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Vapor-Phase Vibrational Spectrum of Glycolic Acid, $CH_2OHCOOH$, in the Region 2000−8500 cm^{-1}

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This work presents an analysis of the previously unobserved vapor-phase spectrum of glycolic acid in the IR/near-IR region (2000−8500 cm^{-1}). The focus is on distinguishing between the O−H stretches of both the acid and alcohol functional groups by using intermediate resolution FTIR spectroscopy. Vibrational transitions due to combination bands and overtones were assigned and relative intensities were obtained. The contribution of a rotational isomer to the vibrational spectrum of $CH_2OHCOOH$ at 353 K is discussed. Theoretical calculations of harmonic frequencies and anharmonicities are reported on the two lowest energy conformers of glycolic acid and provide supporting evidence for the proposed assignments.

Introduction

Carboxylic acids are some of the most important types of organic molecules in the atmosphere.[1] Low vapor pressure carboxylic acids have been found to make up a substantial fraction of organic compounds in aerosols.[1−5] Higher vapor pressure acids, such as formic acid and acetic acid, have been studied in the atmosphere in a variety of environments.[6−9] $CH_2OHCOOH$ (glycolic acid) is the simplest α-hydroxycarboxylic acid. It has been found to account for 3.55 ± 2.26% of organic content of aerosols in a polluted troposphere[1] and is recognized by atmospheric modelers as a significant atmospheric oxidation product.[10] Despite its atmospheric importance, the fundamental spectroscopy of vapor-phase glycolic acid has not been examined to date.

Recent studies have been carried out on the spectroscopy and photochemistry of overtones in an atmospheric context[11] but few have focused on organic alcohols and acids.[12,13] Glycolic acid presents an interesting spectroscopic system because it contains two functional groups with O−H oscillators. Previous work on glycolic acid has been confined to matrix studies,[14,15] microwave spectroscopy,[16,17] and ab initio calculations.[17,18] Matrix studies observed the two O−H oscillators in almost perfect accidental degeneracy.[14] Theoretical studies have focused on understanding the different rotational isomers of glycolic acid.[17,18] Extremely useful microwave studies have provided the structures for different conformers of glycolic acid.[16,17]

This work presents an analysis of the vapor-phase spectrum of glycolic acid in the IR/near-IR region (2000−8500 cm^{-1}). It focuses on distinguishing between the O−H stretches of both the acid and alcohol functional groups as well as assigning vibrational transitions due to combination bands and overtones. An important connection to previous work[19] is made by examining the contribution of a rotational isomer to the vibrational spectrum of $CH_2OHCOOH$ at 353 K. Theoretical calculations of harmonic frequencies and anharmonicities were carried out on the two lowest energy conformers of glycolic acid and provide supporting evidence for peak assignments.

Theory and Calculations

The lowest energy geometry for $CH_2OHCOOH$ was obtained from microwave spectroscopy.[16] This geometry was optimized and harmonic frequencies were obtained by using the B3LYP/6-311++G[2d,2p] method within the Gaussian 98 suite of programs.[20] This theoretical method and basis set had been used in previous work on O−H containing compounds to obtain harmonic frequencies which most closely matched experiments.[21−23] The same method and basis set were used to obtain a one-dimensional potential energy curve as a function of O−H bond distance while leaving all other structural parameters fixed. Nine-point grids centered about the equilibrium bond distances, obtained from the optimized B3LYP geometries, of 0.968 Å for the acid O−H group and 0.967 Å for the alcohol O−H group were used with a step size of 0.05 Å. This was carried out in order to obtain the anharmonicities for the O−H stretches in each geometry.[21,24,25] The calculated local mode anharmonicities were then combined with the normal mode harmonic frequencies to predict the fundamental and first overtone peak positions. The same calculations were utilized for the next lowest energy conformer of glycolic acid. The rotamer was optimized again by using density functional theory with the B3LYP functional and starting from the literature geometry.[17] Equilibrium bond distances of 0.9618 and 0.968 Å were used for the acid and alcohol groups respectively in order to obtain anharmonicities for each O−H stretch in the rotational isomer. The calculated harmonic frequencies and anharmonicities were scaled by factors of 0.9985 and 0.872, respectively. These scaling factors have been used previously for B3LYP calculations on O−H stretching transitions and are the only empirical values that have been utilized with the B3LYP/6-311++G[2d,2p] method.[19,21−24]

Experimental Section

The absorption spectrum of $CH_2OHCOOH$ vapor was measured in the IR/NIR from 2000 to 8500 cm^{-1}. An optical flow cell (100 cm path length) containing the sample has been

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described previously.[21,26−28] The cell was wrapped with copper foil, heating tape, insulation, and a layer of aluminum foil. Thermocouple gauges were placed on the cell walls between the glass or copper foil and the heating tape to monitor the external temperature. The temperature of the gas inside the cell was measured by inserting a thermocouple into the cell while gases were flowing through at conditions similar to those used in the experiment. Because these experiments were done in a flow cell and because there have not been any previous IR cross sections reported it was not possible to measure the partial pressure of $CH_2OHCOOH$. The cell utilized wedged CaF_2 windows to prevent internal reflections so that spectra could be obtained at resolutions up to 0.1 cm^{-1}.

Vapor-phase $CH_2OHCOOH$ was generated by bubbling N_2 through a melted sample of Aldrich 99 wt % of $CH_2OHCOOH$ with the temperature maintained at 363 ± 5 K and a flow rate of 300 standard cubic centimeters per minute (sccm). The melted glycolic acid sample was prepared by vacuum sublimation at 313 ± 10 K for 5 days. All $CH_2OHCOOH$ measurements were made at a cell temperature of 353 ± 5 K. The IR spectrum of glycolic acid showed no detectable CO or CO_2 but did contain substantial amounts of H_2O. The interference from H_2O was minimized by spectral subtraction of H_2O vapor measured under the same experimental conditions.

Light from the spectrometer was focused through the cell with a path length of 100 cm. $CH_2OHCOOH$ spectra were recorded in the range of 2000−8500 cm^{-1} with resolutions of 1 and 0.1 cm^{-1}. The experiments used a quartz halogen source, InSb detector, and CaF_2 beam splitter. For $CH_2OHCOOH$, 1000 scans were coadded for spectra with 1-cm^{-1} resolution and 698 scans were coadded for spectra with 0.1-cm^{-1} resolution. The vibrational-band intensities of observed transitions in $CH_2OHCOOH$ were determined by integrating the area of various bands over regions where the absorbance went to zero. Since the partial pressure of $CH_2OHCOOH$ was unknown, relative intensities and not absolute intensities are reported.

Results and Discussion

Glycolic acid belongs to the C_s point group and thus all 21 of its normal modes are active in the infrared. Many of the observed transitions in the near-IR region are due to overtones and combinations of the fundamental normal modes. The most prominent feature observed in this work is due to the ν_1/ν_2 O−H stretches which are centered near 3585 cm^{-1}. Glycolic acid contains two O−H oscillators that are almost isoenergetic. The calculations done in this work show that the ν_1 mode consists primarily of O−H stretch in the carboxylic acid functional group while the ν_2 mode is caused by the O−H stretch in the alcohol group. This differs from previous theoretical work that assigned the alcohol group as ν_1 and the acid group as ν_2.[14] A summary of the normal modes and calculated harmonic frequencies of glycolic acid that are relevant to this work are presented in Table 1. A summary of all observed vibrational transitions, integrated intensities relative to the combined ν_1 and ν_2 O−H stretches, and assignments is presented in Table 2.

Spectra were collected at a resolution of 0.1 cm^{-1} to better investigate the overlapping ν_1 and ν_2 transitions. Spectra of ν_1 and ν_2 recorded at both 1- and 0.1-cm^{-1} resolutions are presented in Figure 1. Water vapor has been subtracted to the best of the authors' ability, but several residual water lines remain in the high-resolution spectrum. However, it is clear that the ν_1/ν_2 band has a well-defined P−Q−R branch structure. If ν_1 and ν_2 overlap then their transition frequencies lie within 10 cm^{-1} of each other. This would leave the band shape of the combined transitions relatively unperturbed.

TABLE 1: Summary of Selected Normal Modes of Glycolic Acid and Harmonic Frequencies Calculated with the B3LYP/6-311++G[2D,2P] Method

relevant normal modes	description	calcd harmonic freq (cm^{-1})
ν_1	O−H stretch acid	3756.5
ν_2	O−H stretch alcohol	3740.2
ν_3	CH_2 symmetric stretch	3018.3
ν_4	C═O stretch	1798.2
ν_5	CH_2 scissor	1489.5
ν_6	CH_2 wag − CO−H bend alcohol − C−C stretch + CH_2 scissor (ref 14)	1464.1
ν_7	CO−H bend alcohol + C═O ip wag + C−O acid stretch + CO−H bend acid − C−C stretch (ref 14)	1350.5
ν_8	CH_2 wag + CO−H bend alcohol − CO−H bend acid (ref 14)	1295.6
ν_9	CO−H bend acid − C−O stretch acid − C−O stretch alcohol (ref 14)	1169.7
ν_{15}	CH_2 asymmetric stretch	3040.6

TABLE 2: Observed Transitions and Relative Intensities in Glycolic Acid

freq (cm^{-1})	assignment	integration region (cm^{-1})	rel intensity at 1-cm^{-1} resolution
2851.7	ν_{15}	2795−2980	0.35
2930	ν_3		
3585.5	ν_1/ν_2	3530−3622.5	1
4730.4	$\nu_1/\nu_2 + \nu_9$	4650−4762.5	0.02
4836.1	$\nu_1/\nu_2 + \nu_8$	4762.5−4967.75	0.05
4925.6	$\nu_1/\nu_2 + \nu_7$		
5025.1	$\nu_1/\nu_2 + \nu_6$ or ν_5	4967.75−5062.25	0.01
5366.4	$\nu_1/\nu_2 + \nu_4$	not integrated	
6995.6	$2\nu_1/2\nu_2$	6955−7025	0.05

There are several pieces of evidence that provide support for the feature centered at 3585.5 cm^{-1} to have intensity contributions from both O−H stretches. First, the high-resolution (0.1 cm^{-1}) spectrum in a water-free region allowed for examination of rotational line intensities and spacings. The spectrum showed two distinct series of rotational lines of different intensity. One series was spaced by 0.6 ± 0.1 cm^{-1}, which is approximately two times the ground-state rotational constant A (0.356783325 cm^{-1}) for glycolic acid.[16] The second series was spaced by 0.2 $\pm$ 0.05 cm^{-1}, which is approximately two times the ground-state rotational constant B (0.13512789 cm^{-1}).[16] The intensity of the series spaced by 0.6 ± 0.1 cm^{-1} is approximately twice that of the series spaced by 0.2 ± 0.05 cm^{-1}. The calculations in this work showed that both O−H stretches correspond to a dipole moment change in the a/b inertial plane. The carboxylic acid O−H stretch oscillates nearly parallel to the a inertial axis while the O−H stretch of the alcohol primarily oscillates parallel to the b inertial axis. Thus, the observed intensity pattern may indicate two distinct overlapping transitions with different rotational line spacings. This evidence is consistent with previous matrix work[14] that assigned both O−H stretching transitions to one feature at 3561.3 cm^{-1}. Finally, calculations from the present work show that each O−H stretch should contribute equally (within 5%) to the IR absorption intensity. Thus, the band almost certainly contains both the ν_1 and ν_2 transitions with both transitions contributing significant intensity.

The first overtones of the ν_1/ν_2 stretches were centered about 6995.6 cm^{-1}. A 1 cm^{-1} resolution spectrum of this region is shown in Figure 1. The integrated intensity of these transitions is 0.05 relative to the fundamental ν_1/ν_2 modes. This factor of 20 intensity drop is consistent with that of strong acids,[22,27] organic acids,[13,29] and alcohols.[12,13] Figure 1 shows the noticeably asymmetric shape of the overtone transition. Although the

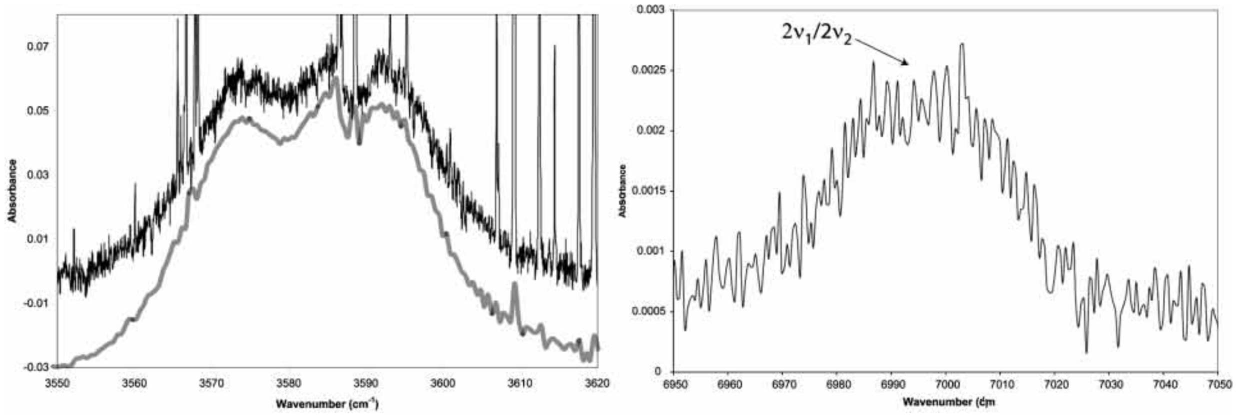

Figure 1. Expanded spectra of ν_1/ν_2 of glycolic acid at 0.1-cm^{-1} resolution (1-cm^{-1} resolution offset below in gray) and $2\nu_1/2\nu_2$ at 1-cm^{-1} resolution are shown. Water vapor was subtracted from all spectra, but residual water lines remain in the high-resolution spectrum. Analysis of the high-resolution spectrum in a water-free region revealed two distinct series of rotational lines spaced by approximately 0.6 and 0.2 cm^{-1}.

TABLE 3: Calculated O−H Stretch Harmonic Frequencies, Anharmonicities, and Peak Positions

	calcd harmonic freq (cm^{-1})	calcd anharmonicity (cm^{-1})	predicted peak position (cm^{-1})	predicted overtone position (cm^{-1})
O−H stretch acid	3756.5	87.4	3581.7	6988.2
O−H stretch alcohol	3740.2	89.6	3561.0	6942.8
rotamer O−H stretch acid	3828.0	85.4	3657.2	7143.6
rotamer O−H stretch alcohol	3755.7	81.9	3591.9	7020.0

full-width at half-maximum (fwhm) of the overtone (37 ± 4 cm^{-1}) is comparable to that of the fundamental (32 ± 2 cm^{-1}), the band shape appears to have a broad low-energy tail that was not observed in the fundamental O−H stretching region. This suggests that the O−H stretches of the acid and alcohol might be separating in the overtone region due to their different anharmonicities. If the second overtone region (10 200−10 500 cm^{-1}) were observed one would expect an even greater degree of separation between these transitions.

Calculations done on the O−H stretching transition frequencies for both the acid and alcohol groups are summarized in Table 3. The peak position for the acid O−H stretch was calculated to be 3581.7 cm^{-1} and differs from the observed peak position by 3.8 cm^{-1}. The alcohol O−H stretch calculations are not in good agreement with the observed peak position since they give a predicted peak position of 3561.0 cm^{-1}. Assuming that the transition at 3585.5 cm^{-1} contains ν_1 and ν_2 overlapping almost completely, the alcohol calculations give a peak position that is 25.2-cm^{-1} red-shifted from the observed value. This was unexpected given the good agreement between experiment and theory for the acid O−H stretch.

The discrepancy between the alcohol group's theoretical and observed O−H stretching peak position can be explained by considering intramolecular hydrogen bonding between the alcoholic hydrogen and the carbonylic oxygen.[14] Previous work compared the frequency of the alcoholic O−H stretch in glycolic acid to that in methanol and inferred that strong intramolecular hydrogen bonding was likely.[14] Also, the relative energies of the two lowest energy conformers (Figure 2) suggest that there is energetic stabilization by stronger hydrogen bonding in the lowest energy conformer.[17] It is possible that the theoretical treatment of the O−H stretching vibration is unsatisfactory. The local mode anharmonicity calculations are the most suspect since the hydrogen-bonded O−H stretch is not expected to be adequately describable by simple O−H oscillation. However, this work cannot rule out if normal mode harmonic frequencies calculated with Gaussian 98 are also a source of error.

Vibrational frequency and anharmonicity calculations were carried out on the second lowest energy rotational isomer of glycolic acid (Figure 2) and are also reported in Table 3. These calculations were performed in order to offer an explanation for the narrow features to high-energy of the Q-branch in the overtone region (7003 cm^{-1}). Interference from gas-phase water prevented a definitive observation of such features in the fundamental ν_1/ν_2 region. Previous SCF/4-31G calculations on vibrational frequencies of glycolic acid rotamers were useful but were not of sufficient accuracy to compare with this experimental work.[18] Similar blue-shifted spectral features have been observed in H_2SO_4[19,28] and were assigned as rotamers. The results of the present work show a predicted peak position for the alcohol O−H stretch at 3591.9 cm^{-1} and a predicted overtone position of 7020.0 cm^{-1}. The calculations on the alcohol O−H stretch in the rotamer should be affected less by hydrogen bonding due to its different geometry. The acid O−H stretch has a predicted peak position of 3657.2 cm^{-1} and a predicted overtone position of 7143.6 cm^{-1}. These calculations suggest that the feature at 7003 cm^{-1} is caused by the alcoholic O−H stretch of the second lowest energy conformer of glycolic acid. Previous theoretical work calculated this isomer to be 8.285 kJ/mol above the lowest energy geometry.[17] At the temperature of these experiments (353 K) it is predicted, using Boltzmann statistics, that 6% of glycolic acid molecules are in this configuration. Therefore, assuming the cross-section is comparable to that of the equilibrium geometry, O−H stretching transitions from the rotamer should be observable in near-IR spectra.

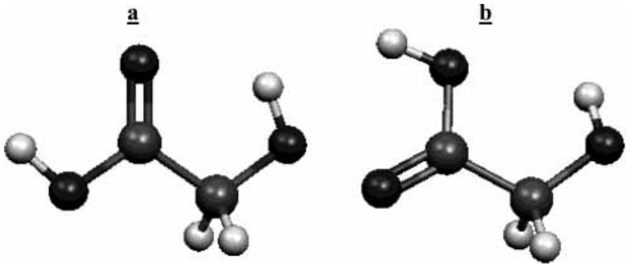

Figure 2. Geometries of glycolic acid in its (a) lowest energy and (b) second lowest energy (8.3 kJ/mol) conformers.

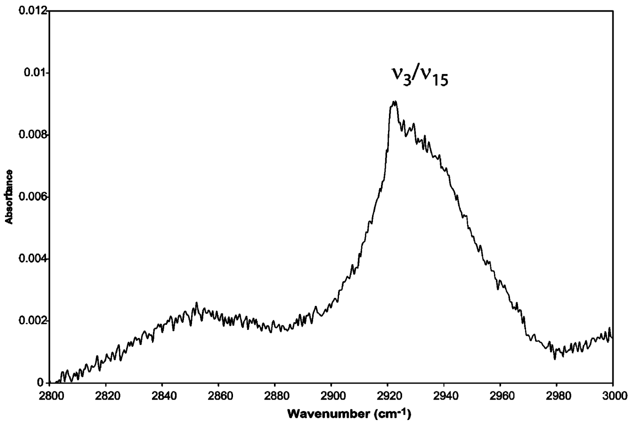

Figure 3. Expanded spectrum of ν_3 and ν_{15} of glycolic acid at 1-cm^{-1} resolution.

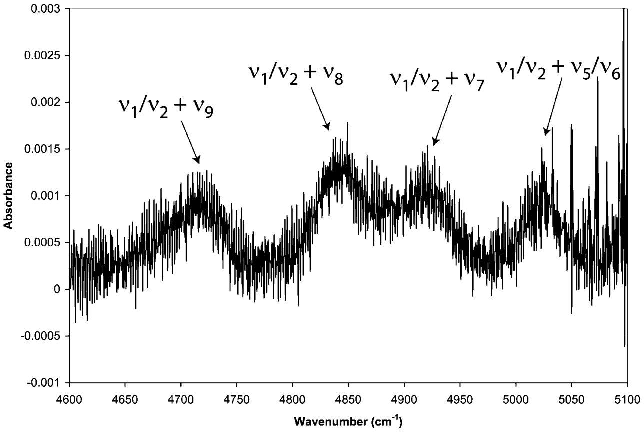

Figure 4. Expanded spectrum of combination bands of glycolic acid at 1-cm^{-1} resolution.

The C−H stretching transitions were observed in the region 2795−2980 cm^{-1} and are shown in Figure 3. Previous matrix work[14] assigned the higher energy C−H stretch as ν_3. Harmonic frequency calculations in the present work find the asymmetric stretch (A″ symmetry) is 22.3 cm^{-1} higher in energy than the symmetric stretch (A′ symmetry). However, because of the difficulty in distinguishing between these transitions, this work relies on the matrix assignments.[14] The integrated intensity of the C−H stretching region was found to be 0.35 that of the O−H stretching region.

Many combination bands involving the ν_1/ν_2 O−H stretches were observed in the region 4500−5500 cm^{-1} and examples are shown in Figure 4. These bands were assigned based on the observed frequency of the ν_1/ν_2 O−H stretch combined with previous matrix observations of lower frequency modes.[14] The assignments are further supported by the fact that the low-frequency modes that appear in combination with the O−H stretches were observed with strong IR intensities in the matrix studies. The band positions and relative intensities are summarized in Table 2. It should be noted that the feature at 5366.4 cm^{-1} was not integrated due to interference from gas-phase H_2O. The observation of such a group of combination bands involving the O−H stretch has interesting implications regarding mode coupling and vibrational energy transfer.

Conclusion

The results presented here include the first vapor-phase vibrational spectrum of glycolic acid. The fundamental and first overtone of the O−H stretches were observed and found to contain ν_1 (acid O−H stretch) and ν_2 (alcohol O−H stretch) overlapping almost completely. Analysis of the band shapes and rotational structure of these transitions provided evidence for this fact but suggested that the modes would be distinguishable by (1) recording spectra at a resolution of at least 0.01 cm^{-1} or (2) measurements of $3\nu_1/3\nu_2$ or higher. In addition, C−H stretching transitions were observed as well as several combination bands involving the ν_1/ν_2 O−H stretches. Relative intensities were measured and mode assignments were made where possible.

An interesting observation was the analysis of the narrow feature at 7003 cm^{-1}. Inspired by previous work on O−H containing molecules which showed similar spectral features,[19,28] this work calculated vibrational frequencies of the second lowest energy rotational isomer and compared the results to observed spectra. The results suggest that this feature is due to the overtone of the O−H stretch of the alcohol group in the rotamer of glycolic acid. These conclusions are significant for dealing with the vibrational spectra of polyatomic molecules with rotational isomers.

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