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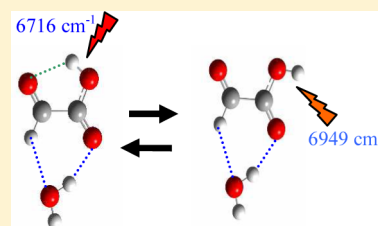
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Light-Induced Opening and Closing of the Intramolecular Hydrogen Bond in Glyoxylic Acid

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S Supporting Information

ABSTRACT: The isomerization process of glyoxylic acid (GA) conformers and their complexes with a water molecule were studied in a low temperature argon matrix. The research target was to understand how starting conformation and complexation affects the near-IR (NIR) induced conformer interconversion. The most stable GA conformer (Tc) is characterized by an intramolecular hydrogen bond, and it is found to undergo light-induced conformer interconversion slower than the open (Tt) conformer. Upon complexation with water, the isomerization processes slow down in the case of the Tc conformer, whereas for the Tt-based complex the influence of water is negligible on the isomerization process.



INTRODUCTION

Glyoxylic acid (GA), HCOCOOH, is the simplest α -oxoacid possessing both an aldehyde and a carboxylic acid structural unit. It plays an important role in biology and appears in the metabolism of living cells.¹

Glyoxylic acid has also been a model compound when considering intramolecular hydrogen bonding and rotational isomerism.^{2,3} It is known that such internal interaction can have a large impact on the physical and chemical properties of the molecule. Recently, it has been shown that for glyoxylic acid, pyruvic acid and oxalic acid the intramolecular hydrogen bonding plays a crucial role in high-overtone induced unimolecular decomposition reaction^{4–6} or in the isomerization processes.^{6,7}

Glyoxylic acid has been computationally predicted to represent four distinctive conformers characterized by relative positions of the carboxylic and aldehyde groups (Figure 1).^{8–12}

The lowest energy conformer (Tc) is characterized by an intramolecular hydrogen bond. The Tc form is predicted to be computationally more stable than Tt conformer by 6.4 kJ mol^{−1} by the CBS-Q method,¹² whereas the experimental value is 5.0 kJ mol^{−1}.⁸ At ambient temperature, the small difference in energy between these two structures and the barrier equal to ca. 48 kJ mol^{−1}³ results in the Tt conformer population being approximately one-third that of the Tc conformer. Both Tc and Tt conformers have been observed and spectroscopically characterized in the gas phase^{4,8,13–17} as well as in low temperature matrices.^{18,19} There is no experimental evidence for the two higher energy conformers, which are achieved by rotation around the C–C bond producing cis-carbonyl conformers Ct and Cc. According to existing DFT calculations, the rotation from Tc to Cc has an energy barrier of 79 kJ mol^{−1}, and the barrier from Tt to Ct is estimated to be 63 kJ mol^{−1}.¹²

In the presence of water, aldehydes and to a lesser extent ketones have the ability to form geminal diols by the hydration

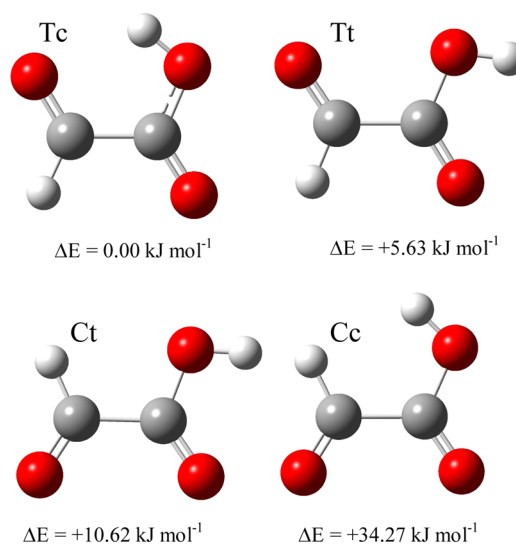


Figure 1. Conformers of the glyoxylic acid molecule.¹⁹

of the carbonyl group.²⁰ Additionally, small complexes with a few water molecules might have an important role in catalyzing reactions in atmospheric chemistry.²¹ For example, in a water restricted environment pyruvic acid forms both 2,2-dihydroxypropanoic acid and hydrogen bonded complexes with a single water molecule.²² Also, glyoxylic acid is known to form 2,2-dihydroxyacetic acid upon interaction with water. The glyoxylic acid monohydrate is the commercially available form of glyoxylic acid, and its crystal structure is known to be stabilized by hydrogen-bond networks.²³

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Recently, employing the matrix isolation technique, we identified and characterized the 1:1 hydrogen bonded complexes between GA and water.¹⁹ In solid argon, the lowest energy conformer of GA binds most favorable the water molecule to the opposite side of the intramolecular hydrogen bond in the molecule (structure Tc-H₂O [B] in Figure 2).

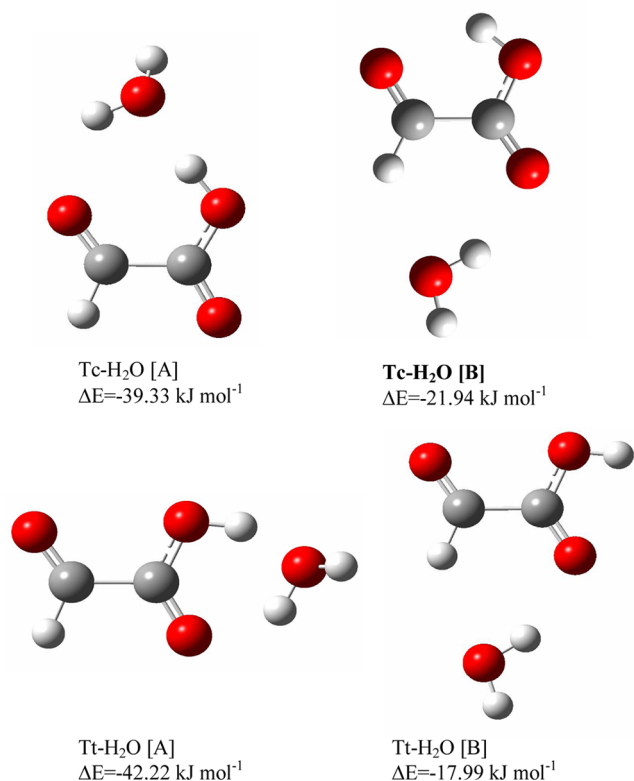


Figure 2. Experimentally observed in argon matrix structures and calculated interaction energies (B3LYP/aug-cc-pVTZ) of the Tc and Tt conformers with H₂O.¹⁹

For this structure the strengthening of the intramolecular hydrogen bond was found, which is manifested by the 18 cm⁻¹ shift of the $\nu(\text{OH})$ mode comparing to the Tc monomer. According to theoretical calculations, the experimentally most abundant Tc-H₂O [B] complex is the second lowest energy structure formed by Tc conformer, and it is predicted to be +8.0 kJ mol⁻¹ higher in energy than the most stable structure where the water is inserted into the internal hydrogen bond (Tc-H₂O[A] in Figure 2). The latter structure was also observed in Ar matrix but the population of it was much lower when compared with Tc-H₂O[B]. In the case of Tt conformer, equally abundant Tt-H₂O [A] and Tt-H₂O [B] structures (Figure 2) were identified in solid Ar.¹⁹

There are many examples of isomerization processes induced by fundamental, combination, first-overtone or high-overtone excitation leading to the formation of less stable carboxylic acids conformers isolated in solid rare gases.^{24–32} Nevertheless, much less work has appeared on the isomerization of systems with intramolecular hydrogen bond.^{6,7,33–35}

Here, we present experimental results and discuss the first-overtone (2 $\nu(\text{OH})$) induced isomerization reactions in the GA molecule isolated in argon matrix. The effect of the intermolecular interaction with water molecule on the OH

group rotation in the two most stable Tc and Tt conformers is also discussed.

■ EXPERIMENTAL AND COMPUTATIONAL DETAILS

Glyoxylic acid is a white powder with a melting point ca. 50 °C. It is commercially available as a monohydrate (98%, Sigma-Aldrich). However, by careful drying of the system all diol and water can be removed from the GA sample as follows: The powder sample of the GA monohydrate was placed into a small bulb connected with a glass U-tube attached to the vacuum line. The system was then heated using heating tapes to ca. 40 °C and pumped simultaneously. The water was pumped out readily and the white foamy sample of HCOCOOH was found to condense on the U-tube walls. Additional drying steps were performed by pumping the U-tube whereas the GA sample was moved back and forth several times between the two side arms of the U-tube by heating tapes.

The matrix samples were prepared by passing high purity argon (Messer, 5.0) through the glass U-tube that contained dry GA heated to 50 °C. The matrix-to-sample ratio could not be determined but matrices containing monomeric GA species could be obtained by optimizing the temperature and the gas flow rate. The GA/H₂O/Ar matrices were prepared by sweeping the H₂O/Ar (1/800 – 1/2000) mixture over dry GA sample in the U-tube. The gaseous mixtures were deposited onto a CsI substrate kept at 15–20 K in a closed cycle helium cryostat (APD-Cryogenics, ARS-2HW) equipped with KBr windows. The sample temperature was maintained with temperature controller (Scientific Instruments 9700) equipped with a silicon diode and a resistive heater.

Infrared spectra were recorded in a transmission mode with a 0.5 cm⁻¹ resolution using Fourier transform IR spectrometer (Bruker IFS 66) equipped with a liquid N₂ cooled MCT detector.

Conformational changes were selectively induced by the NIR radiation of an Optical Parametric Oscillator (OPO) of OPOTEK pumped with the 355 nm laser line of a pulsed (10 Hz, 5 ns) Quantel Nd:YAG laser. The line width of the Idler (NIR) output was about 7 cm⁻¹, the pulse energies were 5–8 mJ. For irradiation, the NIR laser beam with about 0.8 cm diameter was unfocused. The OPO wavelength was automatically controlled and calibrated by the wavemeter integrated into system with additional access to the closed-loop tuning function allowing the wavelength to be tuned with a higher level precision. The pulse energy was monitored by the power and energy meter (Thorlabs) equipped with pyroelectric energy sensor. It is important to note here that the effect of the Globar source of the FTIR spectrometer on the conformational changes of the studied system was checked and no Globar-light-induced reactions were observed in our system.

The exact wavelength of the OPO system used for excitation of the first overtone of the $\nu(\text{OH})$ mode of each of the studied systems was first probed in the region of rough estimate position of the first overtone band using data from theoretical anharmonic calculations. Afterward, the most efficient energy pumping channel, i.e., the band maximum, was located by scanning the isomerization efficiency in 1 nm steps.

To support the experiments, calculations at the B3LYP/aug-cc-pVTZ level of theory, as implemented in the Gaussian 09 package of computer codes, were used.³⁶ The anharmonic wavenumbers used to estimate the anharmonic constants and first overtones were obtained by Barone's method³⁷ and

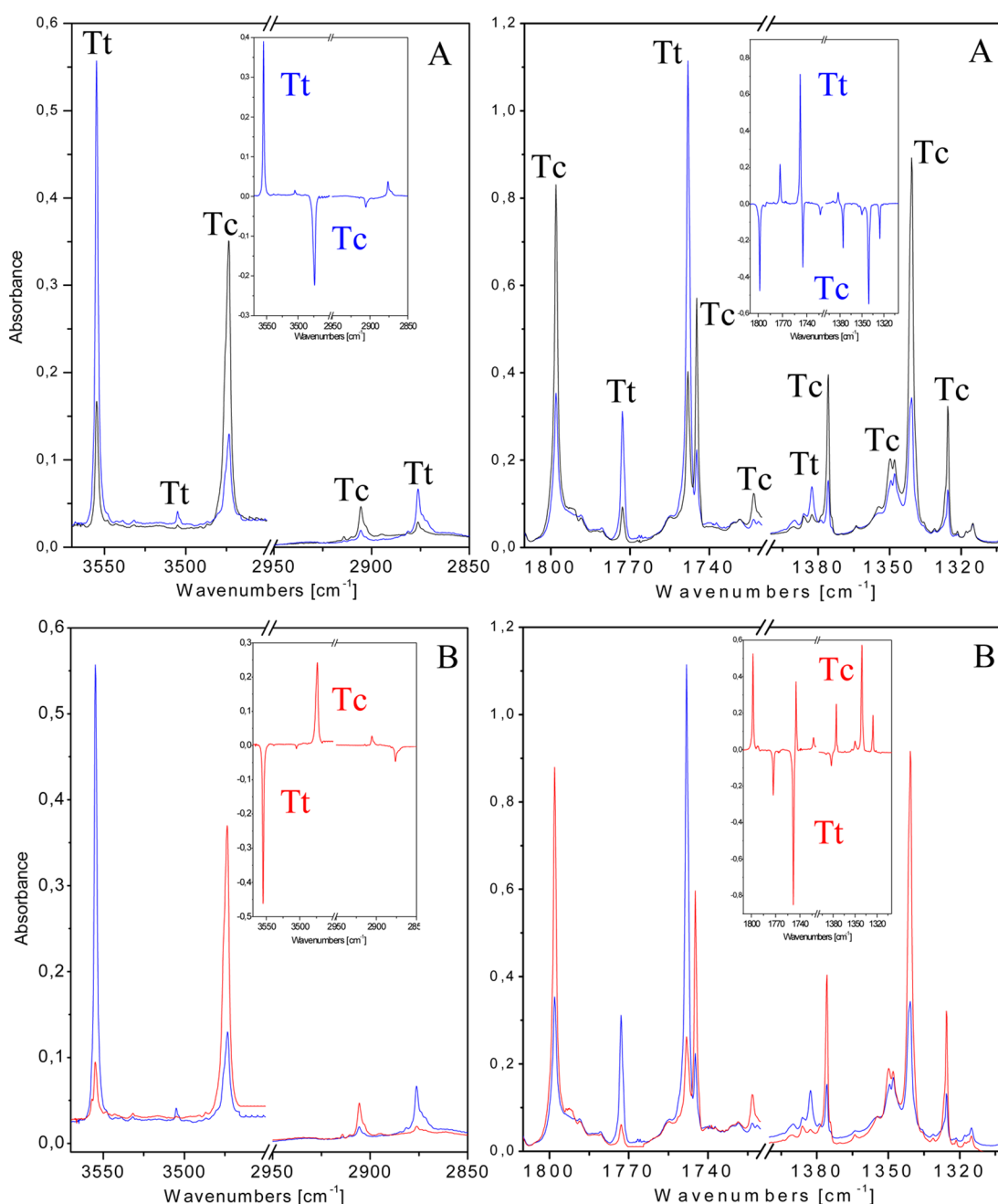


Figure 3. Representative regions of IR spectra of the GA/Ar matrix before and after NIR irradiation. (A) Spectra obtained before (black) and after (blue) 80 min of irradiation at 6775 cm^{-1} . (B) Spectra obtained before (blue) and after (red) 60 min of irradiation at 6959 cm^{-1} . The insets present the difference IR absorbance spectra demonstrating the Tc to Tt (A, blue) and Tt to Tc (B, red) isomerization induced by NIR irradiation. The matrix temperature during the measurements and irradiation processes was 15 K.

thereafter the infrared anharmonic intensities of fundamental and first overtone transitions were calculated.

RESULTS AND DISCUSSION

Glyoxylic acid Monomer Isomerization. Computationally, four minima exist on the potential energy surface of the GA molecule, but only the two most stable structures (Tc and Tt) have been experimentally identified in low temperature matrices.^{18,19}

In the present study, NIR irradiation was used for selective isomerization of the Tc and Tt conformers, which results in the depletion of the selected conformer and the enrichment of the other one. The irradiation at 6775 cm^{-1} , which corresponds to

the first overtone transition of the OH stretching mode of the Tc conformer, induces the Tc \rightarrow Tt isomerization. On the other hand, the back reaction, Tt \rightarrow Tc, was observed upon irradiation at 6959 cm^{-1} .

The analysis of the intensity changes of the particular bands belonging to different conformers upon irradiation enables the unambiguous grouping of the spectral bands to two different structures.

In the observed spectra of GA there are two close lying bands at 1748.0 and 1744.5 cm^{-1} in the carbonyl stretching region of the spectrum (Figure 3). These bands were previously assigned to the C=O stretching mode of the aldehyde group ($\nu_{\text{C=O}_{\text{ald}}}$) in the Tc conformer isolated in different matrix sites.¹⁸

Recently, on the basis of anharmonic calculations and matrix annealing studies, we suggested that the 1748.0 cm^{-1} absorption belongs to the Tt structure whereas the 1744.5 cm^{-1} band is due to the Tc conformer.¹⁹ This assignment is confirmed here by the experiment employing irradiation at 6775 cm^{-1} . Upon $\text{Tc} \rightarrow \text{Tt}$ isomerization the 1748 cm^{-1} feature increases significantly, and simultaneous depletion of the 1744.5 cm^{-1} band is observed (Figure 3A). Additionally, the weak band at 1723.0 cm^{-1} , which was formerly assigned as $\nu(\text{C}=\text{O})_{\text{ald}}$ of the Tt conformer¹⁸ decreases upon 6775 cm^{-1} irradiation. Therefore, it belongs to the Tc conformer, and on the basis of anharmonic data¹⁹ it can be assigned as the first overtone transition of the C–C stretching mode ($2\nu(\text{CC})$).

In the region of $\nu(\text{CH})$ modes (Figure 3A) an increase of the band at 2872.0 cm^{-1} is clearly visible. This confirms that this band belongs to the Tt conformer, as previously tentatively assigned.¹⁹ Moreover, conformer-selective isomerization enables us to assign the band at 3505.5 cm^{-1} to the combination mode of the C=O stretches of carboxyl and aldehyde groups ($\nu(\text{C}=\text{O})_{\text{carb}} + \nu(\text{C}=\text{O})_{\text{ald}}$) (Figure 3A). This band is hardly seen in the spectra of the freshly deposited matrix before the 6775.0 cm^{-1} irradiation.

The isomerization processes in the studied system mentioned above can be regarded as intramolecular hydrogen bond opening and closing processes. In the $\text{Tc} \rightarrow \text{Tt}$ isomerization induced by the irradiation at 6775 cm^{-1} the interaction between OH group and the O atom of the aldehyde moiety is broken, whereas in the $\text{Tt} \rightarrow \text{Tc}$ process upon the irradiation at 6959 cm^{-1} the intramolecular hydrogen bond is closed. Figure 4 shows the evolution of the Tc and Tt bands

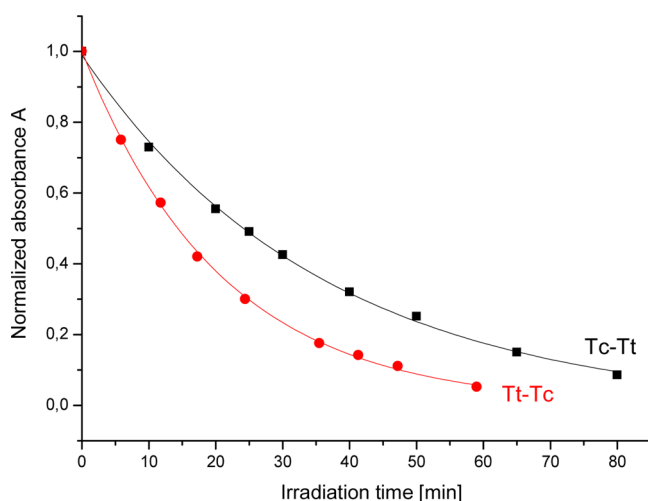


Figure 4. Evolution of the abundances of Tc (black squares) and Tt (red dots) conformers with time upon irradiation at 6775 cm^{-1} ($\text{Tc} \rightarrow \text{Tt}$ process) and 6959 cm^{-1} ($\text{Tt} \rightarrow \text{Tc}$ process) lines. Solid lines represent the best fits using the first-order decay kinetics formula. $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 36 min for the $\text{Tc} \rightarrow \text{Tt}$ process and 20 min for $\text{Tt} \rightarrow \text{Tc}$ isomerization. Therefore, the estimated half-life is equal to 25 and 14 min for the $\text{Tc} \rightarrow \text{Tt}$ and $\text{Tt} \rightarrow \text{Tc}$ processes, respectively.

versus 6775 and 6959 cm^{-1} irradiation time. The OH stretching modes were used to obtain the normalized integrated absorbance values. It can be seen from this Figure that $\text{Tt} \rightarrow \text{Tc}$ process is slightly faster than the $\text{Tc} \rightarrow \text{Tt}$ reaction.

The excitation of the first overtone of either of the two GA conformers is an overbarrier reaction because the energy

deposited in the system exceeds the theoretically predicted barrier height for the isomerization process.

According to the anharmonic vibrational calculations at the B3LYP/aug-cc-pVTZ level of theory, the $\nu(\text{OH})$ first overtone absorption cross section of Tt is larger than that for Tc conformer. The integrated intensity ratio $I_{2\nu(\text{OH})\text{Tt}}/I_{2\nu(\text{OH})\text{Tc}}$ for the first overtone is equal to 1.49. This is in agreement with Takahashi et al.⁴ who reported the integrated absorption cross section of $2\nu(\text{OH})_{\text{Tt}}$ to $2\nu(\text{OH})_{\text{Tc}}$ ratio equal to 1.48. These results indicate that the energy intake to the system via excitation of the first overtone of OH stretching mode can be ca. 1.5 times larger for the Tt conformer than for Tc. On the other hand, the exponential time constant ratio $\tau_{\text{Tt}}/\tau_{\text{Tc}}$ observed experimentally (Figure 4) is equal to ca. 1.8 pointing out a faster isomerization process from the Tt conformer to Tc comparing with the reverse $\text{Tc} \rightarrow \text{Tt}$ conversion. Taking into account the aforementioned ratios, one can see that the energy intake into Tt system is ca. 1.5 times more efficient than into Tc system, whereas the isomerization $\text{Tt} \rightarrow \text{Tc}$ process is 1.8 times faster than $\text{Tc} \rightarrow \text{Tt}$ isomerization process. Therefore, the energy dissipation for Tc conformer appears to be more substantial than for the Tt form, and the energy transfer into the isomerization coordinate (rotation about C–O axis) is less efficient for the Tc structure than it is for the Tt conformer.

Besides the band intensity, one has to take into consideration the full width at half-maximum (fwhm) value of the vibrational band, which could affect the amount of energy deposited in the first overtone $\nu(\text{OH})$ mode of GA conformers. This factor is very important, especially for the systems with the intramolecular $\text{O}\cdots\text{H}-\text{O}$ hydrogen bond, because of the broadening of the higher overtone absorption lines. For example, for pyruvic acid in the gas phase the experimental value of fwhm for $\nu(\text{OH})$ is equal to 37 cm^{-1} whereas for $2\nu(\text{OH})$ it is 69 cm^{-1} , and it becomes hundreds of wavenumbers broad in higher overtone transitions.⁵ Also, the intramolecular hydrogen bond is stronger in pyruvic acid than in glyoxylic acid.^{4,5} For GA isolated in an argon matrix the fwhm of $\nu(\text{OH})$ equals 4 cm^{-1} . Following the example from gas phase experiment,⁵ we expect a value not more than twice as large for $2\nu(\text{OH})$. This estimate is similar to the line width of the Idler (NIR) output used in the irradiation experiments. In our preliminary probing of the isomerization efficiency of the Tc conformer at the irradiation lines differing by 1 nm, the quantum yield of the process decreased significantly at the lines by 1 nm above or below the line corresponding to the band center. This abbreviates that the width of the first overtone band is relatively small, and that during the experiment the irradiation wavelength chosen is targeted on the main part of the vibrational band. In conclusion, taking into account both the absorption cross section and the band widths, no comprehensive explanation for the observed rate differences can be given.

The IVR (intramolecular vibrational energy redistribution) processes connected with the intramolecular hydrogen bond have also to be taken into account. In the Tc conformer intramolecular contact can provide an additional channel for energy dissipation. The energy deposited in the $\nu(\text{OH})$ mode can be transferred to the aldehyde moiety via the hydrogen bridge causing rapid IVR process, which is not the case in the Tt system. Such energy dissipation via intramolecular hydrogen bond has been recently suggested for 1-propanol in solid argon.³⁴

In addition, the role of dark processes in the system was tested by keeping the matrix in darkness for 17 h after initial irradiation. After this period the relative intensities of Tc and Tt conformers did not change, which suggests that the isomerization by intramolecular tunneling does not occur or is very slow.

Glyoxylic Acid–Water Complex Isomerization. The glyoxylic acid molecule forms a hydrogen bonded complex with a single water molecule, and four different structures have been experimentally identified in low temperature matrix (Figure 2).¹⁹ Irradiation of the complex Tc–H₂O [B] at 6716 cm^{−1}, which is in resonance with the first overtone of $\nu(\text{OH})$ of GA in the complex, results in the decrease of the bands belonging to Tc–H₂O [B] (Figure 5A).

Simultaneously, the weak bands in the vicinity of the Tt monomer absorptions increase. These bands were previously assigned to the Tt–H₂O complex characterized by the structure Tt–H₂O [B], analogous to the Tc–H₂O [B] complex (Figure

2).¹⁹ This states that the excitation of the $2\nu(\text{OH})$ mode in the Tc–H₂O [B] complex induces the isomerization reaction leading to the Tt–H₂O [B] complex as shown in the Figure 6.

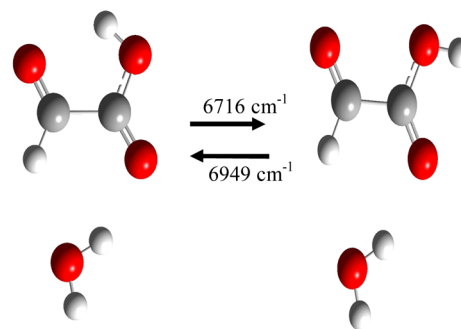


Figure 6. Suggested processes taking place upon irradiation at 6716 and 6949 cm^{−1}.

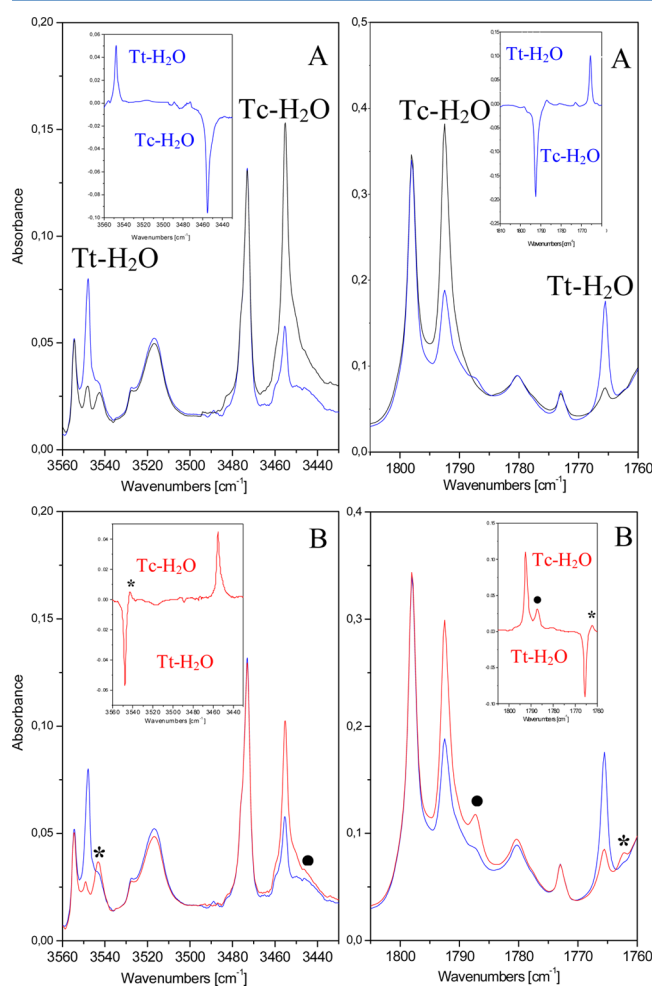


Figure 5. Representative regions of IR spectra of GA/H₂O/Ar matrix before and after NIR irradiation. (A) Spectrum obtained after deposition in the dark (black) and after 6716 cm^{−1} irradiation (blue). (B) Spectrum obtained before (blue) and after 6949 cm^{−1} irradiation (red). The insets present the difference IR absorbance spectra demonstrating the Tc–H₂O to Tt–H₂O (A, blue) and Tt–H₂O to Tc–H₂O (B, red) isomerization induced by NIR irradiation. The matrix temperature during the measurements and irradiation processes was 15 K. The origin of the bands marked with * and ● is explained in the text.

The intensity of the bands due to the GA monomers present in the matrix do not change during the complex transformations, which suggests a good selectivity of the induced processes between the complex and isolated monomer.

The NIR-induced isomerization process enriches the amount of the Tt–H₂O complex as compared with freshly deposited matrix. Therefore, the experiment allows unambiguous identification of some additional absorptions due to the complex compared to known experimental data.¹⁹

Upon irradiation at 6716 cm^{−1} new bands belonging to Tt–H₂O [B] can be identified as follows: 2893.0 cm^{−1} (νCH mode), 1738.5 cm^{−1} ($\nu\text{C}=\text{O}_{\text{ald}}$), 1391.0 cm^{−1} (δCH), 1129 cm^{−1} (γCH), 646.0 cm^{−1} ($\delta\text{C}=\text{C}=\text{O}_{\text{ald}}$), and 510.0 cm^{−1} ($\gamma\text{OH}+\gamma\text{skel}$), as well as a band at 1138.0 cm^{−1} ($2\delta\text{C}=\text{C}=\text{O}_{\text{ald}}$). Besides the newly observed bands due to the glyoxylic acid modes perturbed upon complexation, two new absorptions appear in the OH stretching vibration region of the water molecule. They are observed at 3716.0 and 3577.0 cm^{−1} and are due to the $\nu_{\text{as}}(\text{OH})$ and $\nu_{\text{s}}(\text{OH})$ modes of H₂O in the 1:1 complex with GA. Both positions of the bands and the observed upon-complexation frequency shifts agree well with the anharmonic vibrational data reported previously¹⁹ for the glyoxylic acid–water complex characterized as the Tt–H₂O [B] structure presented in Figures 2 and 6.

The reverse isomerization reaction, leading from the Tt–H₂O [B] structure to Tc–H₂O [B], was achieved by irradiation of the matrix at 6949 cm^{−1} (Figures 5B and 6). This corresponds to the first overtone of the OH stretching mode of GA in the Tt–H₂O [B] complex. In analogy to the GA monomer case, upon irradiation the bands due to the Tt–H₂O [B] complex decrease whereas the Tc–H₂O [B] absorptions increase (Figure 5B). However, one phenomena observed in the Figure 5B deserves a closer look. As can be seen, the bands in close vicinity of the Tt–H₂O [B] absorptions gain intensity (e.g., bands at 3543 and 1762 cm^{−1}, marked with asterisk in Figure 5B) besides the increasing Tc–H₂O bands. These features have their counterparts also in other regions of the Tt–H₂O spectrum. Because of the position close to the main Tt–H₂O bands it is not clear if the absorptions already increase slightly upon Tc–H₂O → Tt–H₂O process or not (Figure 5A). We think that these absorptions belong to the Tt–H₂O system embedded in unrelaxed matrix cage. This is a plausible explanation that is in agreement with the observation that the weak absorptions diminish in the isomerization experiment

conducted at higher temperature (20 K), and that they disappear successively upon matrix annealing. This indicates that at higher temperatures these unrelaxed matrix sites relax to form the most stable Tt–H₂O local trapping site.

Besides the bands due to the unrelaxed Tt–H₂O system, upon 6949 cm^{−1} irradiation new bands in the close vicinity of the Tc–H₂O [B] bands appear (Figure 5B, the bands marked with dots). Similarly to the Tt conformer complexed with water, the counterpart Tc–H₂O absorptions are observed in other spectral regions as well. The explanation of the origin of these features can be analogous to previous explanation of relaxed and unrelaxed trapping sites. The unrelaxed Tc–H₂O trapping site is transformed readily to the lowest energy structure upon matrix annealing. Isomerization performed at higher matrix temperatures efficiently decreases the intensity of these vibrational bands.

Similar trapping site differences were not observed for the GA monomer. Alas, the GA–water complexes are bigger in size and experience stronger sterical constraints in the rigid matrix environment.

To obtain insight on the effect of the water molecule attached to the glyoxylic acid on the isomerization process, we performed kinetic measurements of the Tc–H₂O → Tt–H₂O and the Tt–H₂O → Tc–H₂O processes. These results are presented in Figure 7. In analogy to the GA monomers, the

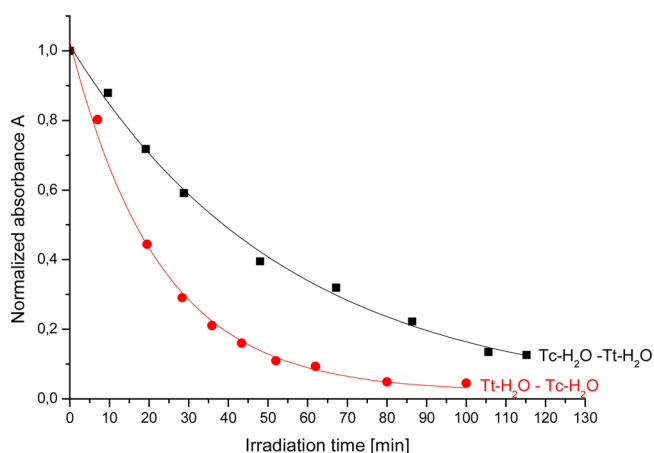


Figure 7. Evolution of the abundances of Tc–H₂O (black squares) and Tt–H₂O (red dots) conformers with time upon irradiation at 6716 cm^{−1} (Tc → Tt process) and 6949 cm^{−1} (Tt → Tc process) lines. Solid lines represent the best fits using the first-order decay kinetics formula. $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 57 min for the Tc → Tt process and 24 min for Tt → Tc isomerization. The estimated half-life is equal to 39.5 and 16.6 min for the Tc → Tt and Tt → Tc processes, respectively.

isomerization of Tt–H₂O to Tc–H₂O is faster than the reverse process from Tc–H₂O to Tt–H₂O. On the other hand, if we consider the estimated half-life of the processes, which equals 39.5 and 16.6 min for Tc–H₂O and Tt–H₂O, respectively, it becomes clear that complexation slows down the isomerization process as compared with the GA monomers.

Interestingly, in the case of the Tt conformer the interaction with water molecule affects the isomerization process only slightly, $\tau = 20$ vs 24 min for Tt monomer and its water complex, respectively. The Tc conformer, on the other hand, seems to be more sensitive to the intermolecular hydrogen bonding with water molecule. The presence of water slows down the process almost twice as compared with the Tc

monomer ($\tau = 36$ vs 57 min). This is in analogy with the lower efficiency of isomerization upon complexation with water, as was observed for formic acid molecule.³⁸ For FA, the light-induced process was observed to be several orders of magnitude less efficient for the water complex compared to the FA monomer. However, in the FA–H₂O complex, the water molecule was directly attached to the OH moiety of the carboxylic group and the isomerization process required not only trans–cis conformational change but also a structural rearrangement of the complex.

In the experimentally most abundant Tc–H₂O [B] and Tt–H₂O [B] systems studied here, water is not directly attached to the OH moiety (Figures 2 and 6), which undergoes the rotation about the C–O bond. Nevertheless, in the Tc–H₂O complex water attaches itself in semicyclic structure employing two intermolecular hydrogen bonds. As follows, it also involves the intramolecular hydrogen bond, resulting in a downward shift of the ν OH band by 18 cm^{−1} of GA in the complex with respect to the monomer band position.

The ratio of the anharmonic intensities $I_{2\nu(\text{OH})\text{Tt-H}_2\text{O}}/I_{2\nu(\text{OH})\text{Tc-H}_2\text{O}}$ for the $2\nu(\text{OH})$ overtone calculated for Tc–H₂O and Tt–H₂O is equal to 1.43. This value is similar to that calculated for the GA monomers. Therefore, a much slower conformational change observed for the Tc–H₂O complex than for the Tt–H₂O complex, can be only partly due to the absorption cross section difference. Again, the IVR process plays an important role in the studied system. In the case of the Tc monomer an additional energy dissipation channel exists via the intramolecular hydrogen bond compared to the Tt monomer. For the Tc–H₂O complex two additional interactions are present. There are two intermolecular hydrogen bonds between water and glyoxylic acid molecule besides the intramolecular hydrogen bond. The energy deposited in the system via $2\nu(\text{OH})$ transition can be redistributed to isomerization reaction coordinate but also dissipated via the hydrogen bonds. The latter IVR channel via intramolecular hydrogen bond to the aldehyde moiety, and further to water molecule via intermolecular hydrogen bond could have a notable decreasing effect on the efficiency of the isomerization process. Thus, the existence of the additional internal energy dissipation channel could be a relevant factor in explaining the differences in isomerization rates observed.

Even though the GA–H₂O complexes are characterized by low-lying intermolecular vibrational transitions which can couple with the lattice phonons resulting in energy transfer in the supermolecular system, this seems not to be a competing energy dissipation channel with respect to the intramolecular IVR process in the first place. In the long run, the whole system cools down via interactions with the environment, but this is not a determining factor for the differences found for the isomerization processes in the GA monomers and its water complexes.

CONCLUSIONS

The isomerization kinetics has been followed for Tc and Tt monomers upon NIR irradiation. It is shown that the Tc → Tt transition is by a factor of ca. 1.8 slower than the Tt → Tc process. This observation is connected to the smaller absorption cross section for $2\nu(\text{OH})$ of the Tc conformer as compared with Tt. Nevertheless, the contribution of the intramolecular hydrogen bond present in the Tc conformer is considered important to the vibrational energy dissipation in the system.

The kinetic profiles of the $\text{Tc-H}_2\text{O} \rightarrow \text{Tt-H}_2\text{O}$ and $\text{Tt-H}_2\text{O} \rightarrow \text{Tc-H}_2\text{O}$ isomerization reactions suggest that the interaction with water decreases the efficiency of the isomerization process of the Tc conformer, whereas it has only a slight effect on the Tt system. The most probable explanation can be that the vibrational energy deposited in the system is also transferred via inter- and intramolecular hydrogen bonds instead of being localized only on the isomerization reaction coordinate.

■ ASSOCIATED CONTENT

■ Supporting Information

Full ref 36. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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