-C_3-C_4	119.03
C_3-C_4	1.39	C_3-C_4-C_{10}	118.14
C_4-C_{10}	1.39	C_4-C_{10}-C_9	119.05
C_{10}-C_5	1.47	C_{10}-C_9-O_1	120.65
C_5-C_6	1.40	C_9-O_1-C_2	122.14
C_6-C_7	1.41	C_8-C_9-C_{10}	119.59
C_7-C_8	1.40	C_{10}-C_5-C_6	119.86
C_8-C_9	1.42	C_5-C_6-C_7	119.95
C_9-O_1	1.42	C_6-C_7-C_8	120.03
C_2-O_{11}	1.42	C_7-C_8-C_9	120.13
C_3-H_{12}	1.07	O_{11}-C_2-O_1	119.54
C_4-C_{13}	1.54	O_{11}-C_2-C_3	119.63
C_{13}-H_{14}	1.07	C_2-C_3-C_{12}	120.51
C_{13}-H_{15}	1.07	C_4-C_3-H_{12}	120.45
C_{13}-H_{16}	1.07	C_3-C_4-C_{13}	120.97
C_5-H_{17}	1.07	C_{10}-C_4-C_{13}	120.88
C_6-H_{18}	1.07	C_4-C_{13}-H_{15}	109.47
C_7-O_{19}	1.07	C_4-C_{13}-H_{14}	109.47
O_{19}-C_{20}	1.43	C_4-C_{13}-H_{16}	109.47
C_{20}-O_{21}	1.43	C_7-C_8-H_{26}	119.91
C_{20}-O_{22}	1.43	C_9-C_8-H_{26}	119.95
C_{22}-H_{23}	1.07	C_{10}-C_5-H_{17}	120.06
C_{22}-H_{24}	1.07	C_6-C_5-H_{17}	120.07
C_{22}-H_{25}	1.07	C_7-C_6-H_{18}	120.02
C_8-H_{26}	1.06	C_5-C_6-H_{18}	120.02
		C_7-O_{19}-C_{20}	109.47
		C_8-C_7-O_{19}	120.00
		C_6-C_7-O_{19}	119.96
		O_{19}-C_{20}-C_{22}	119.99
		O_{19}-C_{20}-O_{21}	120.00
		C_{20}-C_{22}-H_{23}	109.47
		C_{20}-C_{22}-H_{24}	109.47
		C_{20}-C_{22}-H_{25}	109.47
		C_9-C_{10}-C_4	119.01
		C_9-C_{10}-C_5	120.43

Table 2 — Definition of internal coordinates of 7-acetoxy-4-methyl coumarin

No(i) Stretching	Symbol	Type	Definition
1-4	r_i	C-H	C3-H12, C5-H17, C6-H18, C8-H26
5-10	r_i	C-H (methyl)	C13-H14, C13-H15, C13-H16, C22-H23, C22-H24, C22-H25
11-21	T_i	C-C	C2-C3, C3-C4, C4-C10, C10-C5, C5-C6, C6-C7; C7-C8, C8-C9, C9-C10, C10-C5, C5-C6, C6-C7, C4-C13, C20-C22
22-25	Q_i	C-O	C2-O1, C9-O1, C7-O19, C20-O19
26-27	Q_i	C=O	C2-O11, C20-O21
In-plane-bending			
28-33	β_i	Ring 1	O1-C2-C3, C2-C3-C4, C3-C4-C10, C4-C10-C9, C10-C9-O1, C9-O1-C2
34-39	β_i	Ring 2	C8-C9-C10, C9-C10-C5, C10-C5-C6, C5-C6-C7, C6-C7-C8, C7-C8-C9
40-47	δ_i	C-C-H	C2-C3-H12, C4-C3-H12, C10-C5-H17, C6-C5-H17, C5-C6-H18, C7-C6-H18, C7-C8-H26, C9-C8-H26, H26, C9-C8-H26
48-53	δ_i	C-C-H(Methyl)	C4-C13-H14, C4-C13-H15, C4-C13-H16, C20-C22-H23, C20-C22-H24, C20-C22-H25
54-59	α_i	H-C-H	H14-C13-H15, H14-C13-H16, H15-C13-H16, H23-C22-H24, H23-C22-H25, H24-C22-H25
60-61	Φ_i	O-C-C	O19-C7-C6, O19-C7-C8
62-65	ν_i	O-C-C(O)	O11-C2-C3, O11-C2-O1, O21-C20-C22, O21-C20-C19
Out-of-plane bending			
66-69	ω_i	C-H	H12-C3-C2-C4, H17-C5-C10-C6, H18-C6-C5-C7, H26-C8-C7-C9
70-71	ω_i	C-C	C13-C4-C3-C10, C22-C20-O19-C7
72-76	ω_i	O-C	O11-C2-O1-C3, O19-C7-C8-C6, O21-C20-O19-C22, O21-C20-C19-C7, O21-C20-C22-(H23-H24-H25)
77-78	ω_i	C-O	C20-O19-C7-C6, C20-O19-C7-C8
Torsion			
79-84	t_i	t Ring 1	O1-C2-C3-C4, C2-C3-C4-C10, C3-C4-C10-C9, C4-C10-C9-O1, C10-C9-O1-C2, C9-O1-C2-C3
85-90	t_i	t Ring 2	C8-C9-C10-C5, C9-C10-C5-C6, C10-C5-C6-C7, C5-C6-C7-C8, C6-C7-C8-C9, C7-C8-C9-C10.
91-92	t_i	τ C-CH$_3$	C10 (C3)-C4-C13-(H14-H15-H16), O19-C20-C22-(H23-H24-H25)
93-94	t_g	butterfly	O1-C9-C10-C5, C8-C9-C10-C4

been found at 3140, 3098, 3080 cm^{-1} in Raman and 3100 cm^{-1} in IR for the title compound. The C-H in-plane and out-of-plane bending vibrations have also been identified and presented in Table 4.

C-O *vibrations* — The presence of the carbonyl group in a molecule often gives rise to the appearance of the medium intensity band in the single bonded stretching region 1350-1200 cm^{-1}. A great deal of structural information can be desired for the exact position of carbonyl stretching absorption peak. The interaction of carbonyl group with other groups present in the system does not produce such a drastic and characteristic changes in the frequency of C-O stretch as does by interaction of N-H stretch. Further, if a compound contains a carbonyl group the absorption caused by C-O stretching is, generally, among the strongest present. The C-O stretching vibrations of 7A4MC are identified at 1331, 1266,

1250, 1217, 1198, 1171 cm^{-1} in IR and 1333, 1198 cm^{-1} in the Raman band. The assignments proposed for carbonyl groups of the title compound are in very good agreement with the assignment of Chithambarathanu *et al*[11].

C-C *vibrations* — The bands between 1400 and 1650 cm^{-1} in the aromatic and hetero aromatic compounds are assigned to C-C stretching vibrations[12,13]. Therefore, the C-C stretching vibrations of 7A4MC are observed at 1727, 1695, 1625, 1566, 1525, 1475, 1446, 1417, 1398, 1390 cm^{-1} and 1698, 1624, 1568, 1507, 1447, 1390 cm^{-1} in IR and Raman spectra, respectively. The in-plane and out-of-plane bending vibrations of C-C group are also listed in Table 4.

CH$_3$ *group vibrations* — For the assignments of CH$_3$ group frequencies, nine fundamental vibrations can be associated to each CH$_3$ group. Three

Table 3 — Definition of local symmetry coordinates of 7-acetoxy-4-methyl coumarin

No(i)	Symbol[a]	DefiniTion[b]	No(i)	Symbol[a]	DefiniTion[b]
1-4	CH	r_1, r_2, r_3, r_4	40-41	CH_3 ipb	$(-\alpha_{54}-\alpha_{55}-2\alpha_{56})/\sqrt{6}$,
5	CH_3 ss	$(r_5+r_6+r_7)/\sqrt{3}$			$(-\delta_{57}-\delta_{58}-2\alpha_{59})/\sqrt{6}$
6	CH_3 ips	$(2r_5+r_6+r_7)/\sqrt{6}$	42-43	CH_3 opb	$(\alpha_{54}-\alpha_{55})/\sqrt{2}$, $(\alpha_{57}-\alpha_{58})/\sqrt{2}$
7	CH_3 ops	$(r_6-r_7)/\sqrt{2}$	44-45	CH_3 ipr	$(2\delta_{48}-\delta_{49}-\delta_{50})/\sqrt{6}$,
8	CH_3 ss	$(r_8+r_9+r_{10})/\sqrt{3}$			$(2\delta_{51}-\delta_{52}-\delta_{53})/\sqrt{6}$
9	CH_3 ips	$(2r_8+r_9+r_{10})/\sqrt{6}$	46-47	CH_3 opr	$(\delta_{49}-\delta_{50})/\sqrt{2}$, $(\delta_{52}-\delta_{53})/\sqrt{2}$
10	CH_3 ops	$(r_9-r_{10})/\sqrt{2}$	48	bOC	$(\phi_{60}-\phi_{61})/\sqrt{2}$
11-21	CC	$T_{11},T_{12},T_{13}\ T_{14},T_{15},T_{16}\ T_{17},T_{18},T_{19}$	49-50	bOC	$(\nu_{62}-\nu_{63})/\sqrt{2}$, $(\nu_{64}-\nu_{65})/\sqrt{2}$
		T_{20},T_{21}	51-54	ωCH	$\omega_{66}, \omega_{67}, \omega_{68}, \omega_{69}$
22-25	CO	$Q_{22},Q_{23},Q_{24}\ Q_{25}$	55-56	ωCC	ω_{70}, ω_{71}
26-27	CO	Q_{26},Q_{27},	57-61	ωOC	$\omega_{72}, \omega_{73}, \omega_{74}, \omega_{75}, \omega_{76}$
28	R_1 trigd	$(\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33})/\sqrt{6}$	62-63	ωCO	ω_{77}, ω_{78}
29	R_1 symd	$(-\beta_{28}-\beta_{29}+2\beta_{30}-\beta_{31}-\beta_{32}+2\beta_{33})/\sqrt{12}$	64	tR_1trig	$(\tau_{79}-\tau_{80}+\tau_{81}-\tau_{82}+\tau_{83}-\tau_{84})/\sqrt{6}$
30	R_1 asymd	$(\beta_{28}-\beta_{29}+\beta_{31}-\beta_{32})/2$	65	tR_1sym	$(\tau_{79}-\tau_{81}+\tau_{82}-\tau_{84})/\sqrt{2}$
31	R_2 trigd	$(\beta_{34}-\beta_{35}+\beta_{36}-\beta_{37}+\beta_{38}-\beta_{39})/\sqrt{6}$	66	tR_1asym	$(-\tau_{79}+2\tau_{80}-\tau_{81}-\tau_{82}+2\tau_{83}-\tau_{84})/\sqrt{12}$
32	R_2 symd	$(-\beta_{34}-\beta_{35}+2\beta_{36}-\beta_{37}-\beta_{38}+2\beta_{39})/\sqrt{12}$	67	tR_2trig	$(\tau_{85}-\tau_{86}+\tau_{87}-\tau_{88}+\tau_{89}-\tau_{90})/\sqrt{6}$
33	R_2 asymd	$(\beta_{34}-\beta_{35}+\beta_{37}-\beta_{38})/2$	68	tR_2sym	$(\tau_{85}-\tau_{87}+\tau_{88}-\tau_{90})/\sqrt{2}$
34-37	bCH	$(\delta_{40}-\delta_{41})/\sqrt{2}$, $(\delta_{42}-\delta_{43})/\sqrt{2}$,	69	tR_2asym	$(-\tau_{85}+2\tau_{86}-\tau_{87}-\tau_{88}+2\tau_{89}-\tau_{90})/\sqrt{12}$
		$(\delta_{44}-\delta_{45})/\sqrt{2}$, $(\delta_{46}-\delta_{47})/\sqrt{2}$	70-71	tCH_3	τ_{91}, τ_{92}
38-39	CH_3 sb	$(-\delta_{48}-\delta_{49}-\delta_{50}+\alpha_{54}+\alpha_{55}+\alpha_{56})/\sqrt{6}$,	72	Butterfly	$(\tau_{93}-\tau_{94})/\sqrt{2}$
		$(-\delta_{51}-\delta_{52}-\delta_{53}+\alpha_{57}+\alpha_{58}+\alpha_{59})/\sqrt{6}$			

[a]These symbols are used for description of the normal modes by TED in Table 4
[b]The internal coordinates used here are defined in Table 2

Table 4 — Vibrational assignments of fundamental frequencies (in cm^{-1}) of 7-acetoxy-4-methylcoumarin

Sl.No	Species	Observed Frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Assignments (% TED)
		FTIR	FT-RAMAN		
1	a′	—	3140(vw)	3146	νCH(99)
2	a′	3100(vw)	—	3104	νCH(98)
3	a′	—	3098(w)	3094	νCH(96)
4	a′	—	3080(s)	3088	νCH(97)
5	a′	3046(w)	—	3041	CH_3ss(98)
6	a′	3020(w)	—	3023	CH_3ss(96)
7	a′	—	2933(ms)	2933	CH_3ips(90)
8	a′	2960(vw)	—	2966	CH_3ips(98)
9	a′	1727(w)	—	1719	νCC(91)
10	a′	1695(w)	1698(ms)	1699	νCC(89)
11	a′	1625 (s)	1624(vs)	1621	νCC(92)
12	a′	1566(w)	1568(s)	1569	νCC(90)
13	a′	1525(w)	—	1531	νCC(88)
14	a′	—	1507(w)	1516	νCC(87)

Contd

Table 4 — Vibrational assignments of fundamental frequencies (in cm^{-1}) of 7-acetoxy-4-methylcoumarin — *Contd*

Sl.No	Species	Observed Frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Assignments (% TED)
		FTIR	FT-RAMAN		
15	a′	1475(vw)	—	1484	νCC(86)
16	a′	1487(w)	—	1499	CH$_3$ipb(85)
17	a′	1453(w)	—	1450	CH$_3$ipb(84)
18	a′	1446(w)	1447(w)	1449	νCC(85)
19	a′	1417(ms)	—	1417	νCC(82)
20	a′	1398(w)	—	1396	νCC(81)
21	a′	1390(vw)	1390(vw)	1390	νCC(80)
22	a′	1373(s)	1375(s)	1375	CH$_3$sb(82)
23	a′	1364(vw)	—	1367	CH$_3$sb(83)
24	a′	1331(w)	1333(s)	1327	νCO(82)
25	a′	1266(s)	—	1264	νCO(83)
26	a′	1250(w)	—	1253	νCO(81)
27	a′	1217(s)	—	1216	νCO(78)
28	a′	1198(ms)	1198(vs)	1203	νCO(79)
29	a′	1171(w)	—	1168	νCO(78)
30	a′	—	1159(w)	1160	bCH(79)
31	a′	1131(vs)	—	1128	bCH(77)
32	a′	—	1125(w)	1123	bCH(75)
33	a′	1050(w)	—	1054	bCH(74)
34	a′	—	1035(vw)	1044	R$_1$trigd(72)
35	a′	1026(vw)	—	1032	R$_1$symd(71)
36	a′	1019(s)	—	1024	R$_{1a}$symd(70)
37	a′	985(ms)	984(w)	993	R$_2$trigd(73)
38	a′	981(vw)	—	992	CH$_3$ipr(71)
39	a′	977(w)	—	977	CH$_3$ipr(69)
40	a′	974(w)	—	970	R$_2$symd(68)
41	a′	962(vw)	—	963	R$_2$asymd(67)
42	a′	825(s)	—	824	bCC(66)
43	a′	—	813(vw)	812	bCC(65)
44	a′	793(ms)	794(w)	798	bCO(68)
45	a′	—	778(vw)	782	bCO(69)
46	a′	764(vw)	—	764	bCO(70)
47	a′	—	755(w)	758	bCO(64)
48	a″	2812(vw)	—	2816	CH$_3$ops(65)
49	a″	2795(w)	2795(w)	2796	CH$_3$ops(63)
50	a″	1163(w)	—	1167	CH$_3$opb(62)
51	a″	1156(s)	—	1153	CH$_3$opb(60)
52	a″	959(vw)	—	959	CH$_3$opr(61)
53	a″	—	945(w)	942	CH$_3$opr(62)
54	a″	904(s)		907	ωCH(60)
55	a″	881(s)	—	880	ωCH(58)
56	a″	860(w)	—	854	ωCH(59)
57	a″	—	850(w)	848	ωCH(61)
58	a″	742(vw)	—	750	tR$_1$trigd(57)
59	a″	736(ms)	—	737	tR$_1$symd(59)

Contd

Table 4 — Vibrational assignments of fundamental frequencies (in cm^{-1}) of 7-acetoxy-4-methylcoumarin — *Contd*

Sl.No	Species	Observed Frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Assignments (% TED)
		FTIR	FT-RAMAN		
60	a″	706(s)	—	708	tR$_1$asymd(58)
61	a″	—	693(ms)	695	tR$_2$ trigd(56)
62	a″	649(s)	650(w)	651	tR$_2$ symd(57)
63	a″	—	610(vw)	610	tR$_2$ asymd(56)
64	a″	—	440(ms)	441	ωCC(55)
65	a″	—	419(w)	424	ωCC(56)
66	a″	409(w)	—	412	ωCO(55)
67	a″	346(w)	—	349	ωCO(54)
68	a″	—	339(vw)	340	ωCO(56)
69	a″	312(ms)	—	312	ωCO(53)
70	a″	160(vw)	—	159	tCH$_3$(51)
71	a″	133(w)	134(w)	132	tCH$_3$(52)
72	a″	103(w)	—	104	butterfly(52)

w-weak, s-strong, ms-medium strong, vw-very weak, vs-very strong, R-ring, b-bending, ν-stretching, symd-symmetric deformation, ω-out-of-plane bending, asymd-antisymmetric deformation, trigd-trigonal deformation, ss-symmetric stretching, ips-in-plane stretching, sb-symmetric bending, ipb-in-plane-bending, ipr-in-plane-rocking, ops-out-of-plane stretching, opb-out-of-plane bending, opr-out-of-plane rocking, t-torsion.
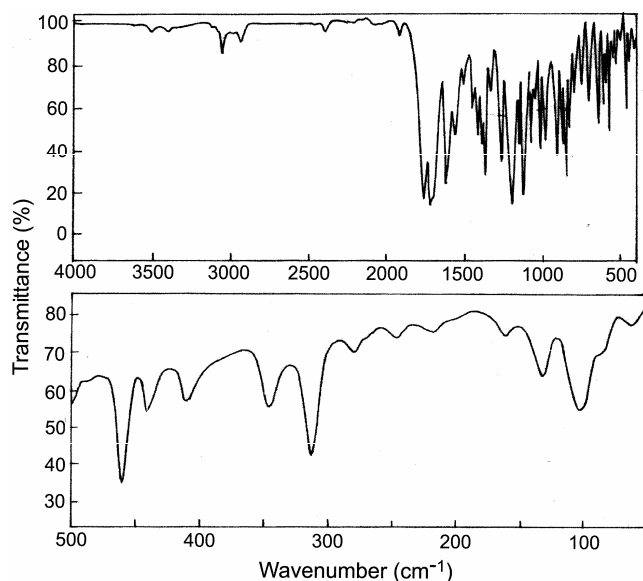

Fig. 2 — FTIR spectra of 7-acetoxy-4-methyl coumarin

Fig. 3 — FT-Raman spectrum of 7-acetoxy-4-methyl coumarin

stretching, three bending, two rocking modes and a single torsional mode describe the motion of the methyl group. The above modes are defined in Table 4. The CH$_3$ symmetric stretching vibrations are established at 3046, 3020 cm^{-1} and CH$_3$, in-plane stretching vibrations are identified at 2960 cm^{-1} in IR, 2933 cm^{-1} in Raman spectra. The CH$_3$ symmetric bending and CH$_3$ in-plane bending frequencies are attributed at 1373, 1364 cm^{-1} and 1487, 1453 cm^{-1}, respectively. These assignments are also supported by
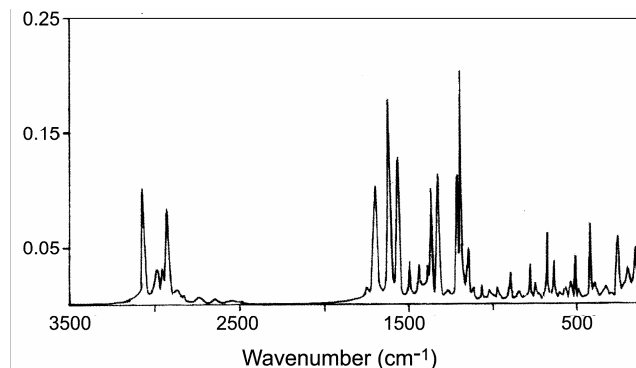
the literature[14,15]. The in-plane rocking and out-of-plane rocking modes of CH$_3$ group are found at 981, 977 cm^{-1} and 959, 945 cm^{-1}, respectively. The bands obtained at 2812 cm^{-1} in IR, 2795 cm^{-1} in both IR and Raman spectra and 1163, 1156 cm^{-1} in IR are assigned to CH$_3$ out-of-plane stretching and CH$_3$ out-of-plane bending modes, respectively. The assignment of the bands at 160, 133 cm^{-1} in IR and 134 cm^{-1} in Raman are attributed to methyl twisting modes.

4 Conclusions

The vibrational properties of 7A4MC have been investigated by FTIR and FT-Raman spectroscopies and were based on DFT calculations at the B3LYP/6-311+G** level. The assignments of the most of the fundamentals of the title compound provided in this

work are quite comparable and unambiguous. The closer agreement obtained between the calculated and the observed frequencies and the TED calculations are also supporting the assignments made for various functional groups present in the molecule. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title compound in the solid phase.

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