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IR, Raman and Ab-initio Calcualtions of Glycolic Acid

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ABSTRACT

Fourier-transform-Raman and infrared spectrum of glycolic acid were recorded and analyzed. The vibrational wavenumbers were examined theoretically using the Gaussian03 set of quantum chemistry codes. The first hyperpolarizability, predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability makes this compound an attractive object for future studies of nonlinear optics. The experimental frequencies are in agreement with the calculated scaled values.

Key words: IR, Raman, HF Calculations, Glycolic acid.

INTRODUCTION

Biodegradable polymers can be efficiently utilized for various purposes such as drug delivery, orthopaedic, dental, and tissue engineering[1-7]. Such sophisticated applications usually require polymers with narrowly defined material properties. For a polymer to be used in drug delivery system, it is desired that it should degrade in prerequisite manner[8-12]. Degradable aliphatic polyesters (bearing ester linkage-CH_2-COO-) are having special significance in drug delivery systems as the ester bonds can be cleaved under physiological conditions in absence of proteolytic activity[13]. Among the polyesters, the polymers derived from α -hydroxy acids have found the most extensive use. Poly (α-hydroxy acids) such as poly (glycolic acid) PGA and poly (lactic acid) having excellent mechanical properties and biological affinity are the most widely studied polymers. However their crystallinity, hydrophobic nature and lack of functional diversity in the back bone have interfered with modulation of their degradation state, mechanical properties and morphology. Studying carboxyl group (COOH) and its interactions are very important in many areas of science: such as surface science[14,15], electrochemistry[16,17], and biology[18,19]. In environment, COOH of humic acid plays a crucial role in speciation, transport and deposition of metal ions[20-23]. It is one of the important groups leading to the reactivity of humic substances[24-26]. Furthermore, trace metals could interact with humic substances as a result of electrostatic attraction and/or formulation of a chelate structure to a charged COO group[25]. COOH of both formic and carboxylic acids possess potentially two proton binding sites namely OH and C=O groups. Proton bound clusters are known to form hydrogen bounded networks[27]. Many proton bounded clusters have been investigated experimentally[28,29] as well as through molecular modeling[30,31]. In the present work, the infrared, Raman and theoretical calculations of the frequencies for glycolic acid are reported.

EXPERIMENTAL

The FT-IR spectrum was recorded using a Perkin-Elmer FT-IR spectrometer. The spectral resolution was 4 cm^{-1}. Standard KBr technique with 1 mg sample per 300 mg KBr was used. The FT-Raman spectrum was obtained on a Bruker IFS 66V NIR-FT instrument equipped with a FRA 106 Raman module. A Nd/YAG laser at 1064 nm with an output on 300mw was used as the exciting source.

Computational details

Calculations of Glycolic acid are carried out with Gaussian03[32] program using the Hartree-Fock/ 6-31G* basis set to predict the molecular structure and vibrational wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers are calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wave number values computed at the HF level contain known systematic errors due to the negligence of electron correlation[33]. We therefore have used the scaling factor value of 0.8929 for HF/6-31G* basis set. Parameters corresponding to optimized geometry of Glycolic acid (Fig. 1) is given in table 1. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The observed Raman and IR bands with their relative intensities, calculated values and assignments are given in Table 2.

The vibrations of the CH_2 group, the asymmetric stretch $\upsilon_{as}CH_2$, symmetric stretch υ_sCH_2, scissoring vibration δCH_2 appears in the region 2925 ± 10, 2855 ± 10, 1463 ± 13 cm^{-1} respectively[34]. The positions of the C-H stretching vibrations are among the most stable in the spectrum. The HF calculation gives $\upsilon_{as}CH_2$ at 2936 cm^{-1} and υ_sCH_2 at 2895 cm^{-1}. The weak band observed in the IR spectrum at 2940 cm^{-1} and 2945 cm^{-1} in Raman spectrum is assigned as the asymmetric CH_2 stretching mode. The symmetrical CH_2 group stretching bands is observed at 2914 cm^{-1} in the IR spectrum. The CH_2 in-plane deformation band which comes near 1463 cm^{-1} in alkenes[35] is lowered about 1440 cm^{-1}, when the CH_2 group is next to a double or triple bond. A carbonyl, nitrite or nitro group each lower the wave number[35] of the adjacent CH_2 group to about 1425 cm^{-1}. In the present case band observed at 1467 cm^{-1} in the Raman spectrum and 1482 cm^{-1} (HF) are assigned to the scissoring mode of CH_2. Absorption of hydrocarbons due to CH_2 twisting and wagging vibration, is observed in the 1350-1150 cm^{-1} region[35,36]. These bands are generally appreciably weaker than those resulting from CH_2 scissoring vibration. The CH_2 wagging and twisting modes are assigned at 1309 cm^{-1} and 1245 cm^{-1} theoretically. These bands are observed at 1357 cm^{-1}, 1264 cm^{-1} in the IR spectrum and at 1233 cm^{-1} in the Raman spectrum. The rocking modes[34] ρCH_2 is expected in the range 895±85 cm^{-1}. The bond calculated at 835 cm^{-1} is assigned as the rocking mode ρCH_2. The band at 814 cm^{-1} in the IR spectrum and 893 cm^{-1} in the Raman spectrum are assigned as ρCH_2 modes for the title compound. The torsional modes are seen in the low wave number range[34].

Carboxylic acids are best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation and even by the C-O stretch and the OH in-plane deformation. The C=O stretching vibration in the spectra of carboxylic acids[34] give rise to a strong band in the region 1725 ± 65 cm^{-1}. In the vapor state the monomer absorbs at a wave number 50 cm^{-1} higher. In the present case we have observed at band at 1729 cm^{-1} in the IR spectrum and 1714 cm^{-1} in the Raman spectrum. The HF calculation gives the mode at 1709 cm^{-1} as $\nu C=O$. The C=O in-plane deformation is weakly to moderately active in the region 725±95 cm^{-1}. In the present case 619 cm^{-1} (HF) and 619 cm^{-1} (IR) are assigned as $\delta C=O$ of carboxylic group. Most

Table 1: Optimized geometrical parameters of the title compound

Bond Lengths (A°)		Bond angles (°)		Dihedral angles (°)	
C1-O2	1.5316	A(2,1,3)	123.3	D(3,1,2,4)	-0.0
C1=O3	1.2117	A(2,1,5)	112.5	D(5,1,2,4)	-180.0
C1-C5	1.4974	A(3,1,5)	124.3	D(2,1,5,6)	58.8
O2-H4	0.9548	A(1,2,4)	114.7	D(2,1,5,7)	-58.8
O8-H9	0.9541	A(1,5,6)	108.9	D(2,1,5,8)	-180.0
C5-H6	1.0809	A(1,5,7)	108.9	D(3,1,5,6)	-121.2
C5-H7	1.0809	A(1,5,8)	111.2	D(3,1,5,7)	121.2
C5-O8	1.4139	A(6,5,7)	108.0	D(3,1,5,8)	-0.01
C5-H9	0.9541	A(6,5,8)	109.9	D(1,5,8,9)	0.03
		A(7,5,8)	109.9	D(6,5,8,9)	120.7
		A(5,8,9)	113.3	D(7,5,8,9)	-120.6

Table 2: Infrared, Raman spectral data and calculated wave numbers and band assignments for Glycolic Acid

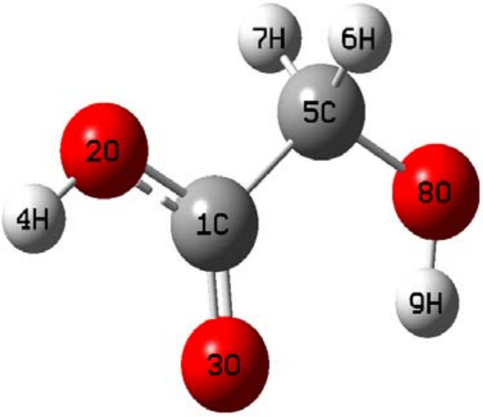
$\upsilon_{(HF)}$ (cm^{-1})	IR intensitie s (KM/Mole)	Raman Activity (Å^4/AMU)	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments
3562	116.77	87.81	3600	-	υOH
3561	83.98	41.45	-	-	υOH
2936	14.24	70.23	2940	2945	υasCH$_2$
2895	12.96	121.07	2914	-	υsCH$_2$
1709	332.76	4.80	1729	1714	υC=O
1482	15.52	15.18	-	1467	δCH$_2$
1421	7.50	2.94	1432	1431	δOH
1309	118.87	3.44	1357		ωCH$_2$
1245	77.29	2.25	1264	1233	τCH$_2$
1218	0.05	13.33	1229	-	δOH
1125	164.17	3.97	1154	1116	υC-O
1047	242.13	5.02	1086	1083	υCO
1030	3.66	0.15	1004	1083	υC-C
835	45.70	7.99	814	893	ρCH$_2$
620	31.16	5.42	-	683	δOH
619	266.68	1.00	619	-	δC=O
499	23.72	3.92	499	496	υC=O
450	33.38	2.61	457	-	δ-C-O, ρ(C=O)O
266	8.42	0.09	-	250	tCOH
223	132.75	2.00	-	-	tCOOH
24	65.77	0.27	-	-	tCH$_2$

υ-stretching; ω-wagging; δ-in-plane deformation ;γ-out-of-plane deformation; ρ-rocking ;τ-twisting; t-torsional; subscript: as-asymmetric; s-symmetric.

carboxylic acids display γC=O in the region 595 ± 85 cm^{-1} which is in the vicinity of that of methyl and ethyl esters. For the title compound the band is at 496 cm^{-1} in the Raman spectrum, 499 cm^{-1} in the IR spectrum and 499 cm^{-1} (HF) is assigned in the γC=O mode. Two bands arising from the C-O stretching and O-H bending appear in the spectra of carboxylic acids near 1320-1210 cm^{-1} and 1440-1395 cm^{-1} respectively[36]. Both of these bands involve some interaction between C-O stretching and in-plane C-O-H bending. The υ(C-O)c mode is reported at 1377 cm^{-1} for sodium salicylate[37] at 1391 cm^{-1} for 4-amino salicytic acid[38] and at 1375 cm^{-1} (IR), 1382 cm^{-1} (HF) for 3,5 dinitro salycytic acid[39]. For the title compound the band observed at 1125 cm^{-1} (HF) and 1116 cm^{-1} Raman and 1154 cm^{-1} in IR are assigned as υ(C-O)c mode. The torsional modes are seen in the low wave number range[34]. The OH stretching mode is observed at 3600 cm^{-1} in the IR spectrum as expected[34]. In the present case HF calculation gives the δOH mode at 1421 and 1432 cm^{-1} (IR) and 1431 cm^{-1} in the Raman spectrum.

In the OH band of oxymethyl group the νOH stretching vibration is expected in the region 3300 ±120 cm^{-1}. In the present case the HF calculation give this value at 3561 cm^{-1} and 3600 cm^{-1} in the IR spectrum. The OH deformation band is expected in the region[34] 1400±40 cm^{-1}. In OH in-plane deformation the bands is observed at 1218 cm^{-1} (HF), 1229 cm^{-1} (IR) are assigned as äOH oxymethyl group. The out-of plane deformation is expected at 640±70 cm^{-1}. In the present case HF calculation gives the mode at 620 cm^{-1} and Raman at 683 cm^{-1} The stretching vibration νCO is expected at 1045 ± 45 cm^{-1}. The band at 1083 cm^{-1} in the Raman spectrum, 1086 cm^{-1} in the IR spectrum and 1047 cm^{-1} (HF) are assigned as ρCO modes for the title compound. The δ-C-O and ρ(C=O) O bands are calculated to be at 450 cm^{-1} (HF) and at 457 cm^{-1} in the IR spectrum. The other modes are also identified and tabulated (Table 2).

For the title compound the bond lengths C_1-O_3=1.2117, C_1-O_2=1.5316, C_5-O_8=1.4139Å and these values are in assignment with the reported values 1.203, 1.2074Å (C=O), 1.361, 1.3487Å(C-O)[40.41]. The ab initio calculation give the O-H bond lengths as O_8-H_9= 0.9541, O_2-H_4=0.9548 Å, where as the reported values are 0.9650, and 0.9533Å[40,41]. At C_1 the bond angle are O_2-C_1-O_3=123.3, O_2-C_1-O_5=112.5, O_3-C_1-C_5=124.3° and the deviation from 120° shows that the interaction between COOH group and the CH_2 group. C_1-C_5=1.4974, C-H=1.0809Å the C-C and C-H bond lengths are 1.4974 and 1.0809 Å which are in agreement with the reported values[42,43]. The C_5-O_8-H_9 angle is 113.3°, which shows hydrogen bond between O_3 and H_9. The calculated first hyperpolarizability of the title compound is 0.562 × 10^{-30} esu and is an attractive object for future studies of nonlinear optics.



CONCLUSION

The IR and Raman spectrum of Glycolic acid were recorded and analysed. The frequencies are calculated theoretically using Gaussian03 software package. The calculated frequencies are found to be in agreement with the experimental values . The geometrical parameters of the title compound are in agreement with the reported values of similar compounds. The vibrational modes are assigned with the help of reported literature.

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