Geometry Optimization and Vibrational Analysis of 3-(4-Fluorophenyl) Propionic acid using Density Functional Theory

G.Velraj*, T.Kavitha, S.Ramachandran and H.Kayalvizhi

Department of Physics, Periyar University, Salem-11, Tamilnadu, India.

Email: gvelraj@yahoo.co.uk.

Abstract

The present work deals with the geometry optimization and vibrational analysis of 3-(4-Fluorophenyl) Propionic acid (34FPA) using quantum chemical calculations. The molecular vibrations of 34FPA were investigated by Fourier transform infrared and FT-Raman spectroscopy with Nd: YAG laser. The geometry, intermolecular hydrogen bond, Vibrational frequencies of the title compound have been investigated with the help of Density Functional theory (DFT) using B3LYP method with 6-311++G(d,p) basis sets.

Keywords: 3-(4-Fluorophenyl) Propionic acid, FT-IR, FT-Raman, DFT

Introduction

Propionic acid is manufactured primarily for the use of preservative and anti-mold agent in animal feed and grain. It is also used as a preservative and flavoring agent in packaged foods such as baked goods and cheese. Calcium propionate and sodium propionate, the salt forms of propionic acid, are used in bread and tortillas to prevent mold. In addition propionic acid is used as a chemical building block for the production of herbicides, pharmaceuticals, dyes, textile and rubber products, plastics, plasticizers, cosmetics, and perfumes [1, 2].

The aim of the present work is to describe and characterize the molecular structure, vibrational and electronic properties of the title compound. A comparison of the experimental and theoretical spectra can be very useful in making correct assignment and understanding the molecular structure relationship.

Experimental Details

The 34FPA sample in solid form purchased from Sigma-Aldrich Chemical Company with a stated purity of 97% is used as such without further purification. The standard KBr technique with 1: 100 mg of sample and KBr was used. The FT-IR spectrum of a sample was recorded in the region 4000-400 cm^{-1} at a resolution of ±4 cm^{-1} using BRUKER Tensor-27 FT-IR spectrometer. FT-Raman spectrum of the sample was recorded using 1064 nm line of **Nd: YAG laser** as the excitation wavelength in the region 4000-100 cm^{-1} on Bruker RFS 27 FT-Raman spectrometer. The liquid nitrogen-cooled Ge detector was used. Five hundred scans were accumulated at a resolution of ±4cm^{-1} using a laser power of 100 mW.

Computational Details

Gaussian09 software [3] was used in the calculations of geometrical parameters, vibrational frequencies etc. All the calculations were performed by using DFT/B3LYP method with 6-311++G (d,p) basis set in this study.

Results and Discussion

Molecular Geometry

The optimized structure given in Figure 1 and structural parameters of 34FPA were calculated at the B3LYP level of theory using 6-311++G (d,p) basis set. The geometry of the molecules under investigation considered to possess C_S point group symmetry and the corresponding minimum energy was calculated to be $E = -598.86165$ a.u. The bond length and bond angle values are tabulated in Table1.
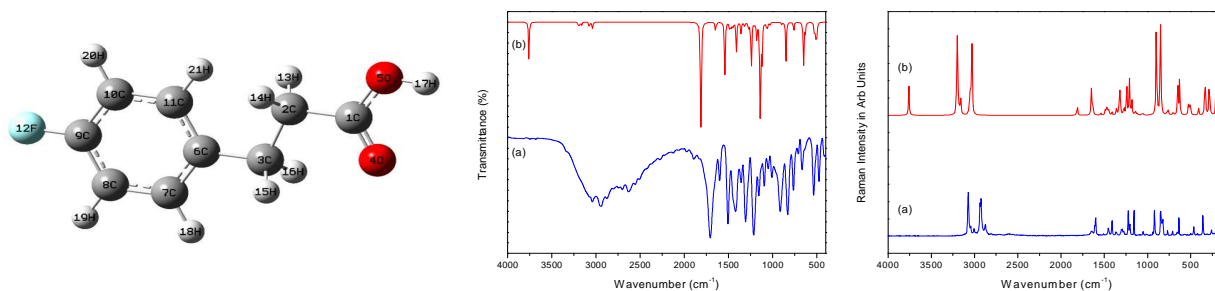
Figure 1.The optimized structure of 34FPA **Figure 2.** *FT-IR spectra: (a) observed; (b) calculated* **Figure 3.** *FT-Raman spectra: (a) observed; (b) calculated*

Table 1. *Optimized geometric data for 34FPA using B3LYP/6-311++G (d,p)*

Bond length	Value ($\overset{\circ}{A}$)	Bond length	Value ($\overset{\circ}{A}$)	Bond angle	Value ($^\circ$)	Bond angle	Value ($^\circ$)	Bond angle	Value ($^\circ$)
C_1-C_2	1.511	C_7-C_8	1.390	C_2-C_1-O_4	126.4	C_6-C_3-H_{15}	109.0	C_9-C_8-H_{19}	119.8
C_1-O_4	1.205	C_7-H_{18}	1.085	C_2-C_1-O_5	111.1	C_6-C_3-H_{16}	109.0	C_8-C_9-C_{10}	121.9
C_1-O_5	1.357	C_8-C_9	1.387	O_4-C_1-O_5	122.4	H_{15}-C_3-H_{16}	105.1	C_8-C_9-H_{12}	118.9
C_2-C_3	1.526	C_8-H_{19}	1.083	C_1-C_2-C_3	112.7	C_1-O_5-H_{17}	107.2	C_{10}-C_9-H_{12}	119.1
C_2-H_{13}	1.095	C_9-C_{10}	1.382	C_1-C_2-H_{13}	107.2	C_3-C_6-C_7	118.5	C_9-C_{10}-C_{11}	118.6
C_2-H_{14}	1.095	C_9-H_{12}	1.357	C_1-C_2-H_{14}	107.2	C_3-C_6-C_{11}	123.7	C_9-C_{10}-H_{20}	119.9
C_3-C_6	1.518	C_{10}-C_{11}	1.396	C_3-C_2-H_{13}	111.7	C_7-C_6-C_{11}	117.8	C_{11}-C_{10}-H_{20}	121.4
C_3-H_{15}	1.094	C_{10}-H_{20}	1.082	C_3-C_2-H_{14}	111.7	C_6-C_7-C_8	121.7	C_6-C_{11}-C_{10}	121.4
C_3-H_{16}	1.094	C_{11}-H_{21}	1.082	H_{13}-C_2-H_{14}	105.8	C_6-C_7-H_{18}	119.3	C_6-C_{11}-H_{21}	120.5
O_5-H_{17}	0.969			C_2-C_3-C_6	115.7	C_8-C_7-H_{18}	118.9	C_{10}-C_{11}-H_{21}	118.0
C_6-C_7	1.402			C_2-C_3-H_{15}	108.7	C_7-C_8-C_9	118.4		
C_6-C_{11}	1.397			C_2-C_3-H_{16}	108.7	C_7-C_8-H_{19}	121.6		

Vibrational Analysis

The 57 fundamental modes of vibrations of the title compound were distributed in to the irreducible representation under C_S symmetry as $\Gamma 3N\text{-}6vib = 37A' + 20A''$. The vibrations of the A' species were in the plane and those of the A'' species are out-of-plane. All the frequencies are assigned in terms of fundamental, overtone and combination bands. All vibrations were active in both Raman scattering and infrared absorption. For visual comparison, the observed and calculated spectra of 34FPA are shown in Figure 2, 3 and Table 2 on a common frequency scale. Comparison between the calculated and observed vibrational spectra helps us to understand the observed spectral features.

C-H Vibrations

Aromatic compounds C-H stretching vibration commonly exhibits strong and medium bands in region of 3120-3000 cm^{-1}[4]. The calculated frequencies which lay in this region at 3041 cm^{-1} and 3072cm^{-1} in the title compound the experimental counter parts are appeared both are FT-IR and FT-Raman spectra, respectively; there was a good agreement between the experimental and calculated frequencies. The C-H symmetric and asymmetric stretching vibrations were occur in the frequency range 3000-2900 cm^{-1} and 3100-3000 cm^{-1}[5]. This is the characteristic region for the ready identification of C-H stretching vibrations. Accordingly, in the studied molecule, symmetric stretching vibrations of C-H were observed at 2876 cm^{-1} and 2936cm^{-1} in the FT-IR and FT-Raman spectra and asymmetric stretching vibrations of C-H were observed at 3006 cm^{-1} in the FT-Raman spectra. The C-H in-plane bending and out-of-plane bending vibrations were observed in the region of 1300-1000 cm^{-1} and 1000-675 cm^{-1}[6,7] for the investigated molecule C-H in-plane bending vibrations were observed at 1306, 1215, 1156, 1095, 1051, 1009 cm^{-1} and 1292, 1203, 1156 cm^{-1} in the FT-IR and FT-Raman spectra. C-H out-of-plane bending vibrations at 915 cm^{-1}, 765cm^{-1}, 710cm^{-1}, 667cm^{-1} and 920cm^{-1}, 822cm^{-1} in the FT-IR and FT-Raman vibrations respectively. The C-H rocking vibrations were observed in the region of 1174-724 cm^{-1} [8]. In the 34FPA compound, rocking vibrations of C-H were observed at 765 and 667 cm^{-1} in the FT-IR spectra.

Table 2*. The observed and calculated frequencies using B3LYP/6-311++G(d,p) and tentative vibrational assignment of 34FPA*

Modes	Experimental frequency(cm⁻¹)		Calculated frequency (cm⁻¹)			Vibrational Assignment (TED%)[b]
	FT-IR	FT-Raman	Scaled value	IR Intensity	Raman Intensity	
A′	3680vw	-	3664	74.62	49.76	υ_s O-H (100)
A′	-	-	3120	2.54	92.86	υ C-H (98)
A′	-	-	3119	3.17	56.16	υ C-H (97)
A′	3041s	-	3103	8.57	22.54	υ C-H (98)
A′	-	3072m	3082	7.87	32.90	υ C-H (96)
A″	-	3006vw	2998	12.78	1.87	υ_{as} C-H (97)
A″		-	2975	0.87	49.02	υ_{as} C-H (96)
A′	2876m	-	2963	12.70	4.60	υ_s C-H (96)
A′	2942s	2936m	2955	1.94	133.24	υ_s C-H (95)
A′	2701m	-	1767	305.58	17.80	υ C-O (40)
A′	1600m	1600vw	1606	17.56	48.33	υ C–C (61)
A′	-	-	1592	4.67	19.05	υ C–C (58)
A′	1506vs	-	1502	121.82	3.25	C-C Ring (81)
A′		1454vw	1448	19.80	14.11	δ C-H (46)
A′	1420s	-	1430	14.03	17.27	δ C-H (45)
A′		1414vw	1410	13.39	9.78	ω C-H (36) + τ Ring (31)
A′	1357m	-	1377	63.16	4.89	ω C-H (61)
A′	-	-	1324	24.66	10.72	ω C-H (48)
A′	1306vs	1292vw	1293	1.19	5.76	β C-H (37)+ υ C-C (29)
A″	-	-	1288	0.09	25.66	t C-H (63)
A′	-	-	1283	9.53	25.89	δ C-H (40) +ω O-H (29) + ω C-H (20)
A′	-	1222w	1242	14.84	15.53	ω O-H (39) + ω C-H (28)+ β O-H (22)
A′	1215vs	1203vw	1209	106.66	54.02	υ C-F (36) + β C–H (31)+ υ C–C (21)
A′	-	-	1177	1.91	57.15	ω C-H (46) + υ C-C(32)
A″	-	-	1171	0.78	1.17	t C-H (66)
A′	1156m	1156w	1150	33.20	25.42	β C-H (59)
A′	-	-	1113	244.28	7.53	β C-H (41) +ω C-H (30)+ β O-H (21)
A′	1095m	-	1093	93.48	2.65	β C-H (67)
A′	1051w	-	1037	19.24	3.34	υ C-C (53) + β C-H (28)
A″	-	-	1022	0.05	1.39	ρ C-H (54)+ β C-H (27)
A′	1009s	-	1005	6.26	0.39	β C-H (71)
A″	-	-	944	0.0026	0.05	γ C-H (73)
A″	915s	920w	921	0.16	0.04	γ C-H (43) + ρ C-H (38)
A′	-	-	874	5.22	153.68	υ C-C (44) + ω O-H (36)
A′	830m	848w	828	11.90	154.56	υ C-C (66)
A″	-	822vw	826	74.37	0.06	γ C-H (51) + ρ C-H (29)
A″	-	-	806	0.32	0.74	γ C-H (63)
A″	765vw	-	757	0.0002	3.16	ρ C-H (48) + γ C-H (38)
A′	710w	-	742	21.60	10.04	γ C-H (64)
A″	667w	-	680	0.47	5.34	ρ C-H (47)+ γ C-H (27)
A′	-	636vw	634	0.15	44.32	τ Ring(77)
A″	-	-	632	86.14	4.38	ω O-H (61) + ρ C-H (33)
A′	-	-	614	21.15	54.86	ρ C-H (36)+ω O-H (33)
A″	536m	-	511	30.30	24.85	ω O-H (35) + ρ C-H(39)
A″	-	-	500	22.70	1.88	γ C-H (41) + ρ C-H (36)
A′	-	-	492	22.66	21.08	ρ C-H (63)
A′	475m	464vw	485	21.49	1.81	τ Ring (71)
A″	416vw	-	409	0.01	0.31	γ C-H (66)
A′	-	-	399	0.20	10.66	τ Ring (74)
A″	-	359vw	325	2.77	79.90	ρ C-F (52) + ρ C-H (33)
A′	-	-	278	1.63	63.25	τ Ring (68)
A′	-	201vw	202	1.57	45.83	τ Ring (71)
A″	-	-	142	0.04	4.12	ρ C-H (44)+ ρ C-F (38)
A′	-	-	89	1.44	3.34	τ Ring(56)
A″	-	-	75	0.25	25.16	ρ C-H (44)
A″	-	-	25	1.59	484.12	τ Ring (54)
A″	-	-	18	0.02	8.35	τ Ring(55)

[a]*vs-very strong; s-strong; m-medium strong; w-weak; vw-very weak* [b]*γ-out of plane bending; β-in plane bending; ρ-rocking; δ-scissoring; υ-stretching υ_s-symmetric stretching; υ_{as}-asymmetric stretching; ω -wagging; t-twisting.*

The C-H scissoring vibrations were observed in the region of 1455-1435 cm⁻¹ [9]. In the present study, scissoring vibrations of C-H were observed at 1420 cm⁻¹ and 1454cm⁻¹ in the FT-IR and FT-Raman spectrum. The C-H wagging vibrations were observed in the region of 1418-1267 cm⁻¹ [10]. Accordingly, in the title compound, wagging vibrations of C-H were observed at 1357 cm⁻¹ and 1414, 1222 cm⁻¹ in the FT-IR and FT-Raman spectra.

C–C Vibrations

The aromatic C-C stretching vibrations were expected in the region of 1625-1400 cm^{-1} [11]. The carbon stretching vibrations of the title compound have been observed at 1600 cm^{-1} in the FT-IR and 1600 cm^{-1} in FT-Raman spectrum.

O-H Vibrations

Hydrogen bonding alters the frequencies of the stretching and bending vibrations. The O-H stretching bands move to lower frequencies usually with increased intensity and band broadening in the hydrogen bonded species [12]. In the title molecule study, the stretching vibrations of hydrogen groups were observed at 3680 cm^{-1} in FT-IR spectrum. O-H in-plane bending vibrations were observed in the region 1250-1152 cm^{-1}. The O-H in-plane bending was observed in 1215cm^{-1} in the FT-IR and 1222, 1203cm^{-1} FT-Raman spectra. The O-H group vibrations are likely to be the most sensitive to the environment, so they showed pronounced shifts in the spectra of the hydrogen-bonded species.

C-O and C-F Vibrations

The band due to C-O stretching vibration was observed in the region of 1850-1550 cm^{-1}. In the present work, the bands observed at 2701cm^{-1} FT-IR spectrum assigned to C-O stretching mode of vibrations, respectively. The C-F stretching modes originate from medium intensity infrared absorptions at 1215 cm^{-1} with counterparts at 1203 cm^{-1} in the Raman spectrum. These values were in accordance with the literature values [13].

Conclusions

In this work, the compound 34FPA was experimentally characterized by means of FT-IR and FT-Raman spectroscopic techniques with laser source for FT-Raman. The calculated geometrical parameters and vibrational frequencies obtained with Density Functional Theory Calculations using B3LYP/6-311++G (d,p) method were in agreement with the experimental values obtained for the investigated molecule.

References

[1]. Propionic Acid Product Information Sheet, the Dow Chemical Company, Form No. 327-00019-0405, 2 (February 2002).

[2]. N. Bizzari, N. Sebastian, with Blagoev, Milen, Propionic Acid, CEH Marketing Research Report: Chemical Economics Handbook, SRI Consulting, 6 November (2007).

[3]. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT (2010).

[4]. G. Varsanyl, assignments for vibrational spectra of seven hundred Benzene derivatives, academic kiaclo, Budapest (1973).

[5]. F.R. Dollish, W.G. Fateley, F.F.Bentley, Charecteristics Raman Freq of Organic Compounds, John Wiley, New York (1974).

[6]. V. Balachandran, J. Mol. Struct. 92, 137 (2012).

[7]. S. Prabu, spectroscopy acta part A: molecular and biomolecuar spectroscopy 103, 45 (2013).

[8]. N.B. Colthup, L.H. Daly, S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York (1990).

[9]. S.A. Brandan, F. Marquez lopez, M. Montejo, J.J. Lopez Gonzalez, A. Ben Altabef, spectrum. Acta part A 751, 422 (2010).

[10]. G.Varsanyl, Vibrational Spectra of Benzene Derivatives, Academic Press, New York (2001).

[11]. V. Krishnakumar, S. Muthunatesan, Spectrochimica Acta Part A., 65, 818 (2006).

[12]. J.P. Merrick, D. Moran, L. Radam, J. Phys. Chem., A 111, 11683 (2007).

[13]. E. Scrocco, J. Tomasi, in: P. Lowdin (Ed.), Advances in Quantum Chemistry, Academic Press, New York, (1978)