Ultra Scientist Vol. 25(1)B, 1-8 (2013).

Vibrational spectroscopic study of 3-hydroxyacetophenone

RAJEEV. T. ULAHANNAN[1], R. RENJITH[1], J.B. BHAGYASREE[1], HEMA TRESA VARGHESE[2], and C. YOHANNAN PANICKER[1]

(Acceptance Date 24th January, 2013)

Abstract

The FT-IR and FT-Raman spectra of 3-hydroxyacetophenone were recorded and analyzed. The vibrational wavenumbers were calculated using HF and DFT methods. The predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability of the title compound is high and the title compound is an attractive object for future studies of non linear optical properties. The calculated HOMO and LUMO energies are -8.868 and -5.469 eV.

Key words: acetophenone, IR, Raman, DFT

Introduction

Carbonyl compounds make a large contribution to the production of free radicals and photooxidants in the atmosphere. Hydroxyacetone and glycolaldehyde have both biogenic and biomass burning sources. Hydroxyacetone and glycolaldehyde are also emitted during biomass burning. Hydroxyacetone and glycolaldehyde are precursors of other atmospherically relevant species[1]. Hydroxyacetone, is an interesting molecule from an astrophysical perspective. This compound exhibits the next level of molecular complexity in species that have carbon backbones with adjacent oxygen atoms, namely, glycolaldehyde[2,3], and ethyleneglycol[4]. In the laboratory, hydroxyacetone is an important starting material in the organic synthesis of gem-diols, acetals, and ketals[5]. If such molecules are synthesized in the interstellar medium, they could lead to the production of complex prebiotic species. In the present study the FT-IR, FT-Raman and theoretical calculations of the wavenumbers of the title compound are reported.

Experimental

The FT-IR spectrum (Figure 1) was recorded using a DR/Jasco FT-IR 6300 spectrometer. The spectral resolution was 2 cm^{-1}. The FT-Raman spectrum (Figure 2) 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[6] 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[7]. 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[7]. The assignment of the calculated wavenumbers is aided by the animation option of Gausview program, which gives a visual presentation of the vibrational modes[8].

Results and Discussion

IR and Raman spectra :

The observed IR, Raman and calculated (scaled) wavenumbers and assignments are given in Table 1. The carbonyl group is contained in a large number of different classes of compounds, for which a strong absorption band due to the C=O stretching vibration is observed in the region[9] 1750–1550 cm^{-1}. If a carbonyl group is part of a conjugated system, then the wavenumber of the carbonyl stretching vibration decreases, the reason being that the double-bond character of the C=O group is less due to the π-electron conjugation being localized. For the title compound, the υC=O mode is seen as a strong band at 1622 cm^{-1} in the IR and at 1644 cm^{-1} in the Raman spectrum and 1629 cm^{-1} theoretically (DFT). But the electron-releasing effect in the C=O double bond causes a polarizability change during vibration, making the Raman band intensity comparable to that of the IR band. Also, here the intermolecular charge transfer takes place via a conjugated phenyl ring path which makes the phenyl ring stretching mode at 1605 (IR), 1603 (Raman) cm^{-1} simultaneously active in the IR and Raman spectra[10]. The deformation bands of the C=O group are also identified (Table 1).

The asymmetric and symmetric vibrations of the methyl group in acetates are expected in the regions[11] 2940–3040 and 2910–2930 cm^{-1}. Aromatic acetyl substituents absorb in a narrow range 3000–3020 cm^{-1} absorption sometimes coincides with the CH stretching mode of the ring[11]. For the title compound methyl stretching vibrations are observed at 3043, 2988 cm^{-1} in the IR spectrum, 3047, 2927 cm^{-1} in the Raman spectrum and at 3052, 2993, 2931 cm^{-1} theoretically. The methyl asymmetric and symmetric deformations are expected in the regions[11] 1390–1480 and 1340–1390 cm^{-1}. The B3LYP calculations give 1467, 1453 and 1338 cm^{-1} as asymmetric and symmetric deformation bands. According to Colthup[12] in acetates the methyl next to the C=O absorbs near 1374 cm^{-1} due to symmetric deformation; the asymmetric methyl deformation absorbs weakly near 1430 cm^{-1}. The methyl rocking generally appears in the regions 1050 ±30 and 975±45 cm^{-1}, as a weak, moderate or sometimes strong band, the wave number of which is coupled to the CC stretching vibrations[11], which occurs in the neighborhood of 900 cm^{-1}. The bands at 1088, 1027 cm^{-1} in IR and 1026

cm^{-1} in the Raman spectrum and at 1081, 1037 cm^{-1} (DFT) are assigned as rocking modes of the methyl group. In O-bonded C(=O)Me group, the C-O stretching vibration exhibits[11] a strong band at 1750 ± 20 cm^{-1}. Esters and lactones have two characteristically strong absorption bands arising from C-O and C-O stretching. The intense C-O stretching vibration occurs at higher wave numbers than that of normal lactones. The force constant of carbonyl band is increased by the electron attracting nature of the adjacent oxygen atom due to inductive effect[13].

The OH group provides three normal vibrations υOH, δOH and γOH. The DFT calculations give the υOH band at 3528 cm^{-1}. The in-plane OH deformation[11] is expected in the region 1400 ± 40 cm^{-1} and the band at 1374 cm^{-1} (IR) and 1379 cm^{-1} (DFT) are assigned as this mode. The stretching of the hydroxyl group with respect to the phenyl moiety υ(C-O) appears at 1222 cm^{-1} in the IR spectrum, 1223 cm^{-1} in Raman spectrum and the calculated value is 1216 cm^{-1}. This band is expected[12, 14] in the region 1220 ± 40 cm^{-1}. The out-of-plane OH deformation is observed at 800 cm^{-1} in the IR spectrum and at 805 cm^{-1}, theoretically, which is as expected[11]. For paracetamol, υ(C-O) is reported[15] at 1240 cm^{-1}.

The υC–H vibrations of the phenyl ring are expected in the region 3000–3110 cm^{-1}. The vibrations assigned to aromatic C–H stretch in the range[11] 3077-3121 cm^{-1} are in agreement with the experimental results, 3145, 3098, 3067 (IR) and 3072 (Raman) cm^{-1}. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring near 1600, 1580, 1490 and 1440 cm^{-1}) are good group vibrations. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers. In the absence of ring conjugation, the band at 1580 cm^{-1} is usually weaker than that at 1600 cm^{-1}. In the case of C=O substitution, the band near 1490 cm^{-1} can be very weak. The fifth ring stretching vibration is active near 1315 ± 65 cm^{-1}, a region that overlaps strongly with that of the CH in-plane deformation. The sixth ring stretching vibration, or the ring breathing mode, appears as a weak band near 1000 cm^{-1}, in mono-, 1,3-di- and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the ring in-plane deformation[11, 14]. The band at 1000 cm^{-1} in the IR spectrum and the one at 992 cm^{-1} (B3LYP) are assigned as the ring breathing mode of the phenyl ring PhI. For the di-substituted benzene υPh modes are seen in the range[11] 1615–1270 cm^{-1}. For the title compound, the bands observed at 1605, 1578, 1499, 1433 cm^{-1} in the IR spectrum and at 1603, 1579 cm^{-1} in the Raman spectrum are assigned as the phenyl ring stretching modes. The DFT calculations give these modes at 1593, 1587, 1494, 1433 and 1323 cm^{-1}. The in-plane bending δCH and the out-of-plane bending γCH of the phenyl ring are expected above 1000 cm^{-1} and below 1000 cm^{-1}, respectively[11]. The in-plane CH deformation bands are assigned at 1290, 1169 cm^{-1} in the IR spectrum, 1277, 1175 cm^{-1} in the Raman spectrum and at 1286, 1171, 1143, 1073 cm^{-1} theoretically (DFT). The out-of-plane CH

deformation modes are observed at 979, 707 cm^{-1} in the IR spectrum and at 955 cm^{-1} in the Raman spectrum. The corresponding theoretically calculated values are 988, 951, 849 and 702 cm^{-1}. The phenyl ring substituent sensitive modes and other modes are also identified and assigned (table 1).

First hyperpoplarizability :

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[16]. Many organic molecules, containing conjugated π-electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy[17, 18]. Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopies has evolved as a subject of research[19]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing and dynamic image processing[17,18]. 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 $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry[20]. The calculated first hyperpolarizability of the title compound is 3.87 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[21].

$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\upsilon_i^{calc} - \upsilon_i^{\exp}\right)^2}$. The RMS error of the observed IR and Raman bands are found to 43.02, 35.42 for HF and 8.62, 6.65 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[22]. The frontier orbital gap helps to characterize the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule[23]. Surfaces for the frontier orbitals were drawn to understand the bonding scheme of the title compound. The

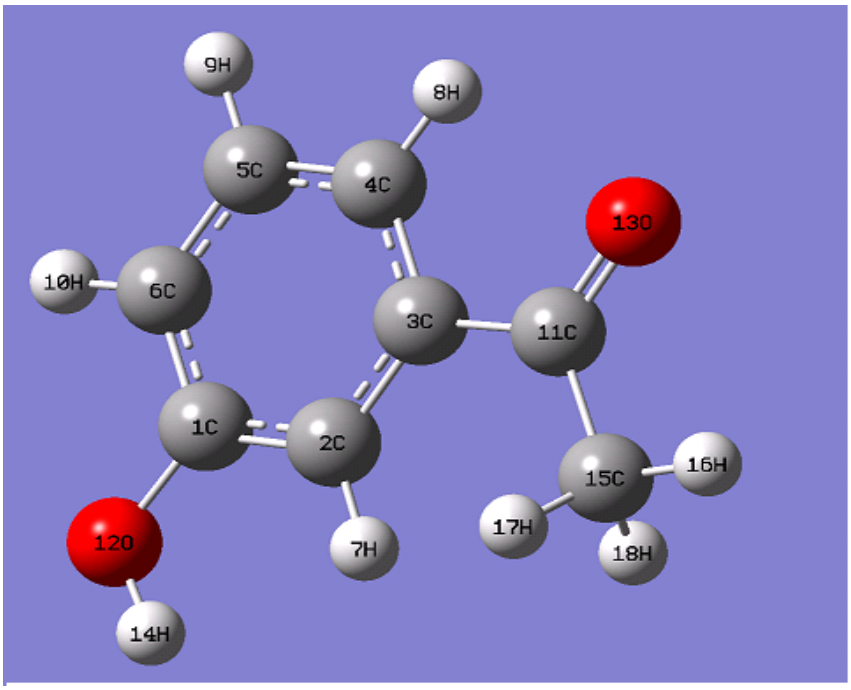
Table 1. Calculated wavnumbers (scaled), observed IR and Raman bands and assignments

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
3614	69.37	97.06	3528	28.13	124.67			υOH
3051	4.17	107.56	3121	6.85	135.30	3145		υCH
3042	3.27	100.53	3114	2.43	90.70			υCH
3015	7.83	93.53	3087	10.06	90.20	3098		υCH
3011	14.08	37.12	3077	12.90	45.03	3067	3072	υCH
2966	10.94	94.51	3052	10.96	93.24	3043	3047	$\upsilon_{as}CH_3$
2917	13.25	49.95	2993	11.40	47.96	2988		$\upsilon_{as}CH_3$
2859	4.07	106.65	2931	3.46	111.52		2927	$\upsilon_{s}CH_3$
1683	175.54	36.72	1629	84.04	23.60	1622	1644	υC=O
1616	36.70	58.82	1593	43.24	46.23	1605	1603	υPh
1608	72.93	34.33	1587	75.31	83.72	1578	1579	υPh
1503	6.17	1.02	1494	3.93	4.59	1499		υPh
1464	15.42	24.39	1467	13.72	25.51			$\delta_{as}CH_3$
1455	18.92	13.54	1453	21.66	11.46			$\delta_{as}CH_3$
1437	49.37	1.00	1433	49.69	1.53	1433		υPh
1400	33.30	3.66	1379	32.35	5.96	1374		δOH
1330	8.86	0.06	1338	17.72	2.76	1344	1344	$\delta_{s}CH_3$
1290	169.93	41.68	1323	3.33	0.12			υPh
1251	25.02	2.49	1286	173.40	47.32	1290	1277	δCH
1204	127.97	0.87	1216	93.93	1.37	1222	1223	υCO
1166	39.00	7.73	1171	6.39	5.24	1169	1175	δCH
1127	136.59	0.86	1143	211.32	5.24			δCH
1087	26.34	2.33	1081	25.08	0.77	1088		ρCH_3
1071	23.86	3.36	1073	9.62	8.82			δCH
1059	0.07	5.03	1037	1.61	2.49	1027	1026	ρCH_3
1047	3.33	0.29	992	3.78	29.54	1000		υPh
993	4.85	30.46	988	1.24	0.43	979		γCH
973	0.01	0.59	951	23.18	8.26		955	γCH

961	17.12	2.79	921	0.26	1.51	915	918	υCC
913	36.63	0.91	887	24.19	2.10	876	878	υCC
882	26.98	2.55	849	23.88	1.21			γCH
838	58.01	1.36	805	37.41	2.92	800		γOH
703	33.81	0.54	702	5.84	14.25	707		γCH
703	5.09	15.22	689	19.40	0.20	689	689	δPh(X)
641	3.33	1.102	628	0.26	0.44	622		δC=O
591	37.04	1.88	590	24.16	1.77		589	δPh(X)
524	2.12	5.10	523	1.68	4.77	522		γPh(X)
504	5.30	0.52	495	4.10	0.61		495	γC=O
474	6.18	1.23	472	5.66	1.35			δPh(X)
436	0.60	0.75	426	0.47	0.49			γPh(X)
365	19.69	3.29	367	15.94	3.91			δCC
354	2.04	4.37	356	1.80	4.99		355	δPh(X)
270	200.68	4.04	348	168.58	4.02			γPh(X)
239	13.22	1.33	235	0.78	1.68		228	δPh(X)
185	4.99	0.02	184	3.75	0.07			tPh
169	0.01	0.09	157	0.10	0.04		155	tPh
150	2.75	4.08	147	1.60	3.86			tCH_3
48	5.74	0.80	59	3.93	0.74			tCH_3

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ-rocking; t-torsion; Ph-phenyl ring; as-asymmetric; s-symmetric; X-substituent sensitive.

calculated HOMO and LUMO energies are -8.868 and -5.469 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[22] of a molecule can be determined as η = (-HOMO+LUMO)/2. The value of η of the title molecule is 1.7 eV. Hence we conclude that the title compound belongs to hard material.



Conclusion

The infrared and Raman spectra of the title compound have been recorded and analysed. Geometry and harmonic vibrational wavenumbers were calculated theoretically using Gaussian09 set of quantum chemistry codes. Calculations were performed at the Hartree-Fock and DFT (B3LYP) levels of theory using the standard 6-31G* basis. The calculated wavenumbers (DFT) agree well with the observed wavenumbers. Calculated infrared intensities, Raman activities and first hyperpolarizability are reported.

References

1. K. M. Spencer, M. R. Beaver, J. M. St. Clair, J. D. Crounse, F. Paulot, P. O. Wennberg, *Atmos. Chem. Phys. Discuss.*, *11*, 23619 (2011).
2. J.M. Hollis, F.J. Lovas, P.R. Jewell, *App. J. Phys. 540*, 107 (2001).
3. A.J. Apponi, D.T. Halfen, L.M.Ziurys, J.M. Hollis, A.J. Remijan, F.J. Lovas, *Appl. J. Phys. 643*, 29 (2006).
4. J.M. Hollis, F.J. Lovas, P.R. Jewell, L.H. Coudert, *Appl. J. Phys. 571*, 59 (2002).
5. T.W.G. Solomons, *Organic Chemistry*, 3rd ed., New York, Wiley (1984).
6. *Gaussian09, Revision B.01*., M.J. Frisch *et al*, Gaussian Inc., Wallingford CT (2010).
7. J.B. Foresman, E. Frisch, *Exploring Chemistry with Electronic Structure Methods, A Guide to using Gaussian*, Pittsburg, PA (1996).
8. *Gaussview Version 5*, R. Dennington, T. Keith, J. Millam, Semichem Inc. Shawnee

Mission KS (2009).
9. G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley and Sons, New York (1981).
10. C. Lin, K. Wu, *Chem. Phys. Lett. 321*, 83 (2003).
11. N.P.G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley: New York (1994).
12. N.B. Colthup, L.H. Daly, S.E. Wiberly, *Inroduction to Infrared and Raman Spectroscopy*, third ed., Academic Press, Boston (1990).
13. R.M. Silverstein, G.C. Bassler, T.C. Morril, *Spectrometric identification of organic compounds*, ed.5, John Wiley and Sons, Singapore (1991).
14. G. Varsanyi, *Assignments of vibrational Spectra of Seven Hundred Benzene Derivatives*, Wiley, New York (1974).
15. A.S. El-Shahawy, S.M. Ahmed, N.K. Sayed, *Spectrochim. Acta 66A*, 143 (2007).
16. Y.R. Shen, *The Principles of Nonlinear Optics*, Wiley, New York (1984).
17. P.V. Kolinsky, *Opt. Eng. 31*, 1676 (1992).
18. D.F. Eaton, *Science 253*, 281 (1991).
19. M. Tommasini, C. Castiglioni, M. Del Zoppo, G. Zerbi, *J. Mol. Struct. 480*, 179 (1999).
20. D.A. Kleinman, *Phys. Rev. 126*, 1977 (1962).
21. T. Joseph, H.T. Varghese, C.Y. Panicker, K. Viswanathan, N. Sundaraganesan, N. Subramanina, M. Dolezal, *Global J. Anal. Chem. 3*, 1 (2012).
22. K. Fukui, *Science 218*, 747 (1982).
23. B. Kosar, C. Albayrak, *Spectrochim. Acta 78A*, 160 (2011).