Ultra Scientist Vol. 25(1)B, 9-16 (2013).

Spectroscopic investigations of methyl trimethylacetate

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(Acceptance Date 24th January, 2013)

Abstract

FT-IR and FT-Raman spectra of methyl trimethyl acetate were recorded and analyzed. The vibrational wavenumbers were computing at HF and DFT levels. The data obtained from theoretical calculations are used to assign vibrational bands obtained experimentally. The results indicate that DFT method is able to provide satisfactory results for predicting vibrational frequencies. The predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability value shows that the title compound is suitable for nonlinear optical studies.

Key words: IR, Raman, DFT, acetate.

Introduction

Pivalic acid is the shortest chain tert-carboxylic acid. Atoms within a molecule occupy space. When atoms are crowded together and overlapped electron clouds, van der Waals repulsions produce a steric hindrance. Steric hindrance may influence conformational equilibria and reactivity. Although steric hindrance is sometimes a unfavorable structure due to less readily reaction, it can provide an escape from undesired side-reactions, can affect varying degrees of rate and energy and can produce the target derivatives which are more resistant to hydrolysis and oxidation than the derivatives from linear chain. Pivalic acid is a key intermediate for the target molecules which require hydrolytic stability and a variety of chemical resistance. Pivalic acid is used mainly in the form of chloride salt (pivaloyl chloride) which were obtained commercially from phosgene. It is used as an intermediate in the production of peroxides and peroxy-esters required for the polymer and agrochemical production. It is used as an intermediate to prepare pharmaceuticals (Ampicillin, Amoxycillin, Cephalosporins). 2,2-Dimethylbutyric acid is the next shortest chain tert-carboxylic acid which have similar application with pivalic acid. Pivalic acid does

occur in nature[1]. A biosynthetic pathway is not known, and it is most likely of anthropogenic origin: pivalic acid esters are established prodrugs. Pivalic acid was considered previously not to be biodegradable: it was and still is an established reference substance in the determination of volatile fatty acid production by rumen microorganisms[2,3]. However, pivalic acid in pharmaceutical wastewater was found to be biodegradable in a methanogenic upflow anaerobic bio-filter process[4] and in the denitrifying stage of a sequencing batch reactor. Vibrational spectroscopic study of acetate group is reported by Ibrahim and Koglin[5]. The assessment of solid state composition of an active salicylanilide compound by FT-Raman spectroscopy reported by Spiegeleer *et al.*[6]. Diclofenac sodium, which consists of a phenylacetate group, a secondary amino group, and a dichlorophenyl ring, is a well known representative of nonsteroidal anti-inflammatory drugs[7]. Computational study of the infrared spectrum of acetic acid, its cyclic dimer, and its methyl ester are reported by Lewandowski[8] *et al.*]. The molecular structure of acetic acid has been studied in the gas phase by both microwave spectroscopy[9,10] and electron diffraction[11]. Ball *et al.*[12] reported the FT-IR study of thermally induced transformations of trimethyl silylmethyl acetate in different temperature ranges. In the present study the FT-IR, FT-Raman and theoretical calculations of the wavenumbers of the Methyl trimethylacetate (methyl pivalate) are reported.

Experimental

The FT-IR spectrum was recorded using a DR/Jasco FT-IR 6300 spectrometer. The spectral resolution was 2 cm^{-1}. The FT-Raman spectrum was obtained on a Bruker RFS 100/s, Germany. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW.

Computational Details :

Calculations of the title compound were carried out with Gaussian09 software program[13] using the HF/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The DFT hybrid B3LYP functional method tends to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data[14]. The wavenumber values computed contain known systematic errors and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets[14]. The assignment of the calculated wavenumbers is aided by the animation option of Gaussview program, which gives a visual presentation of the vibrational modes[15].

Results and Discussion

IR and Raman spectra :

The observed IR, Raman and calculated (scaled) wavenumbers and assignments are given in Table 1. In the spectra of methyl esters, the overlap of the regions in which both asymmetric stretching[16] $\upsilon_{as}CH_3$ absorb with a weak to medium intensity (3020 ± 30 and 2990 ± 40 cm^{-1}) is not large and regularly seen above 3000 cm^{-1}. The symmetrical stretching mod υ_sCH_3 is expected in the range 2920±80 cm^{-1}

in which all the three C–H bonds extend and contract in phase[16]. The bands observed at 2976, 2953, 2935, 2909 in the IR spectrum, 3071, 3047, 3024, 3000, 2952, 2905 cm^{-1} in the Raman spectrum are assigned as the stretching modes of the CH_3 groups. The DFT calculations give values in the range 2930-3055 as these modes. With methyl esters, the overlap of the regions in which methyl asymmetric deformations are active (1460 ± 25 and 1450 ± 15 cm^{-1}) is quite strong, which leads to many coinciding wavenumbers[16]. The DFT calculations give 1491, 1474, 1471, 1466, 1462, 1457, 1453, 1450 cm^{-1} as $\delta_{as}CH_3$ and 1433, 1402, 1375, 1369 as δ_sCH_3 for the title compound. The bands observed at 1488, 1467, 1439, 1400, 1367 cm^{-1} in the Raman spectrum and at 1480, 1462, 1434, 1396, 1366 cm^{-1} in the IR spectrum are assigned as deformation bands of the CH_3 groups. The methyl rock ρCH_3 has been observed at 1185±35 cm^{-1}, often as a shoulder on the low wavenumber side of $\upsilon C(=O)O$ absorption[16]. The second methyl rock[16] absorbs at 1155±35 cm^{-1}. The bands calculated at 1270, 1217, 1195, 1149, 1139, 1028, 1021, 978 cm^{-1} are assigned as rocking modes of methyl group. The bands observed at 1283, 1193, 1155, 1036, 986 cm^{-1} in IR spectrum and at 1289, 1194, 1155, 1122 cm^{-1} in the Raman spectrum are assigned as the rocking modes of the methyl group.

The most characteristic band of esters arises from the C=O stretching vibration occurring at 1750 ± 50 cm^{-1} with a strong to very strong intensity[16]. Methyl esters of α-unsaturated and aromatic carboxylic acids[16] show $\upsilon C=O$ at 1725 ± 20 cm^{-1}. Seth Paul and Van Duyse[17] proposed 1733 ± 5 cm^{-1} for *o*-phtalic esters and Nyquist[18] identified the region 1730±15 cm^{-1} for mono and di-substituted methyl benzoates. The intensity of the carbonyl stretching band can increase through conjugation or formation of hydrogen bonds. The increase in conjugation, therefore, leads to the intensification of the Raman lines and increased IR band intensities. The stretching modes of the carbonyl group of the ester part may be lowered in the presence of conjugation[17]. For the title compound the C=O stretching mode is assigned at 1736 (IR), 1733 (Raman) and at 1745 (DFT) theoretically. The C(=O)O stretching vibration[16] often considered as the C–O–C asymmetric stretch, appears strongly at 1255 ± 60 cm^{-1}, a region in good agreement with that of the υC–O in carboxylic acids (1250 ± 80 cm^{-1}). The band at 1175 cm^{-1} (DFT) is assigned as the υC–O–C mode. The O–C stretching vibration of the O–CH_3 group, coupled with the methyl rock, appears in the wide region 975 ± 125 cm^{-1} with an intensity varying from weak to strong[16]. This vibration is often called the symmetric COC stretching vibration. The band at 944 cm^{-1} given by DFT calculation is assigned as this mode. The δC=O deformation[16] has been found in the region 710 ± 80 cm^{-1} and the band at 743 cm^{-1} (DFT) is assigned to this mode. The γC=O absorption[16] is in the range 625 ± 75 cm^{-1} and the DFT calculation gives this mode at 565 cm^{-1}. The C–C(=O)–O deformation[16] rock absorbs weakly to moderately in the region 435 ± 95 cm^{-1}. For most of the methyl esters, this rock falls in the region 445 ± 60 cm^{-1}. The skeletal C–O–C

deformation[18] appears in the region 325 ± 40 cm^{-1}. Saunders *et al.*[19] found 330 ± 15 cm^{-1} for a series of aliphatic methyl esters. The other deformations modes are also identified and assigned (table 1).

First hyperpolarizability :

Non-linear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase or other physical properties[20]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic image processing[21,22]. Many organic molecules, containing conjugated π electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy[21,22]. Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopies has evolved as a subject of research[23]. The first hyperpolarizability (β_0) of this novel molecular system is calculated using B3LYP/6-31G* method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry[24] of the energy in the external electric field. The calculated first hyperpolarizability of the title compound is 0.262 10^{-30} esu. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

In order to investigate the performance of vibrational wavenumbers of the title compound, the root mean square (RMS) value between the calculated and observed wavenumbers were calculated. The RMS values of wavenumbers were calculated using the following expression[25].

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\upsilon_i^{calc} - \upsilon_i^{\exp}\right)^2}$$ .The RMS error of the observed IR and Raman bands are found to be 20.00, 21.34 for HF and 9.00, 13.28 for DFT methods, respectively. The small differences between experimental and calculated vibrational modes are observed. This is due to the fact that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

Frontier molecular orbitals :

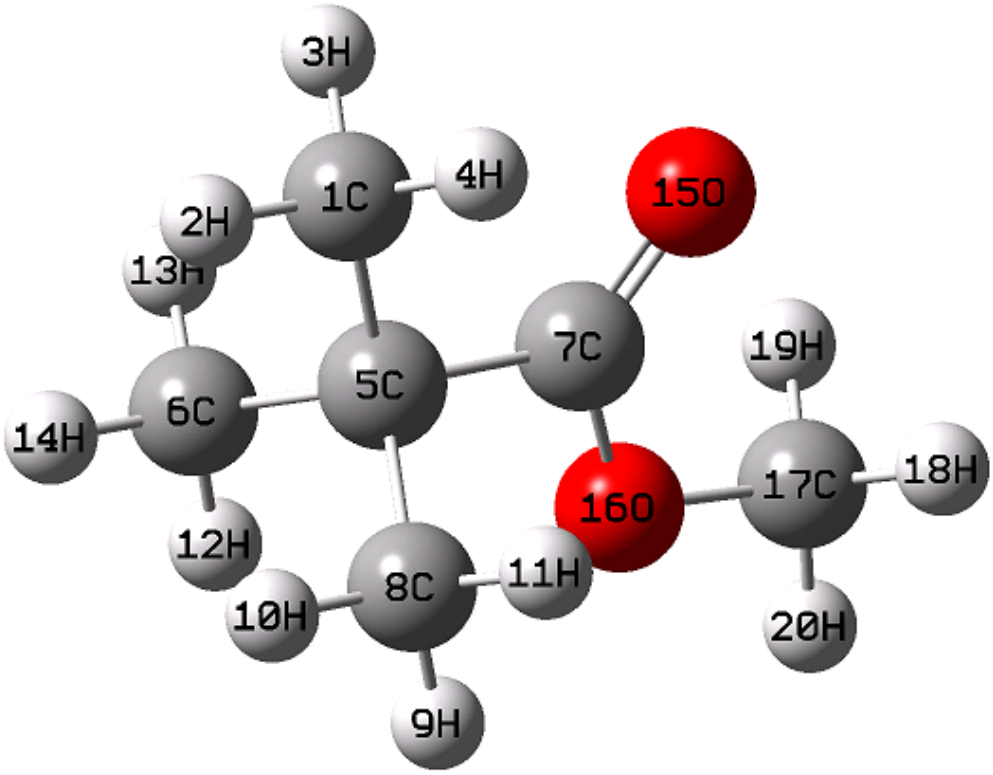
The analysis of the wavefunction indicates that the electron absorption corresponds to a transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to LUMO. Both the HOMO and the LUMO are the main orbital taking part in chemical reaction. The HOMO energy characterizes the capability of electron giving; LUMO characterizes the capability of electron accepting[26]. The frontier orbital gap helps to characterize the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule[27]. Surfaces for the frontier orbitals were drawn to understand the bonding scheme of the title compound. The calculated HOMO and LUMO energies are

Table 1. Calculated wavnumbers (scaled), observed IR and Raman bands and assignments

HF/6-31G*			B3LYP/6-31G*			IR	Raman	Assign-
υ (cm^{-1})	IR_I	R_A	υ (cm^{-1})	IR_I	R_A	$\upsilon(cm^{-1})$	$\upsilon(cm^{-1})$	ments
3048	16.48	70.28	3055	18.19	69.54		3071	$\upsilon_{as}CH_3$
3012	24.08	46.86	3025	23.30	50.25		3047	$\upsilon_{as}CH_3$
2995	40.30	100.48	3019	39.12	89.69		3024	$\upsilon_{as}CH_3$
2992	4.34	20.02	3018	24.73	62.85			$\upsilon_{as}CH_3$
2980	25.63	51.49	3015	0.11	4.85			$\upsilon_{as}CH_3$
2977	53.77	105.47	3007	38.03	87.67		3000	$\upsilon_{s}CH_3$
2960	25.47	56.82	2993	25.16	71.38			$\upsilon_{as}CH_3$
2940	13.80	22.67	2991	12.87	21.99	2976		$\upsilon_{as}CH_3$
2930	28.94	109.77	2954	32.89	111.84	2953	2952	$\upsilon_{as}CH_3$
2928	28.90	230.74	2942	24.91	195.07			$\upsilon_{s}CH_3$
2917	10.72	57.56	2932	11.61	82.38	2935		$\upsilon_{s}CH_3$
2897	43.30	3.90	2930	30.40	1.39	2909	2905	$\upsilon_{s}CH_3$
1696	250.74	3.63	1745	196.43	3.80	1736	1733	υC=O
1498	30.79	1.45	1491	21.40	0.56		1488	$\delta_{as}CH_3$
1483	17.53	4.40	1474	9.01	11.63	1480		$\delta_{as}CH_3$
1481	0.86	30.70	1471	5.38	13.29			$\delta_{as}CH_3$
1480	9.56	8.32	1466	6.91	19.18		1467	$\delta_{as}CH_3$
1474	0.40	51.64	1462	0.09	29.34	1462		$\delta_{as}CH_3$
1473	7.39	10.60	1457	0.06	21.71			$\delta_{as}CH_3$
1468	0.38	24.72	1453	5.79	19.11			$\delta_{as}CH_3$
1463	0.01	0.12	1450	0.04	0.09			$\delta_{as}CH_3$
1452	9.04	5.90	1433	4.43	5.28	1434	1439	$\delta_{s}CH_3$
1428	10.88	0.28	1402	8.59	0.97	1396	1400	$\delta_{s}CH_3$
1404	6.01	1.66	1375	3.45	2.37			$\delta_{s}CH_3$
1380	7.98	1.48	1369	3.47	2.36	1366	1367	$\delta_{s}CH_3$
1265	116.86	0.24	1270	70.46	0.21	1283	1289	ρCH_3
1234	4.54	2.86	1217	3.92	1.01			ρCH_3
1214	1.53	4.93	1195	2.30	2.29	1193	1194	ρCH_3

1195	286.42	3.61	1175	128.94	3.75			υC(=O)O
1167	142.19	4.10	1149	222.48	1.08	1155	1155	ρCH_3
1144	2.68	6.26	1139	0.90	5.25		1122	ρCH_3
1047	13.23	7.49	1028	13.64	6.25	1036		ρCH_3
1043	0.55	6.79	1021	0.23	4.94			ρCH_3
970	0.02	0.01	978	6.76	6.21	986		ρCH_3
961	18.00	10.51	944	0.02	0.01	940		υCOC
925	5.38	9.37	919	2.26	6.61			υCC
920	3.23	10.80	912	1.48	6.91			υCC
833	10.92	10.55	843	12.56	5.94	863		υCC
757	3.49	13.48	767	1.78	9.16			υCC
749	15.13	0.03	743	5.02	0.06			δC=O
566	7.52	9.45	565	2.34	7.68			γC=O
480	4.68	2.88	477	2.70	2.07		489	ρC(=O)O
370	2.21	0.26	366	1.02	0.20			δC-C
346	10.93	0.71	350	11.06	0.63		355	τC=O
330	0.19	1.40	328	0.40	1.16			δC-C
303	13.28	0.72	308	7.04	0.70			δC-C
278	5.97	0.35	277	2.62	0.31			τCH_3
256	0.02	0.04	251	0.06	0.04			τCH_3
244	3.71	0.15	245	1.65	0.12			τCH_3
206	0.89	0.04	202	0.29	0.03			τCH_3
184	4.28	0.15	192	1.67	0.16			τC-O-C
130	3.00	0.02	128	1.18	0.03			τCH_3
112	2.66	0.30	114	1.07	0.45		88	τCH_3
45	1.11	0.35	35	0.65	0.33			τC=O, τOCH_3

as-asymmetric; s-symmetric; υ-stretching; δ-in-plane deformation; ρ-rocking; τ-torsion.



-9.788 and -3.225 eV. The chemical hardness and softness of a molecule is a good indication of the chemical stability of the molecule. From the HOMO-LUMO energy gap, one can find whether the molecule is hard of soft. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft molecules. The soft molecules are more polarizable than the hard ones because they need small energy to excitation. The hardness value[26] of a molecule can be determined as η = (-HOMO+LUMO)/ 2. The value of η of the title molecule is 3.282 eV. Hence we conclude that the title compound belongs to hard material.

Conclusion

The optimized molecular structure, vibrational frequencies, corresponding vibrational assignments of the title compound have been investigated experimentally and theoretically using Gaussian09 software package. The geometry optimization has been carried out using HF and DFT levels. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in IR and Raman spectroscopy of the studied molecule. The calculated infrared intensities and Raman activities are reported. The calculated first hyperpolarizability value shows that the

title compound is suitable for nonlinear optical studies.

References

1. S.S. Schiffman, J.L. Bennett, J.H. Raymer. *Agric. For. Meteorol. 108*, 213 (2001).
2. J.W. Czerkawski, *Br. J. Nutr. 36*, 311 (1976).
3. J.W. Czerkawski, G.Breckenridge. *Br. J. Nutr. 38*, 371 (1977).
4. Y.F. Chen, W.J. Ng, M.G.S. Yap. *Resour. Conserv. Recycl. 11*, 83 (1994).
5. M. Ibrahim, E. Koglin, *Acta Chim. Slov. 51*, 453 (2004).
6. B. De Spiegeleer, B. Baert, N. Diericx, D. Seghers, F.Verpoort, L.V. Vooren, C. Burvenich, G. Slegers, *J. Pharm. Biomed. Anal. 44*, 254 (2007).
7. M. Tuncay, S. Calis, H.S. Kas, M.T. Ercan, I. Peksoy, A. A. Hincal, *Int. J. Pharm. 195*, 179 (2000).
8. H. Lewandowski, E. Koglin, R.J. Meier, *Vib. Spectrosc. 39*, 15 (2005).
9. W. Caminati, F. Scappini, G. Corbelli, *J. Mol. Spectrosc. 75*, 327 (1979).
10. B.P.van Eijck, J.van Opheusden, M.M.M. van Schaik, E.van Zoeren, *J. Mol. Spectrosc. 86*, 465 (1981).
11. J.L. Derissen, *J. Mol. Struct. 7*, 67 (1971).
12. I.K. Ball, P.H. Harrison, A. Torr, *J. Orgmet. Chem. 599*, 185 (2000).
13. *Gaussian09, Revision B.01*., M.J. Frisch *et al.*, Gaussian Inc., Wallingford CT (2010).
14. J.B. Foresman, E. Frisch, *Exploring Chemistry with Electronic Structure Methods, A Guide to using Gaussian*, Pittsburg, PA (1996).
15. *Gaussview Version 5*, R. Dennington, T. Keith, J. Millam, Semichem Inc. Shawnee Mission KS (2009).
16. N.P.G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York (1994).
17. W.A. Seth Paul, A. Van Duyse, *Spectrochim. Acta 28A*, 211 (1972).
18. R.A. Nyquist, *Appl. Spectrosc. 26*, 81 (1972).
19. J.E. Saunders, J. J. Lucier, F. F. Bentley, *Appl. Spectrosc. 22*, 697 (1968).
20. Y.R. Shen, The Principles of Nonlinear Optics, Wiley: New York (1984).
21. P.V. Kolinsky, *Opt. Eng. 31*, 1676 (1992).
22. D.F. Eaton, *Science 253*, 281 (1991).
23. M. Tommasini, C. Castiglioni, M. Del Zoppo, G. Zerbi, *J. Mol. Struct. 480*, 179 (1999).
24. D.A. Kleinman, *Phys. Rev. 126*, 1977 (1962).
25. T. Joseph, H.T. Varghese, C.Y. Panicker, K. Viswanathan, N. Sundaraganesan, N. Subramanin, M.Dolezal, *Global J. Anal. Chem. 3*, 1 (2012).
26. K. Fukui, *Science 218*, 747 (1982).
27. B. Kosar, C. Albayrak, *Spectrochim. Acta 78A*, 160 (2011).