Characterization (FT-Raman, FT-IR Spectra) of 3.5-Dimethoxybenzaldehyde $C_9H_{10}O_3$ and Compared with (DFT)

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Abstract

In this work, both experimental and theoretical study on the FT-IR and Raman spectra of 3.5-dimethoxybenzaldehyde have been carried out. The FT-IR and FT-Raman spectra of the title compound have been recorded in the range of 4000–400 cm^{-1} and 3500–50 cm^{-1} respectively. The molecular geometry and vibrational frequencies in the ground state are calculated using the DFT method and assuming C_S symmetry. The infrared and Raman spectra were also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. The agreement between the calculated and experimental frequencies is very good: always better than 97% for the observed skeletal vibrations. This compound is characterized by the presence of two methyl groups, which makes the attribution of their vibrational modes difficult because of the presence of the low frequency modes attributed to the torsion movements CH_3.

Keywords: FT-Raman, FT-IR, DFT, 3.5-dimethoxybenzaldehyde

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1. Introduction:

This work is a part of a systematic study about the molecular vibrations behavior of 3.5-dimethoxybenzaldehyde in the solid state. One of the interests of these materials lies in the fact that they allow to study in details the influence of the molecular environment to perturb their symmetry. The dimethoxybenzaldehydes (DMBz) are often used as starting materials in condensation reactions forming Schiff base compounds. Schiff base compounds are versatile ligands in numerous metal–organic complexes that are used as a catalyst; it is used as a monomer in the production of various polymers such as polyesters, polyurethanes, and polycarbonates, Examples include C-O coupling reactions [1], the Suzuiki–Miyaura reaction [2], nitroaldol reactions [3] and a wide variety of other reactions [4]. The molecule has coplanar non hydrogen atoms as found in other similar structures [5]. The co planarity of methoxy groups with the benzene ring suggests the presence of a conjugation effect [6]. Herein, we report on one hand the molecular conformation and the spectroscopic behavior spectra of 3.5-dimethoxybenzaldehyde in the solid state. The DFT method has been proven to be a powerful tool in exploring molecular vibration spectra in computational physics, chemistry, and material science [7]. In the

present study, we extend the probing into the application of the B3LYP/6-311G++(d,p) (large basis set). The geometrical parameters of the most optimized geometry obtained via energy calculations were used for the DFT calculations (fig.1). The infrared and Raman intensities were also predicted, based on these calculations, the simulated FTIR and FT-Raman spectra were obtained (fig. 2 and 3). The observed and the simulated spectra agree well. From the experimental spectrum we have found in general the calculated frequencies with a few discrepancies of cm^{-1} from theoretical calculations using functional B3LYP. These differences are due to intermolecular interactions in the crystal. Here we present the results of TFIR and Raman spectroscopy, obtained from the DFT using the functional B3LYP and the basic set 6-311G++(d,p) that we compare with the experimental results observed in TFIR and Raman.

2. Experimental/Theoretical study

2.1. FT-IR Spectroscopy

The FT-IR spectra (500-3500 cm^{-1} region) were recorded on the Jasco (FT/IR-6300) spectrometer at room temperature with with 4.0 cm^{-1} resolution. Each band is characterized by its value of ν at the maximum of absorption.

2.2. Raman spectroscopy

The Raman spectra were made with µ-Raman Bruker Senterra in the range of 3500 to 100 cm^{-1}, equipped with a 100 mW laser source operated at λ =785 nm, and aperture setting about 20 ×1000 µm .

2.3. Quantum chemical calculations

The molecular geometry optimization, energy and vibrational frequency calculations of the title compound were carried out with Gaussian03 software package [8], using the B3LYP functional combined with standard 6-311G++(d,p) basis set, which has proven to give a very ground state geometry (see figure 1). The vibrational modes were assigned by means of visual inspection using the Gaussview program [9].

3. Results and discussion

3.1. Vibrational assignments

The optimized molecular conformation (bondlength and bondangles) of 3.5-dimethoxybenzaldehyde calculated by B3LYP/6-311G++(d,p) is shown in (Fig.1. (a), (b)), Additionally, we present the results of TFIR and Raman spectroscopy, obtained from the DFT using the functional B3LYP and the basis set 311G++(d,p) that we compare with the experimental results observed in TFIR and Raman. The spectra are reproduced in (Fig.2. (a), (b)) and (Fig.3. (a), (b)).

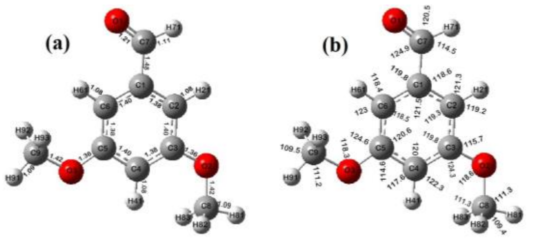

Fig. 1. Molecular conformation of 3.5-dimethoxybenzaldehyde (Cs symmetry) obtained from
B3LYP/6-311G++(d,p) : a) bond length (Å); b) bond angle (°).

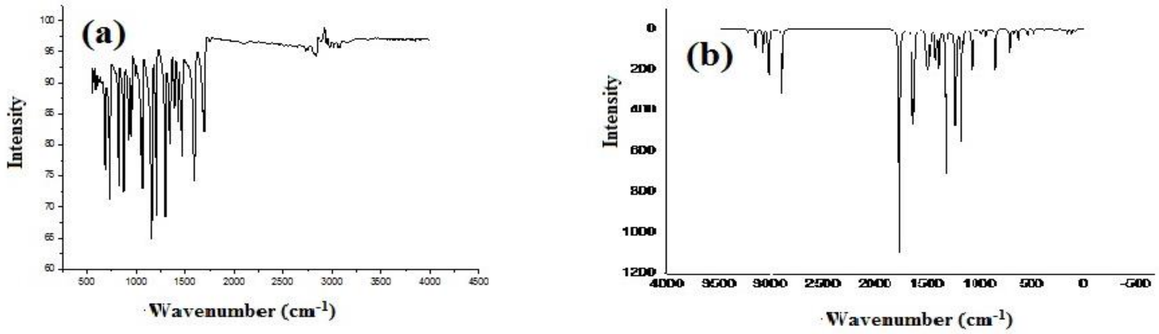

Fig. 2. IR spectra: a) experimental IR spectra; b) Theoretical IR spectra.

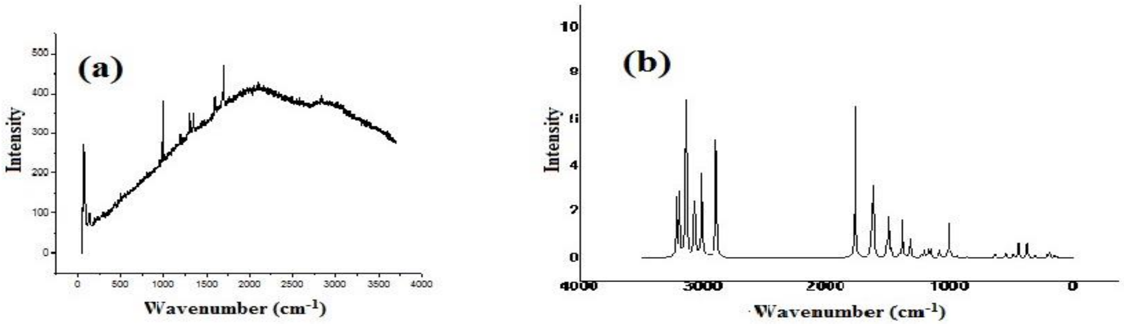

Fig. 3. Raman spectra: a) experimental Raman spectra; b) Theoretical Raman spectra.

From an overall point of view, three frequency domains can be distinguished: 16 frequency modes below 600 cm^{-1}, 34 between 600 and 1700 cm^{-1}, and 10 frequency modes above 1700 cm^{-1}. Among the 60 modes of vibration, 41 modes are active in FT-IR and Raman, 6 are active only in

Raman, 10 are active only in IR and the other 3 modes are not active. It is a fact that the DFT method systematically overestimates the vibrational wavenumbers because of the neglect of anharmonicity effects in the real system [10]. It is easy to discover that the main absorption peaks of the calculated spectra are mainly in accordance with those of the experimental spectra, demonstrating that the calculated results are dependable. However, there are some differences between the simulated spectra and the observed one, due to the thermal agitation animating the atoms at the ambient temperature, which are the conditions under which has taken place our manipulation. There are no imaginary frequencies in the results of vibrational analyses, indicating that all the computations were converged on a true energy minimum. The molecular conformation obtained by B3LYP/6-311G++(d,p) presents the greatest stability with a minimum training energy equal to -574.783 A.U. (Table l).

Table 1. Energy of minimal formation of 3.5-dimethoxybenzaldehyde.

	6-31G(d	6-31G(d,	6-31G	6-31G++(d	6-311G	6-311G(d	6-311G(d,	6 311G++(d
Energy minimum . [u.a.]	-574.620	-574.634	-574.452	-574.657	-574.595	-574.620	-574.771	-574.783

3.1.1. C-H vibration:

-The C-H and C-C related vibrations can help to determine the existence of aromatic rings in a structure. The C-H stretching vibrations of aromatic structures often occur in the range of 3000–3100 cm^{-1}. The nature of substituents has little influence on the band in this region [11]. For 3.5-dimethoxybenzaldehyde, the aromatic C-H stretching vibrations appear at 3018 cm^{-1} in the IR spectrum with weak peaks. Calculated at 3052 cm^{-1}.

-The aromatic C-H in-plane bending modes (Bip C-H) of benzene and its derivatives are observed in the region 1300-1000 cm^{-1} [12]. In IR spectrum, the frequencies 930S, 995W, 1073VS, 1163VS, 1200VS cm^{-1} are assigned to the C-H in-plane bending vibrations, peaks at 991vs and 1194s cm^{-1} were established in Raman spectrum.

-The C-H out-of plane bending (Bop C-H) modes are usually of weak intensity, arising in the region 1000-750 cm^{-1} [12]. In IR spectrum, the C-H out-of-plane bending vibrations are observed at 830VS cm^{-1} and 875VS cm^{-1}, these modes has not been detected in Raman spectrum (Table 2).

3.1.2. Methyl CH_3 vibrations

In aromatic compound, the CH_3 asymmetric stretching vibrations are expected in the range 3000–2925 cm^{-1} and the CH_3 symmetric vibrations are expected in 2940–2905 cm^{-1} the range.

-The symmetric stretching modes (Str sy C-H myth), (no. 52 and 53) calculated at 3008-3013 cm^{-1} give the weak Peak observed at 2842 w cm^{-1} in the Raman and 2885W cm^{-1} in the infrared.

-The four asymmetric stretching modes (Str asy C-H myth), of the methyl group are calculated in the region 3068–3138 cm^{-1} with (DFT) have been observed as broad infrared lines at 2946W and 2981W cm^{-1}. Peaks calculated in the region 1492–1507cm cm^{-1}, are assigned to the scissoring of CH_3 (scis myth). The rocking of CH_3 (rok meth) are found at 1163VS and 1200VS cm^{-1} in IR spectrum and 1194s cm^{-1} in Raman with the predicted frequencies at 1178, 1208 and 1228 cm^{-1} with (DFT). The CH_3 torsional (Tor meth) mode assigned at 150 to 250 cm^{-1}, These excitations of various origins do not facilitate their attributions because of their coupling, in particular between the methyl rotators and the molecular vibrations (see figure 4 and Table 2).

3.1.3. Aldehyde group vibration

The stretching (Str C-H aldehyd) characteristic of the aldehyde functional group absorption is the presence one weak band owing to C-H stretching vibrations. The frequency of this absorption is decreased from the normal C-H stretching position near 2850W cm^{-1} is easily (see Table 2 and Figs. 4.), The presence of absorption bands in this region is due to the symmetric and asymmetric stretching modes of the C-H band with C=O bond (see figure 4 and Table 2).

3.1.4. C= O vibrations

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiply bonded group is highly polar and therefore gives rise to an intense infrared absorption band. In the present study, the strong band observed at 1700s cm^{-1} in IR spectrum and at 1697s cm^{-1} in Raman spectrum , these modes calculated at 1764 cm^{-1}, was assigned to C= O stretching vibrations (Str C= 0) (see figure 4 and Table 2).

3.1.5. Ring group vibration

The C-H and C-C related vibrations can help to determine the existence of aromatic rings in a structure. The

ring stretching (Str ring) vibrations in benzene ring occur in the region 1430–1625 cm^{-1}. In general, the bands are of variable intensity and are observed at 1625-1590, 1575-1590, 1470-1540, 1430-1465 and 1280-1380 cm^{-1} from the frequency ranges. In the present work, the frequencies computed by DFT method at 1324, 1382, 1472, 1490, 1626, 1640 cm^{-1} have been designated to Ring stretching, these modes are observed at 1613S cm^{-1} in the Raman and 1434S, 1564S, 1590S cm^{-1} in the infrared spectra (see figure 4 and Table 2).

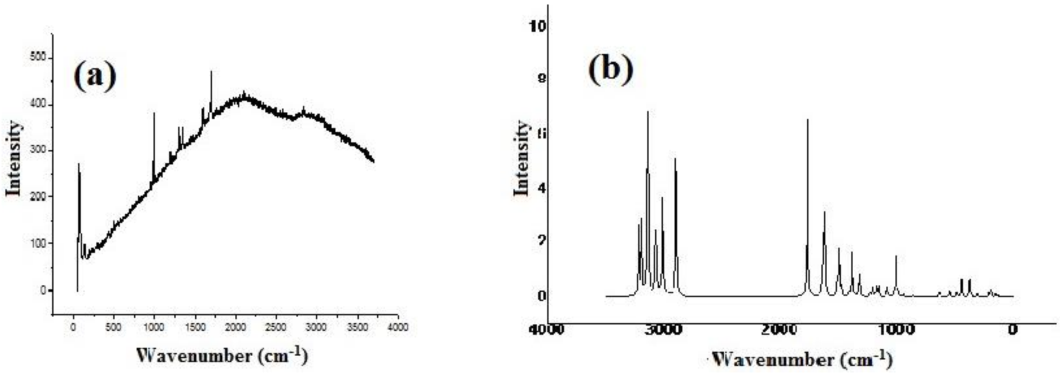

Fig. 4. Atomic displacements in 3.5-dimethoxybenzaldehyde.

Table 2. Comparison of the main calculated and experimental (FT-IR and Raman) vibrational spectra of 3.5-dimethoxybenzaldehyde

No	sym	EXP IR (cm^{-1})	EXP Raman (cm^{-1})	(DFT) B3LYP/6-311G++(d,p))			Assignments
				Cal. frequencies (cm^{-1})	I IR	I RAM	
1	A"		67vs	71	0.58	0.37	W meth
2	A"			88	5.69	0.50	W meth rok ring
3	A"		139w	121	10.3	0.91	W meth rok ring
4	A'			152	7.69	1.16	W meth
5	A'			184	1.44	1.10	W meth
6	A"			187	1.18	3.14	Tor meth
7	A"			203	0.8	1.85	Tor meth

					5		
8	A"			244	1.21	0.04	Tor meth W C-H ald
9	A"			268	2.20	0.11	Tor meth
10	A"			283	2.65	0.03	Tor meth Tor ring
11	A'			301	0.17	2.76	rok ring W meth
12	A'			370	2.21	8.75	rok O-C Bip ring
13	A'			447	5.09	7.84	rok O-C Bip ring
14	A'			484	8.46	2.08	Bip ring
15	A"			540	0.95	0.65	Tor ring Bop C-H
16	A'	558W	500w	545	9.40	2.63	W meth Bop C-H
17	A"			621	0.00	0.93	Bop C-H
18	A'	590W		631	17.8	1.94	W meth Bip ring
19	A"	680S		676	10.5	0.00	Bop C-H
20	A'	730VS		719	39.1	1.39	Bip ring rok C=O
21	A"	830VS		847	59.1	0.00	Bop C-H
22	A"			855	3.1	0.65	Bop C-H

					5		
23	A''	875VS		871	2.78	0.43	Bop C-H
24	A'			938	25.5	1.00	str O-C Bip ring
25	A'	930S	991vs	982	11.0	4.00	Bip C-H W meth
26	A'			1002	1.57	43.7	Breathing ring
27	A''			1021	0.97	2.69	W C-H ald
28	A'	995W		1076	36.5	4.93	Bip C-H str O-C
29	A'	1073 S		1086	54.7	1.04	Bip C-H
30	A'			1154	14.4	5.08	Bip C-H
31	A''			1167	0.53	2.90	rok meth
32	A''			1169	0.77	2.17	rok meth
33	A'	1163VS		1178	203	2.07	rok meth Bip C-H
34	A'		1194s	1208	1.49	6.53	rok meth Bip C-H
35	A'	1200VS		1228	212	2.15	rok meth Bip C-H
36	A'			1275	6.32	0.49	Bip C-H
37	A'	1295VS	1295s	1324	22	14.0	inbrella meth Str ring

					6		
38	A'	1350S	1353s	1382	86	44.4	Str ring inbrella meth
39	A'	1385S		1410	70.9	4.19	rok C-H ald
40	A'			1464	50.3	6.33	inbrella meth Bip C-H
41	A'			1472	24.3	5.25	Str ring Bip C-H
42	A'	1434S		1490	32.6	5.62	inbrella meth Str ring
43	A"			1492	0.98	19.5	scis myth
44	A"			1492	18.8	7.30	scis myth
45	A'			1498	32.3	0.96	scis myth Str ring
46	A'			1506	13.8	4.12	scis myth
47	A'			1507	33.3	4.53	scis myth
48	A'	1564S	1613s	1626	160	80.2	Str ring inbrella meth
49	A'	1590 S		1640	159	19.6	Str ring inbrella meth
50	A'	1697S	1700s	1764	320	139	Str C= 0
51	A'	2850W		2895	114	153	Str C-H aldehyd
52	A'		2842	3008	47.	171	Str sy C-H myth

			w		2		
53	A'	2885W		3013	45.0	155	Str sy C-H myth
54	A''			3068	33.2	54.7	Str asy C-H myth
55	A''	2946W		3075	31.6	48.1	Str asy C-H myth
56	A'	2981W		3138	22.6	121	Str asy C-H myth
57	A'			3138	16.9	129	Str asy C-H myth
58	A'	3018W		3186	1.31	80.1	Str C-H ring
59	A'			3215	1.15	74.7	Str C-H ring
60	A'			3221	4.72	38.2	Str C-H ring

Str: stretching; sy: sym. stretching; asy: asym. stretching; Bip: in-plane-bending; Bop: out-of-plane bending; w: waging; vs: very strong; s: strong; w: weak.

3. Conclusion

Both experimental and theoretical study on the FT-IR, Raman, of 3.5-dimethoxybenzaldehyde have been carried out. The optimized geometry was obtained by using the B3LYP functional combined with 6-311G++(d,p) basis set, The theoretical vibration frequencies present good agreement with the experimental values. The small difference between calculated and experimental wave numbers could be a consequence of the presence of vibrations of the intermolecular interactions in the crystals that were completely missing in the DFT calculation.

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