

Effect of the intra-molecular H-bond of L-lactic acid on its dehydration mechanism: An experimental and computational IR and hybrid DFT-D3 study

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We have studied with hybrid Density Functional Theory (DFT) the intra-molecular hydrogen bond of L-lactic acid and L-lactic-acid analogs with the hydroxyl group on the alpha carbon atom substituted by α -XH (where X = S, Se, Te). The results show there are three types of intramolecular hydrogen bonds that can form only when α -OH is present, whereas other less electronegative functional groups such as -SH, -SeH and -TeH do not exhibit the formation of an intramolecular H-bond. We show that the intra-molecular H-bond formed between the alpha-OH hydrogen and the COOH carbonyl oxygen would enhance the rate of the nucleophilic substitution of alpha-OH to the K⁺ sites for the previously suggested dehydration mechanism of L-lactic to acrylic acids. We find that a temperature range between 190-210 °C would be optimum to maximise the rate of the nucleophilic substitution of the alpha-OH group onto the potassium sites during the dehydration mechanism of L-lactic acid to acrylic acid. Additionally, our hybrid-DFT simulation of the infrared spectrum of the various conformers shows that the lowest energy conformer can be identified by a single vibrational band at 3734 cm⁻¹ whereas the other conformers this vibrational band is split with $\Delta\nu$ that ranges between 6 cm⁻¹ - 176 cm⁻¹. We also find

that the various conformers of acrylic acid can be identified by a double peak for the C=O and O-H vibrations which have $\Delta\nu'$ of $\Delta\nu''$ 24 and 42 cm^{-1} , respectively. This computational study is useful for spectroscopic experimental efforts that try to identify the various conformers of L-lactic acid and acrylic acid and to gain mechanistic insight into the dehydration mechanism over K substituted NaY Zeolites.

Introduction

The industrial production of lactic acid (α -hydroxypropionic) occurs via bacterial fermentation of sugar and starch that contain carbohydrates or by chemical synthesis from acetaldehyde that originates from coal and crude oil.¹ Bacterial fermentation can produce racemic lactic acid consisting of 1:1 mixture of D- and L-stereoisomers or even 99.9% L-lactic acid. L-lactate, the conjugate base of lactic acid, is constantly produced in animals from pyruvate via the enzyme lactate dehydrogenase (LDH) in a process of fermentation during normal metabolism and exercise.

The main industrial use of lactic acid is for the manufacturing of polylactic acid (PLA). Polymer derivatives of lactic acid are biocompatible and biodegradable and are therefore used in medical devices, implants and drug delivery systems.^{2,3} The global annual production of lactic acid was 260,000 tons (excluding PLA) in 2008 and in 2020 it is estimated to be 1,000,000 tons for lactic acid and PLA.⁴ Clealry, there is an increasing need for eco-friendly packaging and there will be a huge market potential in coming years for lactic acid derived plastics.

The dehydration of lactic acid to acrylic acid depicted in Scheme 1 is a very important reaction in the development of green routes for its utilisation, as acrylic acids and its esters are primary building block for all acrylate polymers and plastics.⁵⁻⁷ Therefore the discovery of a catalyst that can efficiently produce acrylic acid from a renewable source is very desirable and would have a significant economic and environmental impact. Currently the industry uses the direct oxidation of propene to produce acrylic acid for which the catalytic dehydration of lactic acid to acrylic acid could become a tantalizing 'green' alternative.⁷ The catalytic conversion of lactic acid to acrylic acid has been shown to be possible with heterogeneous catalysts, such as phosphate impregnated metal oxides with moderate yields (40 - 58 mol%).⁸ Higher yields of 61 mol% have been reported by a base treated calcinated aluminum

phosphate catalyst at reaction temperature of 320 - 375 °C.⁹ KX-modified NaY zeolites have also been found to catalyze the dehydration of lactic acid to acrylic acid and a mechanism has been proposed.¹⁰ In this mechanism the lactic acid adsorbs to potassium cation coordinating through its hydroxyl (-OH) moiety whereas a hydrogen (-H) from the methyl group interacts with the oxygen of a Si-O-Al moiety. These interactions lead to the abstraction of -OH and -H causing acrylic acid to desorb whereas the former adsorbates recombine on the surface of the catalysts forming water which when desorbs regenerating the catalytic site.¹⁰

Understanding the dynamic conformational changes of L-lactic acid as a function of temperature is critical in understanding its adsorption and dehydration mechanism. It has been previously found by van Eijck that lactic acid forms an intramolecular hydrogen bond between the α -hydroxyl group and the C=O of a carboxylate group (conformer **D** in Fig. 2) using microwave spectroscopy in the gas phase.¹¹ Using the semiempirical AM1 and SCF/3-21G method Norris and Gready found 9 conformers for lactic acid with the lowest energy conformer the one where the alpha-OH bond was intramolecularly H-bonded to the OH group of the carboxylic acid (conformer **C** in Fig. 2).¹² Formation of the hydrogen bond leads to a stabilisation of 10 +/- 4 kcal mol⁻¹.¹³ Spectroscopic evidence of two higher energy conformers come from Fausto and co-workers through matrix isolated Fourier transform-infrared (IR) spectroscopy and theoretical calculations at the DFT(B3LYP)/6-311G(d,p) and MP2/6-31G(d,p) levels of theory which showed that conformer **D** is the lowest energy structure.¹⁴

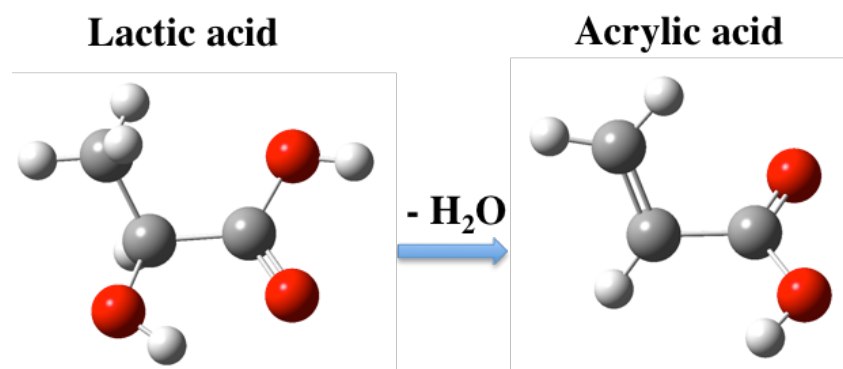


Figure 1. Figure the dehydration of lactic acid to acrylic acid

In this study we have performed a systematic study using hybrid dispersion-corrected DFT of the various H-bonds that form in L-lactic acid and three analogs of lactic acid that have less electronegative elements at the alpha hydroxyl group. First in Section 1.1 we evaluate the temperature at which there is rotational freedom of the carboxylate group. We calculate the relative free energy change with respect to the lowest energy conformer. In Section 1.2 we examine the effect of the electronegativity of the hydroxyl group on the formation of the hydrogen bond. In section 1.3 we simulate the infrared absorption spectrum of the various conformers of lactic acid and suggest a way that the formation of the H-bond can be experimentally confirmed. In section 1.4 we study the effect of basis set on the calculated vibrational frequencies. In section 1.5 we identify the various conformers of L-lactic acid using IR spectroscopy simulations. In section 1.6 we study the various conformers of acrylic acid and in section 1.7 we make an assignment of the vibrational bands in their infrared absorption spectra.

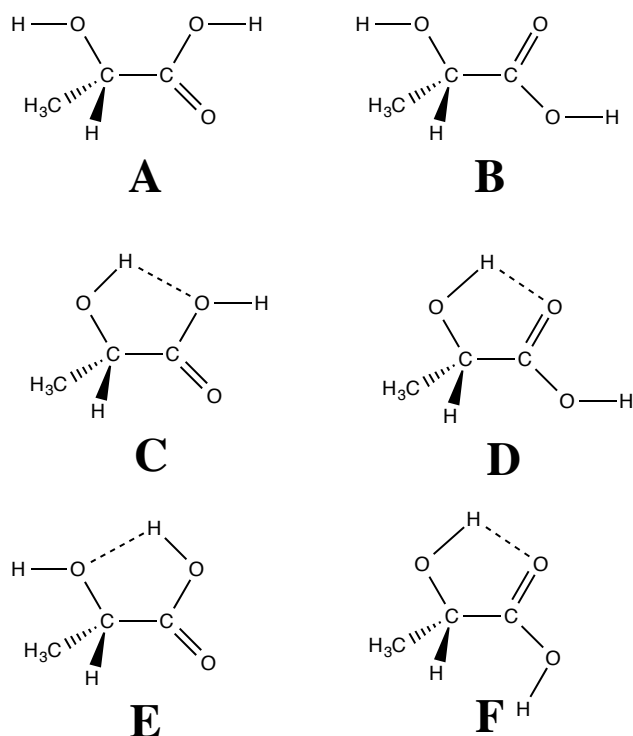


Figure 2. Various local and global minima of L-lactic acid found using the B3LYP-D3/aug-cc-pVTZ method

Computational Methods

DFT calculations have been performed with Gaussian 09¹⁵ with the use of Becke's three-parameter hybrid exchange functional¹⁶ (XC) combined with the Lee-Yang-Parr non-local correlation functional¹⁷, abbreviated as B3LYP. The B3LYP exchange-correlation functional was appropriate, as this would yield accurate oscillator frequencies in modelling IR spectra of adsorbate-metal cluster systems.¹⁸⁻²⁰ For the basis functions, we have used the spherical version (5d, 7f), the correlation consistent augmented valence triple zeta basis set²¹⁻²⁵, abbreviated as aug-cc-pVTZ for C, O, S, Se and H and ECP-121G basis set for Te. Dispersion forces were accounted for with the D3 method by Grimme as implemented in Gaussian 09. The level of theory is abbreviated as B3LYP-D3/ECP-121G(Te),aug-cc-pVTZ(C,O,S,Se,H). Lactic acid was fully optimised and the stationary points have been confirmed using vibrational analysis, by the absence of imaginary vibrational frequencies. The SCF convergence criteria for the root mean square (RMS) density matrix and the total energy were set to 10^{-8} Hartrees/bohr and 10^{-6} Hartrees, respectively.

The simulated IR spectra were performed within the harmonic oscillator approximation where the intensity of each vibrational mode i was taken to be proportional to the square of the derivative of the molecular dipole field with respect to the vibrational coordinate, q_i :

$$\left[\int \psi_{v=0} \frac{\partial \boldsymbol{\mu}}{\partial q_i} \psi_{v=1} dq_i \right]^2 \quad (2)$$

where the harmonic oscillator wavefunctions are used for $\psi_{v=0}$ and $\psi_{v=1}$. We have calculated the dipole derivatives and the force constants from the DFT wavefunction.²⁶

Results and Discussion

The study of conformational changes in L-lactic acid and acrylic acid is important to understand better their mechanism of interconversion. Intramolecular H-bond can affect the conformational dynamics to a great extent as they stabilise intermediate conformations that maximise the strength of the intermolecular interactions. Here we study such conformational changes in L-

lactic acid and determine the temperature of interconversion of the various conformers of L-lactic acid via a simple model described in the following section.

1.1 Temperature of conformational change

Estimation of the temperature of conformational change as a function of activation barriers is derived in this section. For a general isomerisation reaction of the form $A \leftrightarrow B$ we can say that the rate of the forward reaction is given by

$$k_A = e^{-\Delta G_A/RT} \quad (1)$$

and rate of the reverse reaction is given by,

$$k_B = e^{-\Delta G_B/RT} \quad (2)$$

The equilibrium quotient for this isomerisation reaction is given by

$$Q = \frac{k_A}{k_B} \quad (3)$$

So if we substitute the Arrhenius equation into Eqn. 3 the reaction quotient becomes,

$$Q = \exp\left(\frac{\Delta G_B - \Delta G_A}{RT}\right) \quad (4)$$

A reaction where all of A converts to B can be represented well by a reaction quotient of which manifests that the concentration of the products is 100 larger than the concentration of the reactants,

$$Q = 100 \quad (5)$$

Substituting Eqn. 4 into 5 and solving for the temperature yields

$$T = \frac{\Delta G_B - \Delta G_A}{\ln(100)R} \quad (6)$$

Equation 6 can give as the temperature at which an isomer A will turn into isomer B with a ratio in their concentrations of 1:99. For a single barrier process the numerator according to Fig. 3 is just the free energy change of the isomerization reaction ΔG_{rxn}

$$T = \frac{\Delta G_{rxn}}{4.6R} \quad (7)$$

We performed a rigid dihedral scan of L-lactic acid shown in Fig. 2, which shows that the upper bound barrier for the isomerisation of lactic acid from conformer **D** to **C** is 32.5 kJ mol⁻¹. This potential energy landscape shows that reaction coordinate is indeed the dihedral angle. It is therefore evident that from

Eqn. 7 we only have to calculate the energetic difference between the various conformers to estimate the temperature at which the isomerisation occurs.

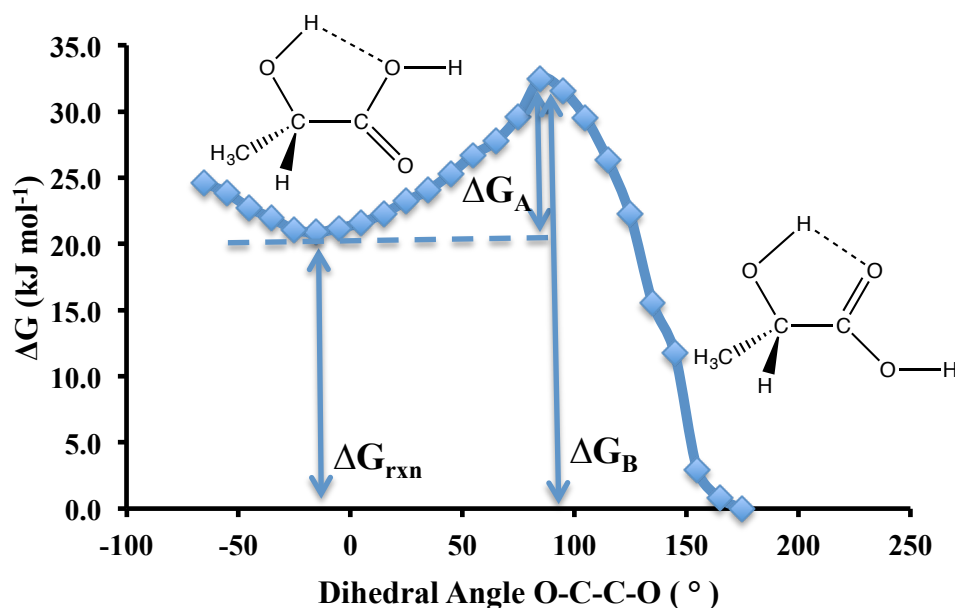
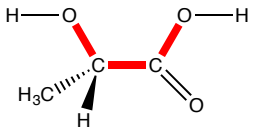
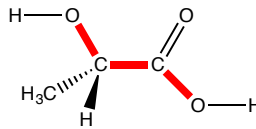
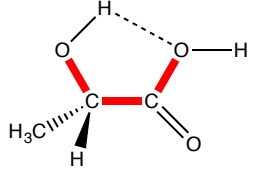
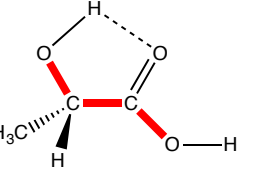
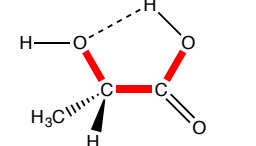
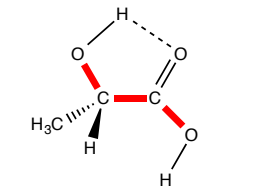


Figure 3. Rigid dihedral scan of O-C-C-O angle of lactic acid starting with the lowest energy conformer (i.e. D) using B3LYP-D3/aug-cc-pVTZ.

From the Gibbs free energy change given in the last column of table 1, we can also estimate the strength of the intra-molecular hydrogen bond formed, which is given by taking the Gibbs free energy difference between conformer **D** and **B**, which is 18.6 kJ mol^{-1} , indicative of a strong H-bond when O-H binds to a C=O group. Previous SCF/3-21G calculations¹² found that this energy difference between the two conformers is 20.9 kJ mol^{-1} which is in good agreement with the value found here. However, their¹² ranking of the relative energies of the conformers finds that conformer **C** is the lowest in energy, whereas we find that conformer **D** is lower by 9.3 kJ mol^{-1} . This result clearly shows that the inclusion of electron correlation and dispersion interactions in our study is necessary to get the correct ordering of the relative stability of the various conformers. The hydroxyl group when bound to the hydroxyl group of carboxylic acid forms a weaker H-bond which is only 8.1 kJ mol^{-1} when comparing the Gibbs free energy change between **C** and **A**. The same type of H-bond, between two hydroxyl groups is found to have a similar strength with the previous, which is 7.5 kJ mol^{-1} , when comparing the Gibbs free energies of conformers **E** and **A**. Therefore the relative strength of the 3 different hydrogen bonds

formed was found to be O-H...O=COH > O-H...O-HC=O > H-O...H-OC=O as it can be seen in conformers **D**, **C** and **E**, respectively.

Table 1. Free energy change and dihedral angle for the various conformers of L-lactic acid with respect to lowest energy conformer with and without the D3-correction at B3LYP/aug-cc-pVTZ level of theory

Labels	Structural Formula	δ ($^{\circ}$)	δ with D3 ($^{\circ}$)	ΔG (kJ mol $^{-1}$)	ΔG with D3 (kJ mol $^{-1}$)
A		-22.7	-24.8	16.8	17.4
B		162.8	163.9	17.8	18.6
C		-31.9	-33.9	9.0	9.3
D		176.0	174.8	0.0	0.0
E		-6.9	-7.8	9.5	9.9
F		175.2	173.6	19.4	19.3

From the various conformers found on the potential energy surface of lactic acid, we can identify 3 different conformational processes. The first is between **A** and **B** in which the dihedral changes by 185.5 $^{\circ}$ while the O-H bonds

are pointing away and not forming an intramolecular H-bond. The reaction temperature for this functional group rotational process is 31 K and therefore this rotation can occur even at room temperature (RT= 25 °C). The second is between **D** and **C** in which the dihedral angle changes by 209°. For these two conformers, the α -hydroxyl group is hydrogen-bonded with the carboxylate carbonyl or hydroxyl group. The enthalpy change for this isomerisation is 9.3 kJ mol⁻¹, which corresponds to an isomerisation temperature of 243 K, which can again happen at RT. The third process is the breaking of the H-bond going from conformer **D** to **B**. This process is endothermic by 18.6 kJ mol⁻¹ and the temperature at which this reaction occurs efficiently is 486 K (213 °C). The last process is expected to have serious implications on the catalytic dehydration mechanism of lactic acid in NaY Zeolites, as the formation of this H-bond below 213 °C enhances the partial negative charge on the alpha-OH oxygen which makes it more reactive towards nucleophilic substitution reactions. In a proposed mechanism¹⁰ of the lactic acid dehydration mechanism, the α -OH group undergoes nucleophilic substitution onto the cationic K⁺ substituted Na⁺ sites of the zeolite NaY as shown in Fig. 8 of Ref. 26. This nucleophilic substitution will be faster if the partial negative charge on the oxygen of the alpha-OH group is more negative. Therefore the H-bond that forms between the alpha-OH hydrogen and the COOH carbonyl oxygen in conformer **D** which happens at temperatures below 213 °C would in principle enhance the rate of the dehydration mechanism. Consequently, it is important that the intramolecular H-bond is present during the dehydration of lactic acid which from our estimate of the rotational barrier of the carboxylate group would happen for temperatures below 213 °C. However, as the temperature of the reaction decreases also the rate decreases. It is therefore evident from these computational data that the rate of the dehydration mechanism of lactic acid is maximised in a very small temperature range between 190 and 210 °C. This temperature range should assist in experimental efforts of increasing the catalytic dehydration mechanism of lactic acid over the potassium substituted Zeolite NaY.

1.2 Effect of electronegativity of α -XH group (where $X = O, S, Se, Te$) on intramolecular H-bond

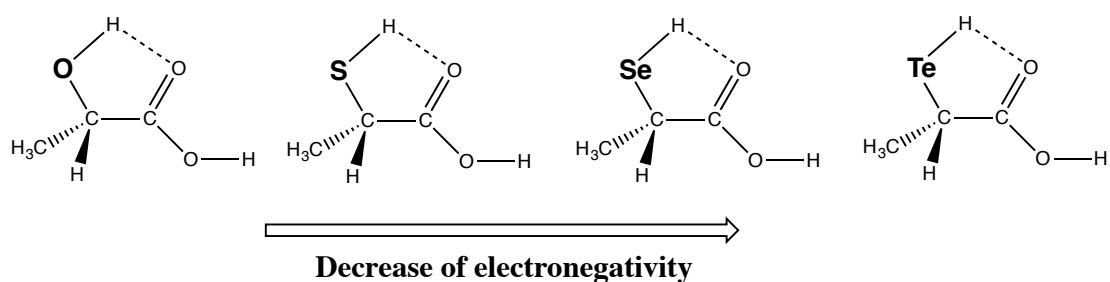


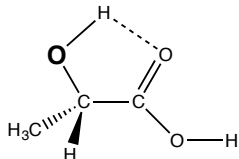
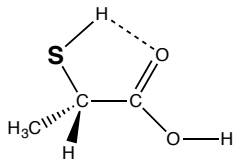
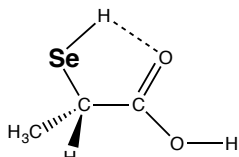
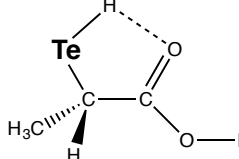
Figure 4. Various lactic acid-like compounds examined for the formation of an intra-molecular H-bond

1.3 Effect of electronegativity on Intramolecular Hydrogen Bonding

We investigated whether the substitution of a less electronegative atom that belongs to the same group of the periodic table has an effect on the intramolecular H-bond formation. The lactic acid like molecules optimised using the D3-B3LYP/CEP-121G method and the D3-B3LYP/aug-cc-pVTZ method are presented in Fig. 4. The same starting structure was used for these full atom optimisations, which was the optimised structure of L-lactic acid using the later method. Certain selected geometric parameters, such as the dihedral angle of the H-bond ($\delta(X-C-C-O)$) and the length of the H-bond measured between the H...O along with the corresponding values of electronegativity of group 6 atoms are tabulated in Table 2. In these results we observe that the $\alpha(X-H)$ which for lactic acid is almost 180° , for all substituted analogs of lactic acid, the same dihedral becomes about 90° , which causes the $\alpha(X-H)$ to become parallel with the C=O bond of the carboxylic acid and be located at a larger intramolecular separation. The larger separation can be seen by the increase of the H...O bond as a function of the decreasing electronegativity (and larger atomic radius) of the group 6 element ($X = O, S, Se, Te$). The formation of the H-bond in just lactic acid is in agreement with the textbook definition of the H-bond that indicates that hydrogen atom that has a covalent link with one of the electronegative atoms (F, N, O) forms an electrostatic link with another electronegative atom in the same or another molecule. We therefore find that among the various lactic acid analogs with O, S, Se and Te only the analog that has a hydroxyl group on the alpha carbon will form a strong H-bond, which can be clearly seen by the

distance of H...O which increases from 2.302 Å for OH to 3.077 Å for SH to 3.226 for SeH to 3.581 Å for TeH. The absence of the hydrogen bond formation can also be observed by the value of the dihedral angle $\delta(\text{X-C-C-O})$ which for X=O is about 180 degrees but for all other analogs that do not form a hydrogen bond this dihedral becomes roughly 90 degrees.

Table 2. Geometric parameters of optimised structures of lactic acid-like compounds where $\alpha\text{-XH}$ (where X = O, S, Se, Te) using the B3LYP-D3/ECP-121G method (and B3LYP-D3/aug-cc-pVTZ in parenthesis).

Labels	Struc. Formula	$\delta(\text{X-C-C-O})$ ($^{\circ}$)	$r(\text{H}\dots\text{O})$ (Å)	H-bond formation	electroneg. Pauling ²⁷
D^a		164.6 (174.8)	2.302 (2.120)	forms	3.44
F		97.3 (93.2)	3.077 (3.008)	does not form	2.58
G		91.9 (89.7)	3.226 (3.139)	does not form	2.55
H		86.1	3.581	does not form	2.10

^a The H-bond strength obtained for lactic acid using the ECP-121G basis is 17.5 kJ mol⁻¹ which compares very well with the value obtained with the aug-cc-pVTZ basis set which is 18.6 kJ mol⁻¹

1.4 Simulated and Experimental infrared spectrum of lactic acid

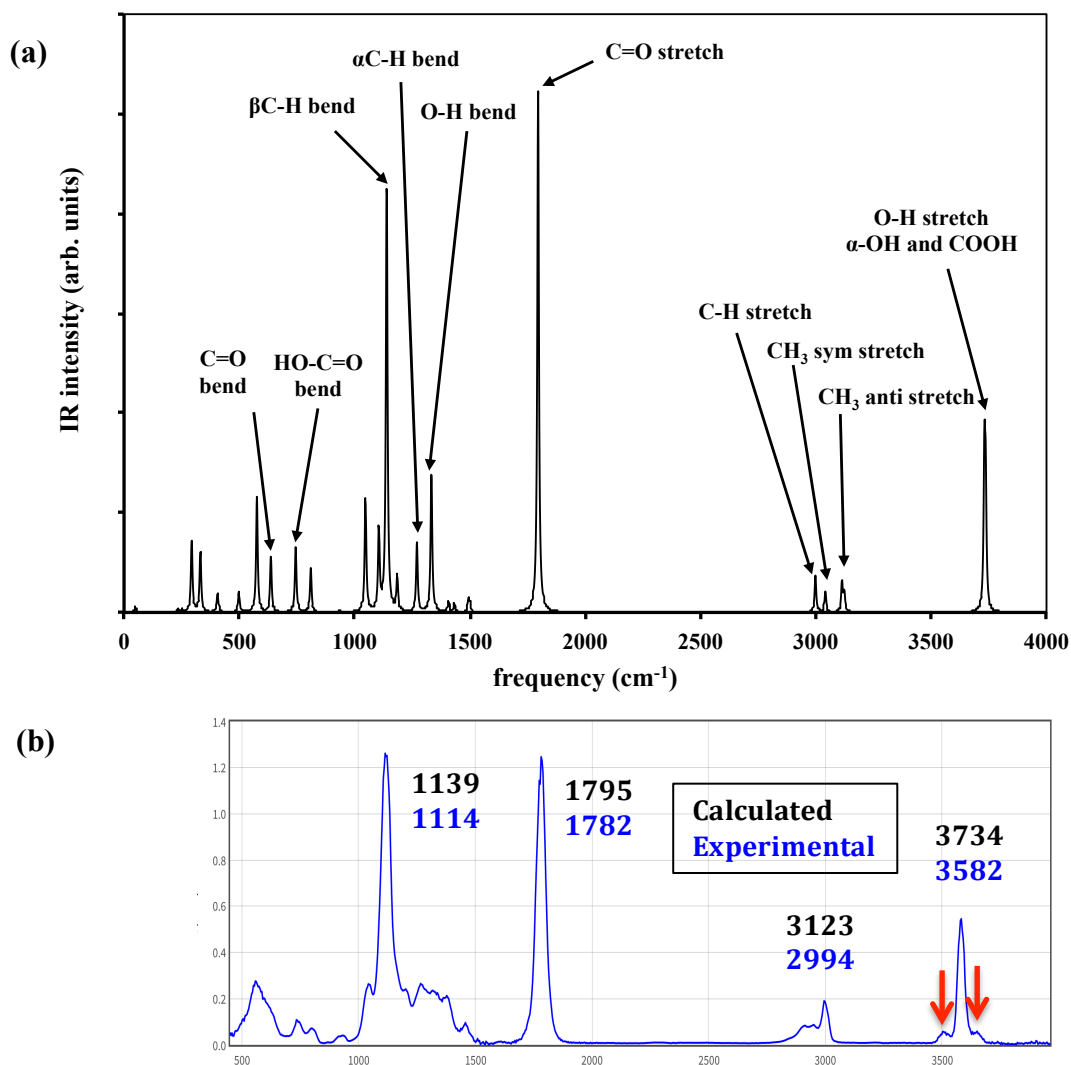


Fig. 5 (a) Calculated infrared spectrum of lowest energy conformer (i.e. conformer **D**) of lactic acid using the B3LYP-D3/aug-cc-pVTZ method and (b) experimental IR spectrum of lactic acid in gas phase.²⁸

The infrared spectrum for the lowest energy conformer of L-lactic acid was calculated in Fig. 5 using the B3LYP-D3/aug-cc-pVTZ method. The tabulated values for the frequency (ν_{IR}), intensity (I_{IR}), bond length (r) and bond angle (ϕ) are tabulated in Table 3. The most intense band is the carbonyl stretching $\nu(\text{C}=\text{O})$ at 1795 cm⁻¹. This peak was previously measured by IR and Raman in aqueous solutions of lactic acid and found to be at 1725 cm⁻¹.²⁹ It was also measured in vibrational absorption spectroscopy experiments of L-lactic acid in CDCl₃ and found to be a double peak at 1745 cm⁻¹ and 1721 cm⁻¹ due to monomeric and aggregated (e.g. monomers, dimers,

trimers) lactic acid, respectively.³⁰ In the experimental IR spectrum from the NIST database, also shown in Fig. 5b, this peak is found at 1782 cm^{-1} . We observe that the relative position of this band depends on how free this carbonyl group is to move. In conformer **B** where there is an absence of a H-bonding interaction between O-H and carboxylate this band is found at 1836 cm^{-1} . When there is a H-bonding interaction between the O-H and the carboxylate O-H, then there is a shift of this band to 1816 cm^{-1} , which happens in conformer **C**. It is noted that this shift of the band should be observable in a highly resolved infrared spectrum. Another peak that we observe is perturbed by the formation of the inter-molecular hydrogen bond is the vibrational peak of the hydroxyl group of the α -OH (3726 cm^{-1}) and the O-H bond of the carboxyl group (3731 cm^{-1}). Around 3100 cm^{-1} there are four rather weak peaks that correspond to the stretching of C-H in β -CH₃. In particular, the antisymmetric C-H stretch of β -CH₃ is found at 3123 cm^{-1} and 3113 cm^{-1} . The symmetric C-H stretch of β -CH₃ is at 3041 cm^{-1} followed by the stretching peak of C-H of α -CH found at 2998 cm^{-1} . The O-H bending mode of α -CH and COOH is found at 1333 cm^{-1} followed by the bending peak of C-H of α -CH (1270 cm^{-1}) and of β -CH (1139 cm^{-1}). The lowest frequency peaks are the bending modes of the COOH group. In particular, the bending of the angle of HO-C=O is at 744 cm^{-1} and that of the C=O group at 637 cm^{-1} . A complete list of these peaks and their intensities as well as selected geometric parameters is given in Table 3.

Table 3 Tabulated values for the infrared frequency (ν_{IR}), infrared intensity (I_{IR}), bond length (r) and bond angle (ϕ) for lactic acid using the B3LYP-D3/aug-cc-pVTZ method.

Vibrational mode	Frequency (cm^{-1})	Intensity (10^{-40} esu ² cm ²)	Bond length (\AA)	Bond angle ($^{\circ}$)
O-H stretch of COOH	3736	73	0.969	108
O-H stretch of α -OH	3731	93	0.967	108
C-H antisym. stretch of β -CH ₃	3123	15	1.088	109
C-H antisym. stretch of β -CH ₃	3113	23	1.088	109
C-H sym. stretch of β -CH ₃	3041	16	1.088	109
C-H stretch of α -CH	2998	28	1.096	109
C=O stretch	1795	685	1.206	124
O-H bend of α -CH and COOH	1333	249	-	-
C-H bend of α -CH	1270	126	-	-
C-H bend of β -CH ₃	1139	905	-	-
HO-C=O bend of COOH	744	203	-	-
C=O bend of COOH	637	206	-	-

1.4 Effect of basis set on vibrational frequencies

It is common to scale calculated IR frequencies in an IR spectrum by a scale factor to lower their values by 3-7%. Usually calculated frequencies are scaled down by this scale factor to take into account limitations of the basis set used, anharmonicity effects and the partial neglect of electron correlation. The well resolved peak in our calculated IR spectrum that shows the best agreement with experiment is the C=O stretching band at 1795 cm^{-1} . Based on the position of this band in our calculated infrared absorption spectrum and the peak that corresponds to monomeric lactic acid we have calculated a frequency scale factor of 0.993. However, we notice that certain peaks agree better than others in the calculated IR spectrum compared to the experimental IR spectrum of lactic acid that was recorded in gas phase. The C-H bend peak of β -CH₃ (exp. 1114 cm^{-1} , calc. 1139 cm^{-1}) are in relatively good agreement with the calculated value at B3LYP-D3/aug-cc-pVTZ. The peaks that involve the stretching of a -H bonds, such as the C-H antisymmetric stretch of β -CH₃ (3123 cm^{-1}) and the O-H stretching frequency (3734 cm^{-1}) overestimate the IR peaks considerably. We have performed a series of calculations with a split basis set on the C, O and the H to understand whether this difference observed mainly for the C-H and O-H stretching frequency could be attributed to the basis set. The results of using a split basis set are shown in Table 4.

Table 4. Comparison of experimental and calculated IR peaks for selected high intensity peaks in the IR spectrum (0 to 4000 cm⁻¹) for lactic acid.

basis on H	basis on C and O	β C-H bend (cm ⁻¹)	C=O stretch (cm ⁻¹)	CH ₃ anti stretch ^a (cm ⁻¹)	O-H stretch ^a (cm ⁻¹)	av. diff. (cm ⁻¹)
cc-pVDZ	cc-pVDZ	1152	1820	3129	3690	79.8
cc-pVDZ	aug-cc-pVDZ	1140	1791	3132	3735	81.5
cc-pVDZ	aug-cc-pVTZ	1139	1795	3108	3724	73.5
aug-cc-pVDZ	aug-cc-pVTZ	1138	1795	3109	3726	74.0
aug-cc-pVTZ	aug-cc-pVTZ	1139	1795	3123	3734	79.8
daug-cc-pVTZ	aug-cc-pVTZ	1139	1795	3123	3734	79.8
aug-cc-pVQZ	aug-cc-pVTZ	1139	1796	3116	3749	82.0
daug-cc-pVQZ	aug-cc-pVTZ	1139	1796	3116	3749	82.0
experimental		1114	1782	2994	3582	

^a taken as the average of two peaks

The average difference (Δx) between experimental IR and theoretical IR peaks is given by,

$$\Delta x = \frac{1}{n} \sum_1^n \sqrt{(x_{exp} - x_{calc})^2} \quad (8)$$

We observe that the Δx between calculated and experimental peaks ranges between 73.5 and 82.0 cm⁻¹. Therefore, we do not observe a significant effect of the basis set on the vibrational frequencies when Dunning's correlation-consistent basis sets are used. The aug-cc-pVTZ basis set generates good result for vibrations that involve C and O. An Δx of 73.5 cm⁻¹ is found when a cc-pVDZ basis set is used on H. So we recommend that if a split basis set is used the cc-pVDZ(H)/aug-cc-pVTZ(C,O) seems to be the best compromise between computational accuracy and computational demand and that it reproduces best experimental IR bands with a frequency scale factor of 0.993.

1.5 Identification of various conformers of lactic acid from IR spectrum

It is useful to be able to identify the various conformer of L-lactic acid from experiment as it could offer the means of studying aspects of the reaction mechanism under in-situ conditions. In Fig. 6 we zoom in on the IR spectrum of the various

conformers of lactic acid for the peaks that correspond to the vibration of the two hydroxyl groups. In all conformers this peak is a doublet, where the peak of the alpha hydroxyl group is higher in frequency by $\Delta\nu$ which is shown in Table 5, along with the frequencies of the O-H of the alpha hydroxyl group ($\nu(\text{OH1})$) and the carboxylate group ($\nu(\text{OH2})$). However, for conformer **D**, this double peak turns into a single peak since the vibrational frequencies are at 3731 and 3736 cm^{-1} , with a $\Delta\nu$ of only 5 cm^{-1} . The same peak which corresponds to the $\nu(\text{C=O})$ in the gas phase spectrum of lactic acid is single peak confirming the dominating occurrence of conformer **D** in the gas phase matrix, in agreement with the relative stability of the various conformers as presented in Table 1. Closer observation of the experimental gas phase IR spectrum shown in Fig. 5b shows that there are additional peaks (shown by the red arrows) lower and higher in wavenumber than the main peak at 3734 cm^{-1} , which suggests that some of the other conformers are also present in the gas phase matrix. The resolution of the experimental IR spectrum does not resolve the individual $\nu(\text{O-H})$ peaks for the six different conformers. From the $\Delta\nu$ measured in the experimental spectrum by fitting 3 Gaussian functions we find that it is 152 cm^{-1} , which is good agreement with the maximum $\Delta\nu$ of 176 cm^{-1} that we find from the calculated IR spectra of L-lactic acid. Based on the relative energetic ordering of the various conformers and their $\Delta\nu$ values from Fig. 6 we estimate that the peaks of the other conformers that are present in the experimental spectrum are the peaks of conformer **C** and conformer **E** both of which lie 9 kJ mol^{-1} higher in energy than the lowest energy conformer **D**. Therefore the relative energetic ordering of the various conformers and their appearance in the IR spectrum are in good agreement.

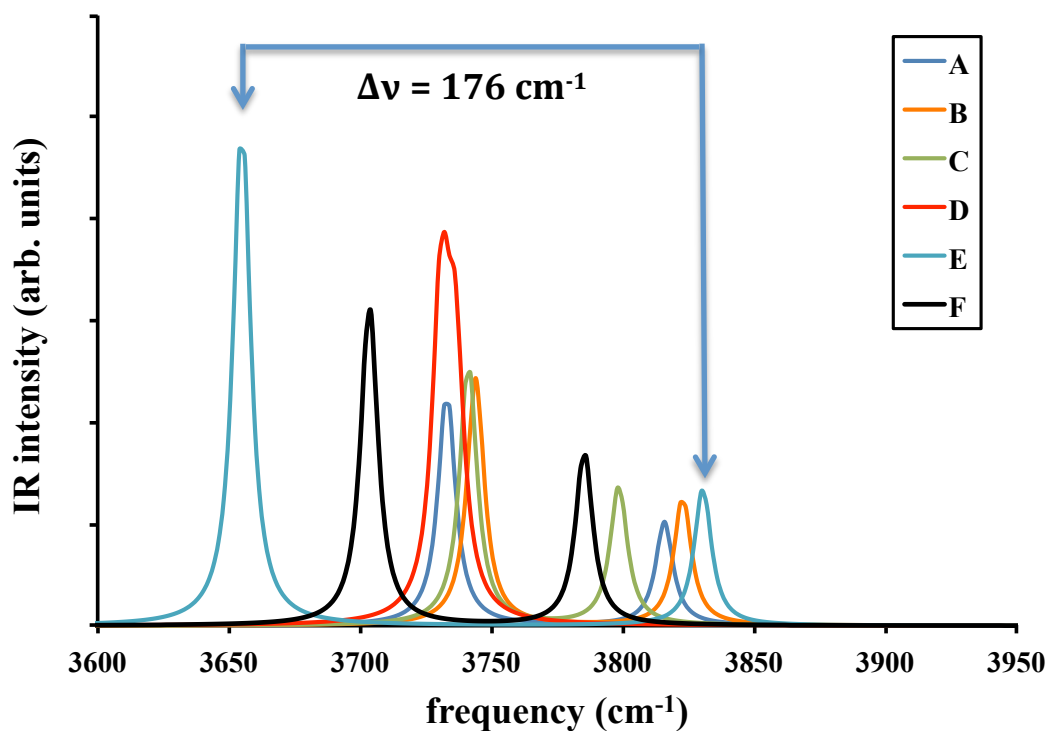


Fig. 6 Calculated infrared spectrum showing O-H vibrations of conformers A-F of lactic acid using the B3LYP-D3/aug-cc-pVTZ method.

As future development of the resolution of these spectroscopic techniques may allow identification of the individual peaks of each conformer we have tabulated in Table 5 a list of all the vibrational frequencies and their intensities for the two hydroxyl groups as well as their absolute separation, $|\Delta\nu|$.

Table 5. Vibrational frequencies and intensities of the O-H vibrational peaks and their absolute wavenumber separation $|\Delta\nu|$ calculated at the B3LYP/aug-cc-pVTZ level of theory

Labels	Structural Formula	$\nu(\text{OH1})$ (cm^{-1})	$I(\text{OH1})$ ($10^{-40}\text{esu}^2\text{cm}^2$)	$\nu(\text{OH2})$ (cm^{-1})	$I(\text{OH2})$ ($10^{-40}\text{esu}^2\text{cm}^2$)	$ \Delta\nu $ (cm^{-1})
A		3816	30.8	3733	71.0	83
B		3823	38.0	3744	75.0	79
C		3799	41.4	3741	79.4	57
D		3731	92.8	3736	73.5	6
E		3831	40.6	3655	156.1	176
F		3703	91.0	3785	52.1	82

1.6 DFT-D3 study of various conformers of acrylic acid

We now consider the conformational landscape of acrylic acid. In table 6 we have calculated at the B3LYP-D3/aug-cc-pVTZ level of theory the various conformers of the molecule. We find that there is a total of 4 conformers (**J-M**) which are the result of the rotation of the carboxylate group and the hydrogen of the hydroxyl group. The lowest energy conformer is conformer **L** which has a dihedral angle for the C-C-C-OH dihedral of 180° and is therefore a completely planar molecule. All other conformer except conformer **J** are planar due to the better overlap of the π -orbitals of the $>\text{C}=\text{C}<$ and $>\text{C}=\text{O}$ bonds. In conformer **J** there is a steric repulsion between the H of the O-H group the C-H of the vinyl group which forces

the geometry of the molecule out of planarity, and the dihedral of the C-C-C-OH becomes -18.9° . This steric repulsion can be estimated by the relative energy of conformer **J** and **K** to be about 22 kJ mol^{-1} .

Table 6. Free energy change for the various conformers of acrylic acid and their dihedral angle with and without the D3-correction at B3LYP/aug-cc-pVTZ level of theory

Labels	Structural Formula	δ ($^\circ$)	δ with D3 ($^\circ$)	ΔG (kJ mol^{-1})	ΔG with D3 (kJ mol^{-1})
J		-16.9	-18.9	23.3	23.2
K		0.0	0.0	1.4	1.3
L		180.0	180.0	0.0	0.0
M		180.0	-180.0	21.1	21.1

In conformer **M** we observe a steric repulsion of the hydrogen of the O-H group and the hydrogen of the vinyl group as the latter O-H bond is not completely parallel to the C-H bond. It is interesting that although there are these steric repulsions, the molecule still has a planar configuration which is a direct result of the delocalised nature of the π -bonds along the C=C-C=O skeleton. The existence of comparable amounts of conformer **L** (s-cis) and conformer **K** (s-trans) has been previously suggested based on microwave spectroscopic measurements of acrylic acid vapors at low pressures.^{31, 32} This observation agrees well with the fact that the relative stability

of the two rotational conformers is very similar with a ΔG of just 1.3 kJ mol^{-1} . Previous theoretical studies of acrylates (i.e. acrolein, acrylic acid, methyl acrylate) using the HF/6-31G* method found that the s-cis conformation is slightly favoured to the s-trans conformation.³³ Studies of the infrared spectrum of solid acrylic acid showed that the molecule dimerises forming mostly cis-cis and trans-trans dimers³⁴ whereas earlier studies both in liquid and in vapor had assigned the IR spectroscopic features to just the trans-trans dimer.³⁵

From the various conformers found on the potential energy surface of acrylic acid, we can identify 4 different conformational processes. The first process is between **K** and **L** in which the dihedral angle C-C-C-O changes by 180° while the π -conjugated system changes from trans to cis. This process has a free energy change of just 1.3 kJ mol^{-1} , which corresponds to a reaction temperature of 34 K which is possible even at RT.

The second process is between **J** and **M** in which the dihedral angle C-C-C-O changes by 163.1° , while the π -conjugated system changes from trans to cis. This process has a free energy change of just 2.1 kJ mol^{-1} , which corresponds to a reaction temperature of 55 K which is possible even at RT.

The third process is one in which there is a rotation of the O-H group between conformer **J** and **K**. This process has a free energy change of 21.9 kJ mol^{-1} , which corresponds to a reaction temperature of 572 K (299°C). The analogous rotation of the O-H group for conformer **L** and **M** has a free energy change of 21.1 kJ mol^{-1} which corresponds to a reaction temperature of 551 K (278°C). It is known that conformers **K** and **L** can dimerise forming trans-trans and cis-cis acrylic acid dimers.³⁴ Based on the calculated temperatures at which the O-H group will rotate into the higher energy conformer **J** and **M**, it is conceivable that above 300°C the dimerisation of these dimers will not be energetically favoured, which may be important in experiments that aim to probe the conformational dynamics of the monomeric forms of acrylic acid.

1.7 Simulated and Experimental infrared spectrum of acrylic acid

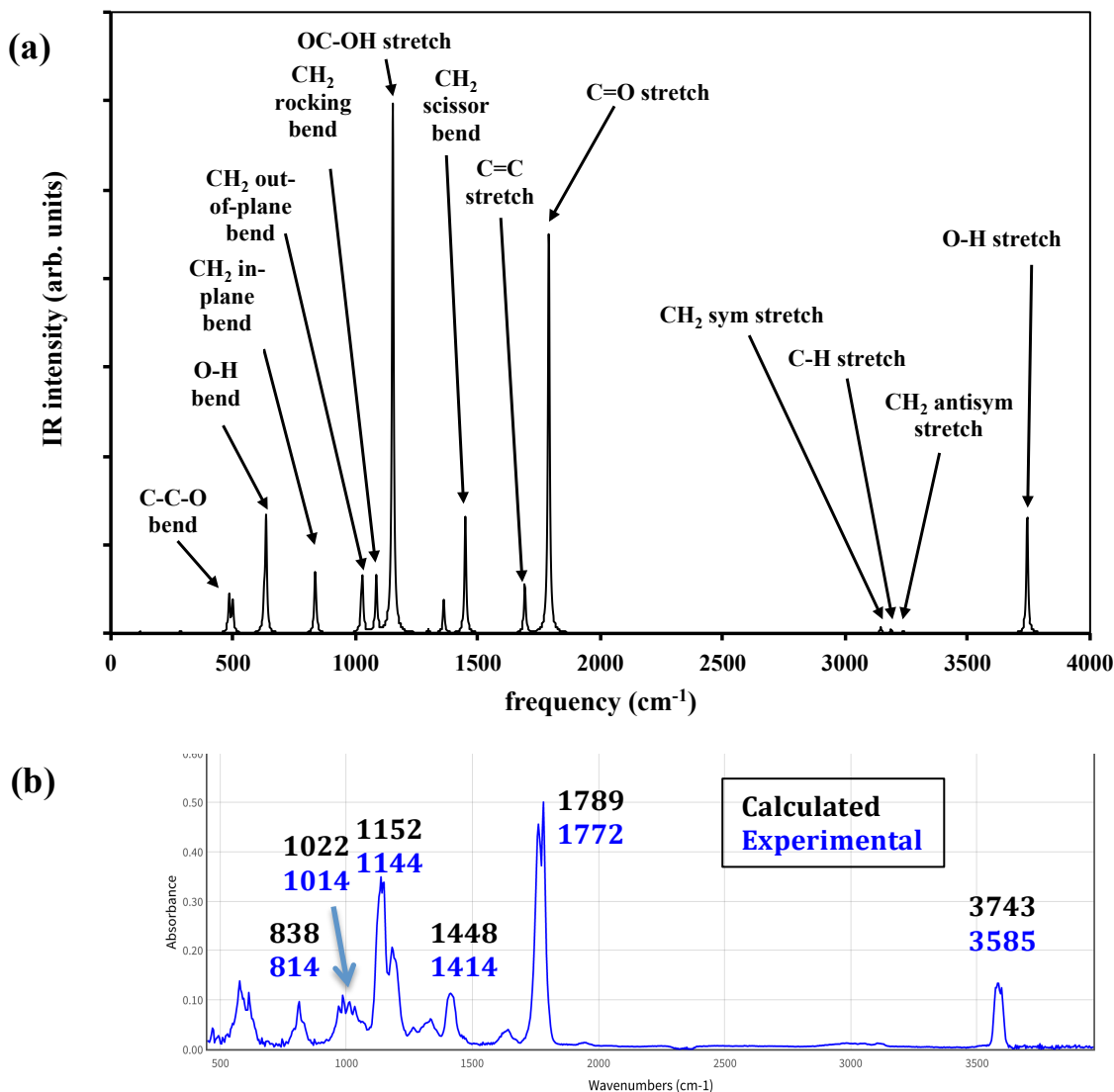


Fig. 7 (a) Calculated infrared spectrum of lowest energy conformer of acrylic acid using the B3LYP-D3/aug-cc-pVTZ method and (b) experimental IR spectrum of acrylic acid in gas phase.²⁸

The infrared spectrum for the lowest energy conformer of acrylic acid was calculated in Fig. 7(a) using the B3LYP-D3/aug-cc-pVTZ method. The values for the frequency (ν_{IR}), intensity (I_{IR}), bond length (r) and bond angle (ϕ) are tabulated in Table 7. The most intense band is the carbonyl stretching $\nu(\text{C}=\text{O})$ at 1789 cm⁻¹ (exp. 1772 cm⁻¹) which appears as a double peak. The separation of the double peak in IR

spectrum of the vapour is $\Delta\nu' = 24 \text{ cm}^{-1}$. From the calculated infrared spectrum showing the vibrational bands for C=O shown in Fig. 8(a) it is clear that the doublet peak cannot be a result of the rotational isomerisation of s-cis (conformer **L**) to s-trans (conformer **K**) as their $\Delta\nu'$ is just 2 cm^{-1} . However the $\Delta\nu'$ between conformer **K** and **L** and that of the other high energy conformers (**J** and **M**) ranges between $24 - 36 \text{ cm}^{-1}$. Based on the separation of the double peak in experimental and calculated IR spectrum, we find that the doublet peak is a result of the O-H bond pointing towards or away from the vinyl hydrogens. Close observation of the structure of the O-H in conformer **J** and **M** shows that there is repulsive interaction between O-H and C-H. In conformer **J** this causes the C=C-C-OH dihedral to become -18.9° whereas in conformer **M** the C-H and O-H bond are not completely parallel. Both these structural features indicate intra-molecular repulsive interactions, which affect the vibrational frequency of the C=O bond.

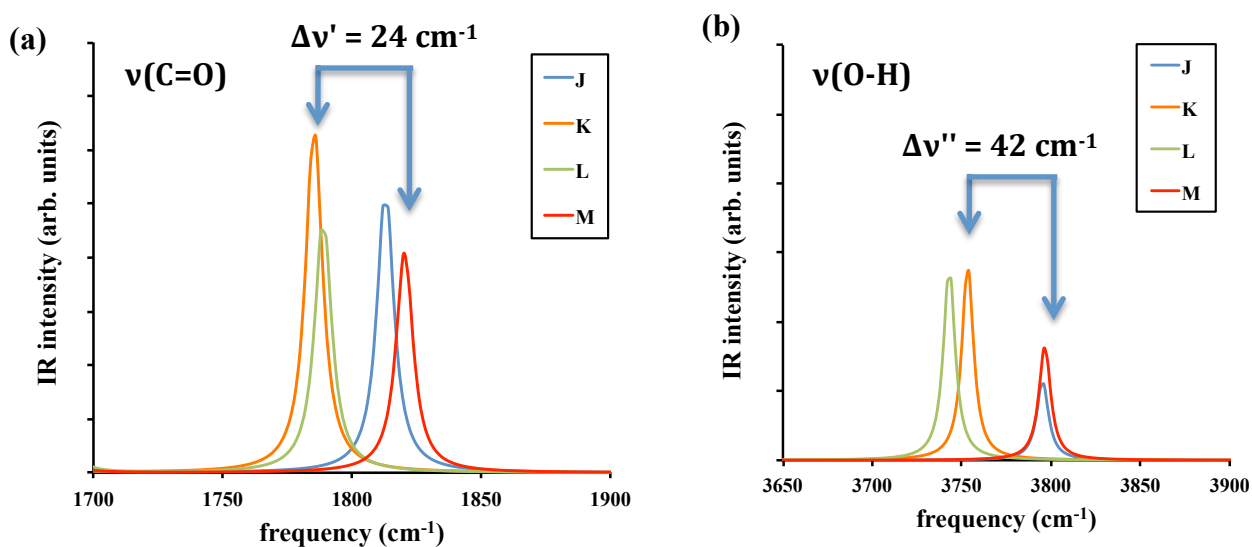


Fig. 8 (a) Calculated infrared spectrum showing (a) C=O and (b) O-H vibration of conformers J-M of acrylic acid using the B3LYP-D3/aug-cc-pVTZ method

The intra-molecular repulsion that affects the vibrational frequency of the C=O bond has also an effect on the peak that corresponds to the vibration of O-H at 3585 cm^{-1} and calculated at 3743 cm^{-1} . This peak compares well to previous experimental assignment of 3541 cm^{-1} based on the IR spectrum of very dilute solutions of acrylic acid in CCl_4 in which it was in monomeric form, evident by a broader peak that narrowed to a single peak upon dilution.³⁶ The differences in

vibrational frequencies of the O-H bond for the various conformer of acrylic acid are shown in Fig. 8(b). They indicate a $\Delta\nu$ of 42 cm^{-1} which suggests considerable broadening of the O-H peak even in the absence of inter-molecular H-bonds. Indeed the experimental IR spectrum of acrylic acid in gas phase (see Fig. 7b) shows evidence of this peak broadening of the O-H band.

We observe that the agreement of calculated and experimental IR peak is not as good as it is for the rest of the peaks, which can be attributed to the fact that in the gas phase matrix, the oscillator strength of the O-H bond will be somewhat weaker, due to hydrogen bonding, which causes the smaller wavenumber of the experimental peak. We observe this phenomenon also for lactic acid where all peaks apart from the O-H peak have good agreement between calculated and experimental value even without frequency scaling. The next intense band is at 1448 cm^{-1} , which corresponds to the CH_2 scissor bending vibration. The next peak which is located at 1152 cm^{-1} has also another peak somewhat higher in wavenumbers. It is not clear what the origin of this double peak is. It could be that it corresponds to the acrylic acid molecules that are dimerised via H-bonding as acrylic acid dimerises forming mostly cis-cis and trans-trans dimers.³⁴ It would be interesting if the concentration of monomeric and dimeric acrylic acids in the gas phase could have some effect on the relative intensity of the two peaks in order to confirm the dimerisation phenomenon. For the next band we observe 4 peaks in the experimental spectrum but only two in the calculated spectrum. The peak with the biggest agreement is the out-of-plane bending of the CH_2 group, which is found at 1022 cm^{-1} and 1014 cm^{-1} in the experimental and calculated IR spectrum, respectively. The in-plane bending of the CH_2 group was found at 838 cm^{-1} and 814 cm^{-1} in the calculated and experimental IR spectrum, respectively. The calculated IR oscillator frequencies are by an average value of 18 cm^{-1} greater than the experimental values, which shows relatively good agreement between experiment and calculation at the B3LYP-D3/aug-cc-pVTZ level of theory. A complete list of these peaks and their intensities as well as selected geometric parameters are given in Table 7.

Table 7 Tabulated values for the infrared frequency (ν_{IR}), infrared intensity (I_{IR}), bond length (r) and bond angle (ϕ) for lactic acid using the B3LYP-D3/aug-cc-pVTZ method.

Vibrational mode	Frequency (cm^{-1})	Intensity ($10^{-40} \text{ esu}^2 \text{ cm}^2$)	Bond length (\AA)	Bond angle ($^\circ$)
O-H stretch	3743	85.3	0.968	107.16
CH ₂ antisym stretch	3238	1.3		
C-H stretch	3187	2.4		
CH ₂ sym stretch	3145	3.7		
C=O stretch	1789 ^a	608.9	1.206	126.18
>C=C< stretch	1691	76.3	1.328	120.42
CH ₂ scissor bend	1448	76.1		
OC-OH stretch	1152	1199.9	1.357	111.14
CH ₂ rocking bend	1084	37.1		
CH ₂ out-of-plane bend	1022	14.5		
CH ₂ in-plane bend	838	37.1	1.481	
O-H bend	634	464.3		
C-C-O bend	498	163.7		

^a average of two peaks

Conclusions

In this hybrid DFT-D3 study we evaluate the temperatures at which the various intra-molecular H-bonds of L-lactic acid form and the conformations of acrylic acid. We find evidence that one intramolecular H-bond in L-lactic acid has an effect and on the proposed reaction mechanism for L-lactic acid dehydration to acrylic acid and that there is an optimum temperature range (190-210 °C) where the catalyst turn-over-frequency would be the greatest. Furthermore, we have systematically studied the IR spectrum of L-lactic acid and acrylic acid. We have identified various characteristics that can identify the various conformers of these compounds via infrared spectroscopy. In particular, the lowest energy conformer can be identified by a single vibrational band at 3734 cm^{-1} whereas the other conformers this vibrational band is split with $\Delta\nu$ that ranges between 6 cm^{-1} - 176 cm^{-1} . We find that the various conformers of acrylic acid can be identified by a double peak for the

C=O and O-H vibrations which have $\Delta\nu'$ of $\Delta\nu''$ 24 and 42 cm^{-1} , respectively. Our study reveals important new findings about the spectroscopic identification of the various conformer of lactic and acrylic acid and the effect that intra-molecular hydrogen bonding in L-lactic acid can have on the dehydration mechanism occurring in potassium substituted NaY Zeolites.

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