



Hydration of pyruvic acid to its geminal-diol, 2,2-dihydroxypropanoic acid, in a water-restricted environment

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ABSTRACT

In this work we present the spectroscopic characterization of 2,2-dihydroxypropanoic acid and its water complexes. Based on this information the water-mediated hydration between pyruvic acid and its geminal diol counterpart, 2,2-dihydroxypropanoic acid, was investigated at very low water concentration at ambient temperatures, using Fourier-transform mid-infrared (FTIR) and nuclear magnetic resonance spectroscopy (NMR). We experimentally observed large concentrations of 2,2-dihydroxypropanoic acid in this water-restricted environment of the carbon tetrachloride matrix. Our observation can be explained by the role of hydrogen-bonded water clusters in promoting the hydration of the carbonyl in pyruvic acid.

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1. Introduction

In the presence of water, aldehydes and to a lesser extent ketones have the ability to form geminal diols by the hydration of the carbonyl group [1–3]. This chemistry has been studied extensively in bulk aqueous media [4–9], where this reaction occurs efficiently and is acid catalyzed. However, little is known about this process at low water concentrations where this mechanism is not applicable. Significant discrepancies between atmospherically measured oxidized organic molecules and predictions of atmospheric models have been observed [10]. Spectroscopic studies of the hydration of oxidized organic molecules in water-restricted environments might contribute to assessments of their atmospheric importance.

This study investigates the hydration of pyruvic acid in a water-restricted environment at ambient temperatures using a carbon tetrachloride matrix. While well known in aqueous solutions, the formation of the geminal diol of pyruvic acid, 2,2-dihydroxypropanoic acid, was not expected in a water-restricted environment. Our present results suggest the possibility of water enhancing the extent of diol formation at low water concentrations.

Pyruvic acid has been previously characterized in the mid-infrared in a carbon tetrachloride matrix [11] and in the gas-phase [12,13]. However, no vibrational spectra of 2,2-dihydroxypropanoic acid, or water complexes of pyruvic and 2,2-dihydroxypropanoic acids, have been reported at ambient temperatures, prior to the present study. A matrix isolation study of methyl diol by Lugez

et al. [14] and recent works by Plath et al. [15] and Axson et al. [16] provide the only infrared spectra of other geminal diols in the literature. Characterization of pyruvic acid hydrates, 2,2-dihydroxypropanoic acid and its hydrates provided in this work using infrared spectroscopy make it possible to investigate the water mediated hydration between pyruvic acid and 2,2-dihydroxypropanoic acid at low water concentration.

The hydrophobic solvent, carbon tetrachloride, was chosen in this study because of its low water solubility. Additionally, pyruvic acid has been shown to stay as a monomer in non-polar solvents, such as carbon tetrachloride, due to its ability to form intramolecular hydrogen bonds [6]. Formation of intramolecular bonds weakens the ability of this molecule to form dimers by intermolecular hydrogen bonds. Accordingly, the carbon tetrachloride matrix is a perfect medium for the observation and characterization of pyruvic acid–water interactions at ambient temperatures. This environment has been shown to be effective to investigate the rotational structure of water [17] and to characterize intermolecular hydrogen-bonded complexes, such as 1,4-butanediol with aprotic solvents [18], *N*-methylacetamide with phenol derivatives [19], nitric acid–water complexes [20,21], ions [22], and water dimer [23]. As shown here, this medium made it possible to observe pyruvic and 2,2-dihydroxypropanoic acid–water complexes, adding to the literature on hydrogen bonded complexes [17,20–22,24,25].

2. Experimental section

2.1. Materials and sample preparation

All materials were purchased from Sigma–Aldrich Chemical Co., Inc. Carbon tetrachloride (Aldrich, >99.5%, anhydrous) was dried

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with silica gel and activated carbon in a closed reservoir. For our qualitative analysis in the mid-infrared spectroscopic studies the aqueous pyruvic acid solutions were prepared by diluting 98 wt.% pyruvic acid (Aldrich, 98%) with Nanopure water (NERL reagent grade water 18 MΩ) by weight. Stock carbon tetrachloride/aqueous pyruvic acid solutions were prepared by vigorously mixing excess 45, 35, 24, 15, 5 and 0 wt.% pyruvic acid aqueous solutions with dried carbon tetrachloride. The mixtures were then transferred to a closed reservoir and allowed to phase separate over night. The carbon tetrachloride/98 wt.% pyruvic acid solution was prepared by vigorously mixing 3 μL of 98 wt.% pyruvic acid with 30 mL of dried carbon tetrachloride.

After phase separation, the carbon tetrachloride layer of each carbon tetrachloride/pyruvic acid solution was transferred from each respective closed reservoir into a glass cell, with a path length of 2.5 cm fitted with calcium fluoride windows. Preparation and conditioning of the glass cell and all glassware to prevent any hydrogen bonding with the glass walls used in this work is described elsewhere [20].

Aqueous pyruvic acid solutions for ^{13}C nuclear magnetic resonance (NMR) spectroscopic studies were prepared by appropriately diluting 98 wt.% pyruvic acid with Nanopure water by weight and were vigorously mixed. The mixtures were then transferred to NMR tubes for spectroscopic analysis.

2.2. Spectroscopic studies

The infrared absorption spectra of the carbon tetrachloride/pyruvic acid layers were measured at room temperature in the mid-infrared with a commercial Fourier transform spectrometer (FTS). A Bruker IFS 66v (InGaAs detector and resolution of 0.25 cm^{-1}) was used for 45, 35, 24, 15, 5 and 0 wt.% carbon tetrachloride/pyruvic acid solutions in the mid-infrared from 2800 to 4000 cm^{-1} .

^{13}C NMR spectra of the aqueous pyruvic acid solutions were obtained with a Varian Inova-400 NMR spectrometer operating at 100.63 MHz. For quantization of the ^{13}C NMR resonances, a 60° excitation pulse of 9.3 μs duration was used for acquisition with a recycle delay of 4.3 s for signal averaging. It was not necessary to use extraordinarily long relaxation delays because the T_1 relaxation time-constant should not change significantly with relative molar concentration. Internal ratios of similar peak intensities within each spectrum were used to determine the relative molar ratio of pyruvic and 2,2-dihydroxypropanoic acids. To eliminate relative intensity variation due to the Nuclear overhauser effect, broadband ^1H inverse-gated decoupling was used such that the decoupler was off during the 3 s relaxation delay. To achieve adequate digital resolution for peak integration, the time-domain NMR signal consisting of 64 K complex points was zero-filled to 256 K prior to application of the Fourier transform.

2.3. Theoretical calculations

The structures of pyruvic acid and 2,2-dihydroxypropanoic acid, as well as the fundamental vibrational mode OH frequencies were calculated using the anharmonic oscillator local-mode (AO) method with the B3LYP [26,27] functional with 6-311++G(3df,3pd) [28–31] basis set on the GAUSSIAN 03 program [31]. The detail of the harmonically coupled anharmonic oscillator (HCAO) method is described elsewhere [32,33]. The potential energy curves with respect to the OH-stretching coordinate used for the local mode vibrational calculation, were obtained by displacing the OH bond length by $\pm 0.2\text{ Å}$ from equilibrium in steps of 0.05 Å while keeping all other structural parameters fixed at their equilibrium values. The points were fit to a Morse potential and the local-mode OH-stretching frequency, $\tilde{\omega}$, and anharmonicity, $\tilde{\omega}_x$, were

Table 1

Experimentally observed and calculated H_2O , CH_3COCOOH , $\text{CH}_3\text{COCOOH}\cdot\text{H}_2\text{O}$, $\text{CH}_3\text{C}(\text{OH})_2\text{COOH}$ and $\text{CH}_3\text{C}(\text{OH})_2\text{COOH}\cdot\text{H}_2\text{O}$ frequencies, oscillator strengths and assignments from 3300 to 3700 cm^{-1} .

Vibrational mode	Calculated frequency (cm^{-1})	Experimentally observed frequency (cm^{-1})
H_2O		
ν_1		3616 ^b
ν_3		3708 ^b
CH_3COCOOH		
Isomer Tce		
$\nu_{\text{OH}}^{\text{acid}}$	3360 ^a	3429 ^b
f	2.09×10^{-5}	
Isomer Tte		
$\nu_{\text{OH}}^{\text{acid}}$	3557 ^a	3561 ^b
$\text{CH}_3\text{COCOOH}\cdot\text{H}_2\text{O}$		
Conformer Tce		
$\nu_{\text{OH}}^{\text{acid}}$	2842 ^a	2975 ^b
Conformer Tte		
f	2.32×10^{-5}	
$\nu_{\text{OH}}^{\text{acid}}$	2808 ^a	2887 ^b
$\text{CH}_3\text{C}(\text{OH})_2\text{COOH}$		
Conformer Tce		
$\nu_{\text{OH}}^{\text{acid}}$	3487 ^a	3429 ^b
f_{acid}	2.03×10^{-5}	
$\nu_{\text{OH}}^{\text{bonding}}$	3566 ^a	
$\nu_{\text{OH}}^{\text{free}}$	3686 ^a	3634 ^b
f_{free}	5.75×10^{-6}	
$\text{CH}_3\text{C}(\text{OH})_2\text{COOH}\cdot\text{H}_2\text{O}$		
Conformer Tce		
$\nu_{\text{OH}}^{\text{acid}}$	2828 ^a	2929 ^b
f_{acid}	2.17×10^{-4}	
$\nu_{\text{OH}}^{\text{bonding}}$	3386 ^a	
$\nu_{\text{OH}}^{\text{free}}$	3669 ^a	3634 ^b
f_{free}	8.26×10^{-6}	

^a Calculated fundamental vibrational mode OH frequencies and oscillator strengths using the anharmonic oscillator local-mode method with the B3LYP/6-311++G(3df,3pd) presented in this work.

^b Experimentally observed or calculated OH-stretching transitions presented in this work.

determined from the second-, third-, and fourth-order derivatives of the potential energy curve according to the equations given by Kjaergaard [32] and Howard and Kjaergaard [34]. Peak assignments along with AO method calculated frequencies are presented in Table 1.

The oscillator strengths of each OH-stretching transition have been calculated within the HCAO local mode model with local mode parameters that were determined with an *ab initio* calculated dipole moment function as described by Low and Kjaergaard [35].

3. Results and discussion

3.1. Characterization of vibrational spectra in the mid-infrared

Pyruvic acid is an α -ketoacid, which is most stable in its ketone form [11,12,36–40], but can exist in its enol form via a keto–enol tautomerism. The flexibility of the $\text{C}-\alpha\text{C}-\text{C}-\text{O}$ chain in the keto and $\text{O}-\alpha\text{C}-\text{C}-\text{O}$ in the enol form allows for many possible conformations [11]. The three thermodynamically stable keto conformations, Tce, Tte, Cte, and the most stable enol form, E1, of pyruvic acid, have been previously observed within a carbon tetrachloride matrix and assigned by Raczyńska et al. [11]. The nomenclature for the keto conformations were taken from Yang et al. [36] and the nomenclature for the enol form was taken from Raczyńska et al. [11]. In this work in addition to observing Tce-, Tte-, Cte- and E1-pyruvic acid conformers we have observed Tce-2,2-dihydroxypropanoic acid and the hydrates of Tce- and Tte-pyruvic acids

and *Tce*-2,2-dihydroxypropanoic. The emphasis in this study is on the lowest energy, reactive *Tce*-pyruvic acid conformer [12,13]. The *Tce*-pyruvic acid conformer is the most stable structure, due to strong intramolecular hydrogen bonding between the carbonyl C=O and the carboxylic OH functional groups [38]. The B3LYP/6-311++G(3df,3pd) optimized structures of the two most stable conformers of pyruvic acid, *Tce*-CH₃COCOOH and *Tte*-CH₃COCOOH, and the two structures of 2,2-dihydroxypropanoic acid,

Tce-CH₃C(OH)₂COOH and *Tte*-CH₃C(OH)₂COOH, are shown in Figure 1. The *Tce*- and *Tte*-pyruvic acid conformers differ by a *trans* and *cis* conformation of the carboxylic hydrogen atom and the carbonyl groups. The *Tte*-pyruvic acid conformer is stabilized by a weaker intramolecular hydrogen bond. Carbon tetrachloride matrix [11] and gas-phase [12] infrared spectra are available in the literature for pyruvic acid, but no vibrational spectra of pyruvic acid water clusters, 2,2-dihydroxypropanoic acid and its water clusters

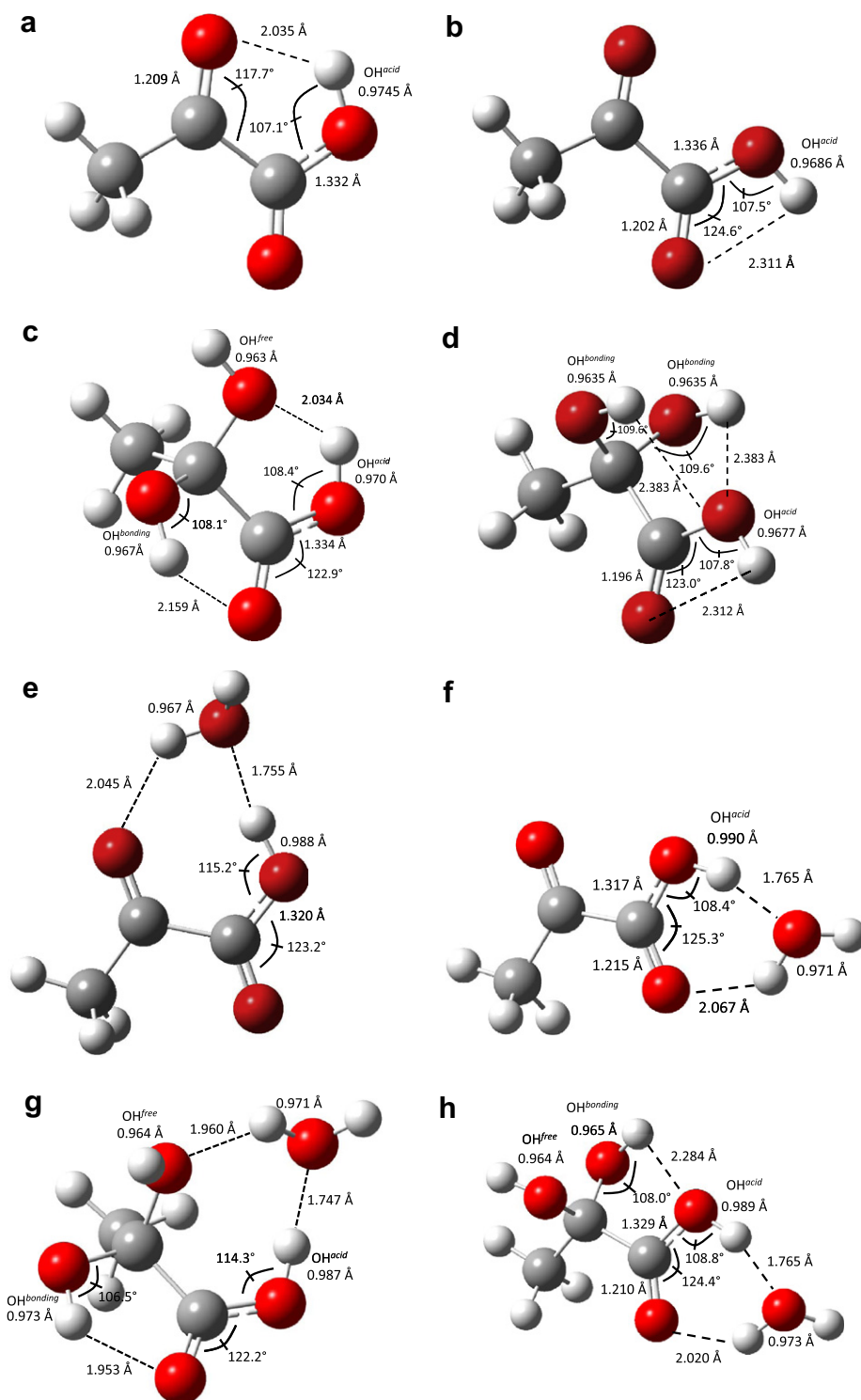


Figure 1. B3LYP/6-311++G(3df,3pd) optimized structures of (a) *Tce*-CH₃COCOOH; (b) *Tte*-CH₃COCOOH; (c) *Tce*-CH₃C(OH)₂COOH; (d) *Tte*-CH₃C(OH)₂COOH; (e) *Tce*-CH₃COCOOH·H₂O; (f) *Tte*-CH₃COCOOH·H₂O; (g) *Tce*-CH₃C(OH)₂COOH·H₂O; (h) *Tte*-CH₃C(OH)₂COOH·H₂O.

have been reported prior to the present study. Figure 2 contains the fundamental vibrational mid-infrared spectra of 45, 35, 24, 15 and 0 wt.% aqueous pyruvic acid solutions in carbon tetrachloride, at room temperature, obtained in this work.

To aid and support assignments of our mid-infrared spectra we conducted an investigation of the hydration of pyruvic acid in aqueous phase via ^{13}C NMR and performed theoretical calculations of the structures and fundamental vibrational frequencies for pyruvic acid, 2,2-dihydroxypropanoic acid and their corresponding water complexes of the most stable conformers. The ^{13}C NMR spectra of aqueous pyruvic acid solutions, shown in Figure 3, indicate that at high water/pyruvic acid ratios new spectral features appear attributed to the presence of 2,2-dihydroxypropanoic acid. Vibrational peak assignments of the infrared spectra along with calculated OH-stretching transitions are presented in Table 1.

The ability of pyruvic acid to hydrate its carbonyl group in the presence of water to form 2,2-dihydroxypropanoic acid and the distinct spectroscopic signatures of these two chromophores allows us to investigate the water-mediated equilibrium. In aqueous solution, these acids could hydrolyze to give H_3O^+ , $\text{CH}_3\text{COCOO}^-$ and $\text{CH}_3\text{C}(\text{OH})_2\text{COO}^-$ ions; however, these species were not observed in this experiment. The spectra shown in Figure 2, indicate that molecular pyruvic and 2,2-dihydroxypropanoic acids and their hydrates are the primary constituents in this water-restricted environment. The spectral features at 3429, 3561 and 3514 cm^{-1} have been previously assigned to the OH-stretches of the four molecular pyruvic acid conformers *Tce*, *Tte*, *Cte* and *E1*, respectively [11,41]. The most stable *Tce*-pyruvic acid conformer appears with the highest intensity as expected. The peak at 3561 cm^{-1} is comprised of overlapped transitions for the *Tte*- and *Cte*-pyruvic acid conformers. Our observations of the OH-stretches of molecular *Tce*-, *Tte*-, *Cte*- and *E1*-pyruvic acid conformers in a carbon tetrachloride matrix are in excellent agreement with previous work in the same environment by Raczynska et al. [11,41], which reported these features at 3430, 3563 and 3516 cm^{-1} respectively. The OH-stretch of molecular *Tce*- and *Tte*-pyruvic acid has been observed in the

gas-phase at 3467 and 3579 cm^{-1} , respectively [12]. Here we measure matrix shifts of 38 and 18 cm^{-1} for *Tce*- and *Tte*-pyruvic acid, respectively, when compared to gas-phase results. The peaks at 3616 and 3708 cm^{-1} are assigned to the symmetric and antisymmetric OH-stretch of molecular water, respectively. Previous work by Kuo et al. [20] have observed the symmetric and antisymmetric OH-stretch of H_2O in a carbon tetrachloride matrix at 3617 and 3708 cm^{-1} , respectively, and we follow their assignments for water.

At high water/pyruvic acid ratios, several new spectral features are observed. A new peak appears at 3634 cm^{-1} and a broad spectrum develops between 2800 and 3100 cm^{-1} . We assign the peak at 3634 cm^{-1} to overlapping free OH-stretching transitions of *Tce*-2,2-dihydroxypropanoic acid and its monohydrate. This assignment was confirmed from our theoretical calculations given in Table 1. Intermolecular hydrogen bonding is expected to produce a significant red-shift of the OH-stretching transitions in the complex [12,14,31,33,42–46]. Therefore we can assign the broad spectrum in the infrared between 2800 and 3100 cm^{-1} to *Tce*- and *Tte*-pyruvic monohydrates (*Tce*- and *Tte*- $\text{CH}_3\text{COCOOH}\cdot\text{H}_2\text{O}$) and *Tce*-2,2-dihydroxypropanoic acid monohydrate (*Tce*- $\text{CH}_3\text{C}(\text{OH})_2\text{COOH}\cdot\text{H}_2\text{O}$). We performed theoretical calculations to obtain structures of monohydrate clusters of *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acids, as shown in Figure 1, as well as their fundamental OH peak positions, to get a firm assignment of the broad spectral feature. The monohydrate formation leads to an increase in the acid OH bond length of *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acids. By comparing the values reported in Figure 1, we see a small increase in OH bond length of 13, 22 and 17 mÅ for *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acids, respectively. The elongation of the OH bond length of the acid OH of *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acid monohydrates is a characteristic of molecules complexed to water and is indicative of intermolecular hydrogen bonding. The most defined peaks centered at 2887, 2929 and 2975 cm^{-1} are assigned to *Tte*- $\text{CH}_3\text{COCOOH}\cdot\text{H}_2\text{O}$,

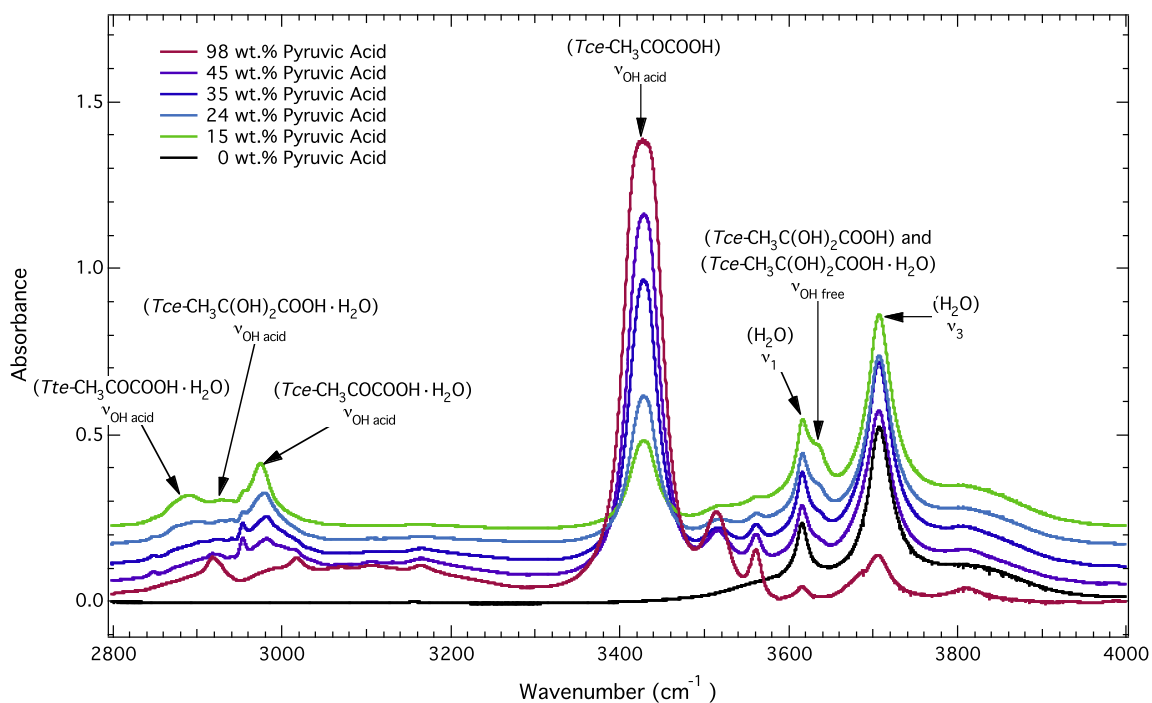


Figure 2. Observed mid-infrared absorption spectra of aqueous pyruvic acid solutions in the carbon tetrachloride layer are shown as a function of weight percent, at 0.25 cm^{-1} resolution from 2800 to 4000 cm^{-1} . *Tte*- and *Cte*- CH_3COCOOH and *E1* conformers of pyruvic acid are also present, but unmarked and spectra have been offset for clarity.

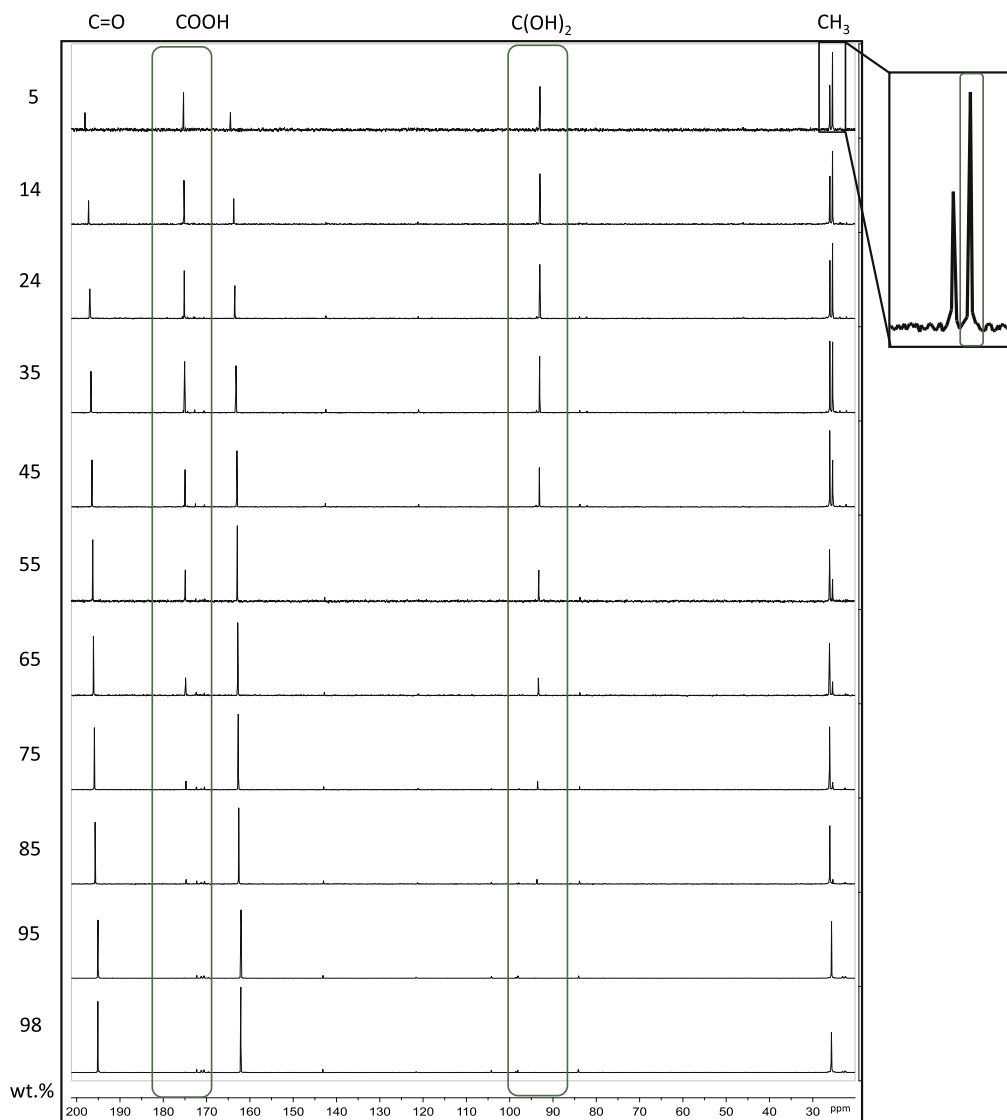


Figure 3. ^{13}C NMR spectra of aqueous pyruvic acid solutions are shown as a function of weight percent. Spectra have been offset for clarity. The features due to 2,2-dihydroxypropanoic acid conformers have been indicated with green boxes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
The integrated area of OH-stretching transitions, the calculated oscillator strengths and the determined concentrations of *Tce*-pyruvic acid and *Tce*-2,2-dihydroxypropanoic acid and its corresponding water complex are shown here.

		<i>Tce</i> -CH ₃ COCOOH	<i>Tce</i> -CH ₃ C(OH) ₂ COOH	<i>Tce</i> -CH ₃ C(OH) ₂ COOH·H ₂ O
Area ^a	15	7.22689	0.860297	
	24	15.9396	0.508982	
	35	33.4019	0.206982	
	45	49.2495	0.115478	
Oscillator strength, f_{01} ^b		2.09×10^{-5}	5.75×10^{-6} 7.16×10^{-6}	8.56×10^{-6}
Concentration, M^a	15	2.14×10^{-5}	2.04×10^{-5}	
	24	4.71×10^{-4}	1.21×10^{-5}	
	35	9.87×10^{-4}	4.92×10^{-6}	
	45	1.46×10^{-3}	8.50×10^{-6}	

^a Due to the overlapping OH-stretching transitions of the free OH on *Tce*-2,2-dihydroxypropanoic acid and its monohydrate, the integrated area was obtained and concentration of the geminal diol was determined.

^b In order to determine the total geminal diol concentration the average oscillator strengths of the free OH on *Tce*-2,2-dihydroxypropanoic acid and its monohydrate were used.

Tce-CH₃C(OH)₂COOH·H₂O and *Tce*-CH₃COCOOH·H₂O respectively. These assignments were aided by the calculated vibrational fre-

quencies for these monohydrates shown in Table 1. The noticeable difference between calculated and observed frequencies is due to a

matrix shift as well as the limitation of theory to accurately predict intermolecular hydrogen bonded OH vibrations [32,33]. In the fundamental region, the red-shift of the acid OH of *Tte*-CH₃CO-COOH·H₂O, *Tce*-CH₃C(OH)₂COOH·H₂O and *Tce*-CH₃COCOOH·H₂O was observed to be 674 cm⁻¹ (3561–2887 cm⁻¹), 500 cm⁻¹ (3429–2929 cm⁻¹) and 518 cm⁻¹ (3429–2975 cm⁻¹), respectively. The theoretical prediction of a red-shift of the acid OH-stretching transitions calculated in this study are expected to be 749 cm⁻¹ for *Tte*-CH₃COCOOH·H₂O, 659 cm⁻¹ for *Tce*-CH₃C(OH)₂COOH·H₂O and 518 cm⁻¹ for *Tce*-CH₃COCOOH·H₂O, in agreement with the experimental results. The vibrational spectra of the acids and their water complexes have been extended to the near-infrared and are described in the supplementary material.

3.2. Water mediated hydration between pyruvic and 2,2-dihydroxypropanoic acids

Our spectroscopic results, as shown in Figure 2 allow for qualitative observation and characterization of molecular *Tce*-, *Tte*-, *Cte*- and *E1*-pyruvic and *Tce*-2,2-dihydroxypropanoic acids and *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acid monohydrates within a water-restricted environment at ambient temperatures. In order to quantitate the extent of the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid, the concentrations of *Tce*-pyruvic acid and *Tce*-2,2-dihydroxypropanoic acid are required. The concentrations were determined by taking the ratio of the integrated area of the acid OH-stretching transition with the corresponding theoretical oscillator strength, shown by Eq. (1), where OH_x represents the acid OH for *Tce*-pyruvic acid or the free OH for *Tce*-2,2-dihydroxypropanoic acid.

$$\frac{\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \text{Area}_{\text{OH}_x} d\tilde{\nu}}{I \cdot \frac{N_A e^2}{4\epsilon_0 m_e c^2 \ln 10} f_{\text{OH}_x}} = [\text{CH}_3\text{COCOOH}] \text{ or } [\text{CH}_3\text{C}(\text{OH})_2\text{COOH}] \quad (1)$$

Due to the overlapping OH-stretching transitions of the free OH on *Tce*-2,2-dihydroxypropanoic acid and its monohydrate it was not possible to separate and determine their individual concentrations. Therefore the total geminal diol concentration was determined by taking the ratio of the integrated area of the free OH-stretching transition with the average of the theoretical oscillator strengths for *Tce*-2,2-dihydroxypropanoic acid and its monohydrate using Eq. (1). The integrated areas of the OH-stretching transitions, the theoretical oscillator strengths and the concentrations for both acids are summarized in Table 2.

$$Q = \frac{[\text{CH}_3\text{C}(\text{OH})_2\text{COOH}]}{[\text{CH}_3\text{COCOOH}]} \quad (2)$$

The extent of the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid is denoted by *Q* and is given by Eq. (2). The *Q* determined for the 45, 35, 24, and 15 wt.% aqueous pyruvic acid solutions in carbon tetrachloride are 2.3×10^{-3} , 6.2×10^{-3} , 3.2×10^{-2} , and 1.2×10^{-1} , respectively. We note that this analysis depends on the accuracy of the calculated relative fundamental intensities of the two peaks. Previous studies have shown that B3LYP intensities give results within a factor of two of the experimental values [42]. On the other hand, when relative intensities are considered, this discrepancy is much smaller, and we have previously compared the B3LYP intensity ratios for the two conformers of pyruvic acid with CCSD(T) results and saw that it was off by less than 10% [13]. Therefore, we believe that the above *Q* values are accurate only to two digits that are reported. The dependence of *Q* on the water concentration suggests that water and water complexes play an important role in the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid. The relative population of 2,2-dihydroxypropanoic acid is much greater than what is expected

from the consideration of one water molecule and we believe that larger water clusters promote the hydration process. The importance of including water complexes in order to account for the observed water dependence in other hydration studies has been stated by Plath et al. [15] and Axson et al. [16] in the observation of the geminal diols of glyoxylic acid and methylglyoxal in the gas-phase, respectively. The work by Gandour [43] and Wolfe et al. [44], have proposed that the hydration of a carbonyl group proceeds in solution via a cyclic transition state containing two or three [44] water molecules. They suggest the formation of a cyclic six- or eight-membered reaction complex, with two or three protons moving more or less synchronously in the transition state. The formation of a cyclic reaction complex to lower the barrier for the hydration reaction of fluoromethanol was shown by Takahashi et al. [25]. Our results are consistent with the proposed hydration mechanisms.

4. Summary

The vibrational spectra of *Tce*-, *Tte*-, *Cte*- and *E1*-pyruvic acid conformers as well as *Tce*- and *Tte*-2,2-dihydroxypropanoic acid and their monohydrates are reported here at ambient temperatures in a water-restricted environment. With this method, we were able to make the first spectroscopic observation of 2,2-dihydroxypropanoic acid and monohydrates of *Tce*- and *Tte*-pyruvic and *Tce*-2,2-dihydroxypropanoic acids in the mid-infrared. The results from this study show that at ambient conditions in this water-restricted environment, pyruvic acid will undergo hydration to form 2,2-dihydroxypropanoic acid.

This investigation of the water-mediated hydration between pyruvic and 2,2-dihydroxypropanoic acids showed that in order to explain the experimentally observed large concentration of 2,2-dihydroxypropanoic acid it is necessary to incorporate intermolecular hydrogen-bonded water complexes in the reaction mechanism. Our findings show that the hydration of pyruvic acid to 2,2-dihydroxypropanoic acid is dependent on the water concentration, which has been observed in gas-phase studies [15,16].

We conclude that significant concentration of the geminal diol of pyruvic acid may form in water-restricted situations typical in environmental chemistry. 2,2-Dihydroxypropanoic acid has different chemical and physical properties than pyruvic acid. These results imply the importance of relative humidity on the partitioning between gas and particle phase [45–47]. Hydration of the carbonyl group will have important consequences to the photochemistry of pyruvic acid and other oxidized organic molecules in the atmosphere [48].

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References

- [1] D.R. Kent et al., J. Chem. Phys. 119 (2002).
- [2] M. Mugnai et al., Mol. Phys. 105 (17–18) (2007) 2203.
- [3] H.E. Krizner, D.O. De Haan, J. Kua, J. Phys. Chem. A 113 (25) (2009) 6994.
- [4] A.J.L. Cooper, A.G. Redfield, J. Biol. Chem. 250 (2) (1975) 527.
- [5] H.J. Buschmann, E. Dutkiewicz, W. Knoche, Ber. Bunsen Phys. Chem. 86 (2) (1982) 129.
- [6] G. Fischer et al., J. Org. Chem. 53 (1) (1988) 214.
- [7] M. Becker, Berich. Bunsen Gesell. 68 (7) (1964) 669.
- [8] M. Becker, H. Strehlow, Z. Elektrochem. 64 (6) (1960) 813.

- [9] H.J. Buschmann, H.H. Fuldner, W. Knoche, Ber. Bunsen Phys. Chem. 84 (1) (1980) 41.
- [10] A. Hodzic et al., Atmos. Chem. Phys. 10 (12) (2010) 5491.
- [11] E.D. Raczynska, K. Duczmal, M. Darowska, Vib. Spectrosc. 39 (1) (2005) 37.
- [12] K. Takahashi et al., J. Phys. Chem. A 112 (32) (2008) 7321.
- [13] K.L. Plath et al., J. Phys. Chem. A 113 (26) (2009) 7294.
- [14] C. Lugez et al., Chem. Phys. 181 (1993) 129.
- [15] K.L. Plath et al., React. Kinet. Catal. Lett. 96 (2) (2009) 209.
- [16] J.L. Axson et al., Proc. Natl. Acad. Sci. USA 107 (15) (2010) 6687.
- [17] M. Kuo, N. Kamelamela, M.J. Shultz, J. Phys. Chem. A 112 (6) (2008) 1214.
- [18] H. Kleeberg, D. Klein, W.A.P. Luck, J. Phys. Chem. 91 (12) (1987) 3200.
- [19] N. Leroux, C. Samyn, T. Zeegers-Huyskens, J. Mol. Struct. 448 (1998) 209.
- [20] M.H. Kuo et al., J. Phys. Chem. C 111 (25) (2007) 8827.
- [21] M.K. Maron, M.J. Shultz, V. Vaida, Chem. Phys. Lett. 473 (4–6) (2008) 268.
- [22] P. Bisson et al., J. Phys. Chem. A 114 (12) (2010) 4051.
- [23] F.M. Nicolaisen, J. Quant. Spectrosc. Radiat. Transfer 110 (18) (2009) 2060.
- [24] A.D. Hammerich, V. Buch, J. Chem. Phys. 128 (11) (2008) 111101.
- [25] K. Takahashi et al., Phys. Chem. Chem. Phys. 9 (29) (2007) 3864.
- [26] A.D. Becke, J. Chem. Phys. 98 (7) (1992) 5648.
- [27] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (2) (1988) 785.
- [28] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (10) (1980) 5639.
- [29] R. Krishnan et al., J. Chem. Phys. 72 (1) (1980) 650.
- [30] T. Clark et al., J. Comput. Chem. 4 (3) (1983) 294.
- [31] M.J. Frisch et al., GAUSSIAN03 C.02 ed., vol. 110, Gaussian Inc., Wallingford, CT, 2004.
- [32] H.G. Kjaergaard, J. Phys. Chem. A 106 (12) (2002) 2979.
- [33] D.L. Howard, P. Jorgensen, H.G. Kjaergaard, J. Am. Chem. Soc. 127 (48) (2005) 17096.
- [34] D.L. Howard, H.G. Kjaergaard, J. Phys. Chem. A 110 (34) (2006) 10245.
- [35] G.R. Low, H.G. Kjaergaard, J. Chem. Phys. 110 (18) (1999) 9104.
- [36] X. Yang et al., Chem. Phys. Lett. 380 (1–2) (2003) 34.
- [37] I.D. Reva et al., J. Phys. Chem. A 105 (19) (2001) 4773.
- [38] C. Chen, S.F. Shyu, J. Mol. Struct. Theochem. 503 (3) (2000) 201.
- [39] Z.Y. Zhou, D.M. Du, A.P. Fu, Vib. Spectrosc. 23 (2) (2000) 181.
- [40] P. Tarakeshwar, S. Manogaran, J. Mol. Struct. Theochem. 430 (1998) 51.
- [41] E.D. Raczynska, K. Duczmal, M. Darowska, Pol. J. Chem. 79 (4) (2005) 689.
- [42] H.G. Kjaergaard, K.J. Bezar, K.A. Brooking, Mol. Phys. 96 (7) (1999) 1125.
- [43] R.D. Gandour, Tetrahedron Lett. 3 (1974) 295.
- [44] S. Wolfe et al., J. Am. Chem. Soc. 117 (15) (1995) 4240.
- [45] L. Bao et al., Atmos. Environ., in press.
- [46] S. Matsunaga, M. Mochida, K. Kawamura, J. Geophys. Res. 109 (2004) D04302.
- [47] R.G. Remorov, C. George, Phys. Chem. Chem. Phys. 8 (2006) 4897.
- [48] D.J. Donaldson, A.F. Tuck, V. Vaida, Chem. Rev. 103 (12) (2003) 4717.