

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/267573366>

Light-induced, site-selective isomerization of glyoxylic acid in solid xenon

ARTICLE *in* CHEMICAL PHYSICS LETTERS · NOVEMBER 2014

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2014.10.023

CITATION

1

READS

21

3 AUTHORS:



Adriana Olbert-Majkut

University of Wrocław

33 PUBLICATIONS 223 CITATIONS

SEE PROFILE



Maria Wierzejewska

University of Wrocław

61 PUBLICATIONS 475 CITATIONS

SEE PROFILE



Jan Lundell

University of Jyväskylä

119 PUBLICATIONS 3,767 CITATIONS

SEE PROFILE



Light-induced, site-selective isomerization of glyoxylic acid in solid xenon



Adriana Olbert-Majkut^{a,*}, Maria Wierzejewska^a, Jan Lundell^b

^a Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

^b Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland

ARTICLE INFO

Article history:

Received 11 September 2014

In final form 9 October 2014

Available online 16 October 2014

ABSTRACT

The isomerization of glyoxylic acid (GA) and its water complex was studied in a low temperature xenon matrix. The aim of these studies was to understand how xenon environment affects the cis-trans GA interconversion upon near infrared irradiation. In solid xenon, the GA conformers are embedded in two different matrix sites. These show up as different vibrational bands of GA that exhibit different kinetic rates of isomerization. Upon complexation with water, the isomerization process slows down. Xenon matrix appears not to affect energy relaxation process via intramolecular or intermolecular hydrogen bond as compared with previous experiments in an argon.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Infrared-induced isomerization of glyoxylic acid (GA) – the simplest α -oxoacid possessing both aldehyde and carboxylic acid structural unit – and its water complexes [1] has been previously studied in argon matrices [2]. It was shown that the most stable GA conformer (Tc) (see Figure 1) characterized by an intramolecular hydrogen bond undergoes light-induced conformer interconversion slower than the open (Tt) conformer. Upon complexation with water, the isomerization process slows down in the case of the Tc conformer, while for the Tt-based complex the influence of water is negligible. It was explained by suggesting 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.

Here, we study the light-induced isomerization of GA and its water complexes in a different environment compared to previous study [2]. It is well known that the properties of trapped species are strongly affected by the matrix preparation method [3]. It is also found that isomerization processes rates are significantly enhanced over the corresponding gas phase values by the presence of the matrix in spite of the steric effects produced by the environment. This result occurs because the matrix opens a vibration \rightarrow lattice phonon modes \rightarrow rotation \rightarrow torsional vibration

energy transfer path [4,5]. In turn, the isomerization is usually slower in an argon matrix than in xenon, and the rate differences appear to be due primarily to differences in the interaction forces rather than the unit cell spacing in Ar and Xe matrices [6].

In this letter, we report the first-overtone ($2\nu_{OH}$) induced isomerization processes of GA and its water complex isolated in a xenon matrix. Besides the isomerization processes rates, the spectral characteristic of the studied system in a Xe matrix is presented.

2. Experimental 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 diols and water can be removed from the GA sample as described elsewhere [2]. The matrix samples were prepared by passing high purity xenon (Messer, 5.0) through the glass U-tube that contained dry GA heated to 50 °C analogically to the experiments in Ar matrix [1,2].

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 Quantel Nd:YAG laser as described elsewhere [2]. Analogically to previous experiment [2] the pulse energy was kept at 4.8 mJ for all experiments. Each experiment was repeated 3 times.

* Corresponding author.

E-mail address: adriana.olbert@chem.uni.wroc.pl (A. Olbert-Majkut).

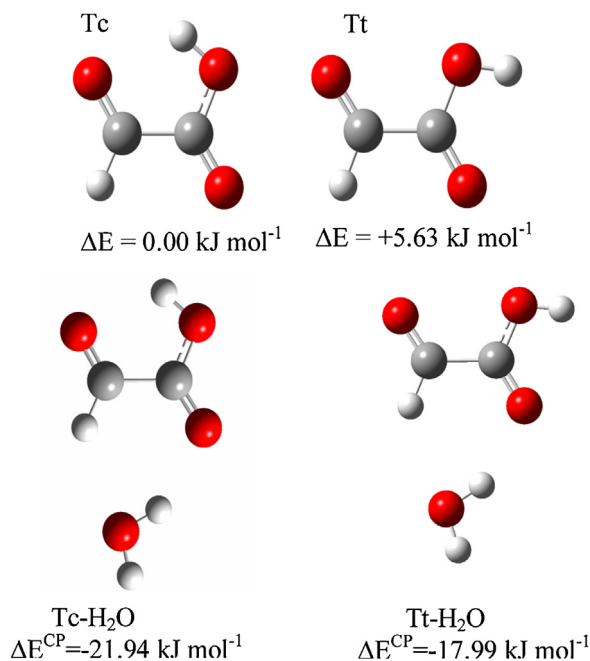


Figure 1. Conformers of the glyoxylic acid molecule and its water complexes experimentally observed in an Ar matrix. The energies correspond to calculated (B3LYP/aug-cc-pVTZ) relative energies (for the monomers) and BSSE-corrected interaction energies (for water complexes) [1].

3. Results and discussion

3.1. Glyoxylic acid monomer in xenon

In our previous studies we reported in details the assignment of bands due to the experimentally observed Tc and Tt conformers isolated in Ar matrix [1]. The same conformers have been also identified in Xe matrix. The abundance ratio of these two systems appeared to be the same in both Ar and Xe environment. The analysis of the intensity changes of the particular bands belonging to different conformers upon NIR-induced selective Tc → Tt and Tt → Tc isomerization irradiation enabled the unambiguous grouping of the spectral bands by two different structures. We were also able to identify some additional bands belonging to the Tc and Tt species as compared with the literature data [7].

In Table 1 are collected the wavenumbers of the bands observed in the spectra of Tc and Tt conformers of GA isolated in xenon matrix and their counterparts identified previously in solid Ar [1]. As can be seen, in the spectra of the GA/Xe matrix the significant matrix shift appears as compared with the GA embedded in argon. Moreover, one can see significant bands splitting due to the site effect.

In Figure 2a and b the spectra recorded for GA/Xe matrix at different temperatures are presented. Careful matrix annealing from 10 K to 50 K followed by cooling down process to 10 K leads to the reversible shift of one of the bands due to Tc conformer (marked as Tc_T) and both bands assigned to Tt conformer (marked as Tt_{T1} and Tt_{T2}). Simultaneously, after the full cycle of annealing process the relative intensities of the two band's components remains unchanged. This excludes the possibility of the thermally stable and unstable sites [8]. It is important to note here, that the barrier between Tc and Tt isomer is too high [9,10] so that a thermally induced isomerization could take place [11]. The described high thermal sensitivity of the position of bands is found mainly for bands associated with the OH moiety and could be due to the trapping of glyoxylic acid conformers in two different matrix cages: in a loose (Tc_L, Tt_L) and a tight (Tc_T, Tt_T) site. In the tight site the close-by Xe atoms interact stronger with the OH moiety of GA

Table 1

Experimental vibrational spectra (in cm⁻¹) of Tc and Tt conformers of GA in xenon matrix.

| Ar matrix ^a | Xe matrix | | Assignment |
|------------------------|------------|------------|-----------------------------|
| Harm | Loose site | Tight site | |
| Tc | | | |
| 3473.5 | 3446.0 | 3436.5 | ν O—H |
| 2905.5 | 2883.4 | 2886.8 | ν C—H |
| 1798.0 | 1791.4 | 1795.8 | ν C=O carb |
| 1744.5 | 1754.0 | 1752.0 | ν C=O ald |
| 1350.0 | 1340.0 | 1337.0 | δ COH/ ν CO |
| 1340.8 | 1322.5 | 1320.8 | δ C—H |
| 1155.5 | – | 1123.0 | ν CO/ δ COH |
| 997.0 | 989.5 | 991.2 | γ C—H |
| 993.0 | | | |
| 871.0 | 872.0 | 877.0 | ν C—C |
| 677.0 | 676.3 | 677.6 | γ skel + γ OH |
| 674.4 | | | |
| 640.3 | 646.0 | 648.6 | δ C—C=O ald |
| 638.0 | 634.0 | 643.0 | |
| 566.8 | 560.2 | 566.7 | γ OH + γ skel |
| 563.7 | | | |
| 499.5 | 504.8 | 504.0 | δ C—C=O carb |
| – | – | – | δ skel |
| | – | – | γ CC |
| Tt | | | |
| 3555.0 | 3514.0 br | 3505.0 | ν O—H |
| | | 3500.9 | |
| 2876.0 | 2850.0 | 2852.0 | ν C—H |
| 2873.5 | | | |
| 1773.0 | 1773.0 | 1772.0 | ν C=O ald |
| 1748.0 | 1747.0 | 1745.0 | ν C=O carb |
| 1382.0 | 1388.2 | 1390.0 | δ COH/ ν CO |
| 1363.0 | 1353.0 | 1358.0 | δ C—H |
| 1118.0 | – | 1116.0 | ν CO/ δ COH |
| 1116.2 | | | |
| 995.0 | 989.5 | 993.3 | γ C—H |
| 857.3 | 877.0 | 868.2 | ν C—C |
| 651.0 | 643.0 | 667.3 | γ skel + γ OH |
| 634.0 | 637.4 | 638.0 | δ C—C=O ald |
| 512.7 | 504.0 | 519.0 | γ OH + γ skel |
| 509.5 | | | |
| 493.5 | – | – | δ C—C=O carb |
| – | | | δ skel |
| – | | | γ CC |

br – broad band.

^a Taken from Ref [2].

isomers, while in the loose site the interactions is weaker. The sites in question might correspond to two- and single-substitutional site, respectively, but a simulation of the matrix environment would be needed to verify this assumption [8].

The annealing process decreases matrix rigidity, and therefore the interactions of GA with Xe atoms become weaker. The stronger interactions are observed at lower temperature when the GA molecules are located in a tight site. Annealing relaxes the matrix and significant band position changes can be observed at 'softer' matrix state at 50 K. Evidently, the position of the bands at higher temperatures converges closer to the loose site position and also towards the band positions observed for the gas phase molecule [12].

3.2. The isomerization of glyoxylic acid upon NIR irradiation

Analogously to the argon matrix experiment [2] the first overtone of OH stretching mode (2 ν OH) of particular conformer was used to induce both Tc → Tt and Tt → Tc isomerization. The exact wavelength used for excitation of the first overtone of the ν (OH) mode of each of the studied conformers was first probed in the region of rough estimate position of the first overtone band using data from theoretical anharmonic calculations. Afterwards, the most efficient energy pumping channel, i.e. the maximum band

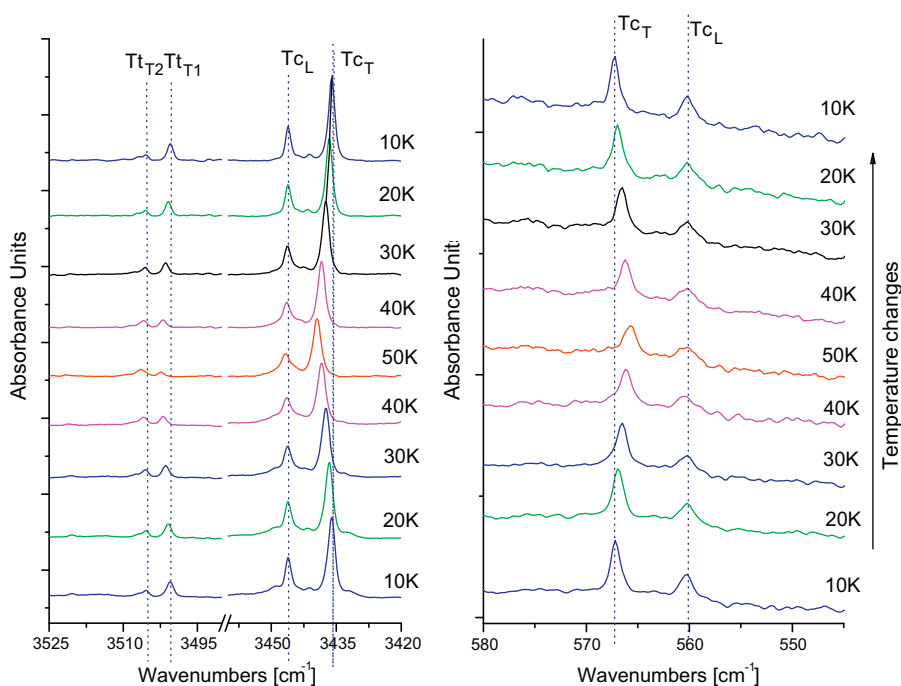


Figure 2. Spectra of the νOH (a) and $\gamma\text{OH} + \gamma \text{skel}$ (b) region of Tc conformer isolated in a Xe matrix.

position, was located by scanning the isomerization efficiency in 1 nm steps as described elsewhere [2].

In comparison to the previous isomerization experiments in argon matrix [2], here NIR irradiation was not only 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 but also for the studies of the isomerization kinetics taking place in particular site the GA isomers were embedded in.

3.2.1. $Tc \rightarrow Tt$ isomerization

The irradiation at 6689 cm^{-1} , which corresponds to the first overtone transition of the OH stretching mode of the Tc conformer isolated in tight site (Tc_T), was used to induce the $Tc_T \rightarrow Tt_T$ isomerization. As can be seen in Figure 3A, upon irradiation the Tc_T band intensity at 3436.5 cm^{-1} decrease. It is accompanied by a simultaneous increase of the intensities of two bands assigned to the Tt conformer in a tight site (Tt_{T1} at 3500.9 cm^{-1} and Tt_{T2} at 3505.0 cm^{-1}). The kinetic profile presented in Figure 3B highlight these observations and points out the lack of intermediate species in the reaction. The optimized exponential time constant for both tight sites of Tt conformer are almost the same being equal to 20.1 and 19.3 min. Moreover, these values perfectly match the exponential time constant determined for the decrease process of Tc conformer isolated in a tight site ($\tau = 19.9\text{ min}$). This clearly points out that both discussed Tt_T bands (Tt_{T1} and Tt_{T2}) correspond to the Tc_T absorption. The double structure of the band due to the Tt conformer in a tight site probably corresponds to two sites of the same symmetry but with slightly different interactions of the vicinal Xe atoms with OH moiety of Tt structure.

Figure 4 presents the changes in the spectra upon irradiation at 6711 cm^{-1} and the kinetic profile of $Tc \rightarrow Tt$ isomerization process of the system embedded in loose site (Tc_L and Tt_L). The 6711 cm^{-1} line corresponds to the first overtone of the OH stretch of Tc isomer in a loose site. As can be seen in the Figure 4A, the band due to the Tc conformer embedded in the loose site (Tc_L) at 3446.0 cm^{-1} decreases and simultaneously the broad band assigned to the Tt isomer in loose site (Tt_L) at 3514 cm^{-1} increases.

Unlike the bands due to the system embedded in the tight site, the absorbance of the Tt conformer in a loose site is broader and this pattern is conserved upon the isomerization process. The broadness of the band is indication of the high degree of freedom of the motions in the spacious matrix cage upon rotation of the OH moiety around C–O bond that was not a case in tight site. It is worth to note here that the Tt_L band does not show a clear doublet structure as was observed for the tight site. Therefore, we cannot exclude that the νOH band due to Tt isomer in the loose site do not exhibit a doublet band structure. For the kinetic search the band as a whole was integrated.

The values of the optimized exponential time constants of Tc_L decay and Tt_L growth point out that $Tc_L \rightarrow Tt_L$ isomerization is a 1:1 reaction. Small discrepancies observed for the τ values might originate from the errors appearing during the bands integration procedure.

The comparison of the kinetic parameters of the isomerization taking place in the tight and loose sites show that the discussed process is about twice faster in the loose site than that in the tight matrix cage. This could be rationalized as follows: Firstly, there are much smaller geometrical constraints in the spacious, loose site making the process much easier and faster to take place. Secondly, in the tight site the energy dissipation from the intramolecular modes of the irradiated system into the lattice phonons might be more efficient than in the loose site because of the strength of interactions with the lattice atoms and thereby due to more efficient coupling with phonons. This process can be viewed as a phonon-assisted intramolecular vibrational energy relaxation (IVR), in which the lattice phonons act like a thermal bath that compensates the energy differences between the relevant intramolecular vibrational states [13,14].

Besides the explanations above it is necessary to note that, while the isomerization process takes place in the tight site the bands due to the system embedded in loose site also slightly decreases. This can be seen in Figure 3. It means that at least part of the energy pumped into the ‘tight-site-isomer’ is used for the isomerization process in loose site. This might be due to the characteristics of the experimental setup used for our experiment. The spectral

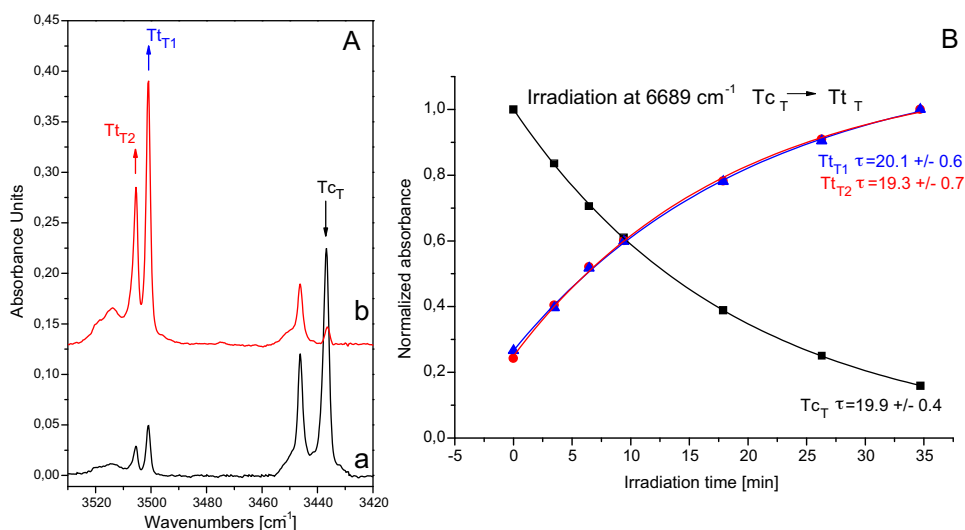


Figure 3. The $T_c \rightarrow T_t$ isomerization in tight site upon irradiation at 6689 cm^{-1} . (A) The spectra of the GA/Xe matrix before (a) and after (b) NIR-irradiation. (B) The evolution of the abundances of T_{cT} (black squares) and T_{tT_1} and T_{tT_2} (blue and red dots, respectively) conformers with time upon irradiation by 6689 cm^{-1} . Solid lines represent the best fits using first order decay kinetics formula $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 19.9 min for T_{cT} band decay and 20.1 and 19.3 min for T_{tT_1} and T_{tT_2} bands' growth, respectively. Matrix temperature during the measurements and irradiation processes was 15 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

width of the laser is ca $6\text{--}7\text{ cm}^{-1}$ and while looking for the proper isomerization wavelength we checked the isomerization quantum yield to find the most optimal line. It might be so that in the region of $2\nu_{OH}$ at the wavelength corresponding to the maximum absorption of the $2\nu_{OH}$ of T_{cT} the bands due to the loose- and tight-site-isomers overlap slightly. On the other hand, the $T_{cL} \rightarrow T_{tL}$ process is highly selective and the intensity of the bands due to the GA molecule embedded in tight site does not change (see Figure 4A). It means that in the vicinity of maximum absorption of $2\nu_{OH}$ of T_{cL} there is no overlapping with the T_{cT} absorption. Nevertheless, at the moment we are not able to say how much energy pumped into the T_{cT} system is transferred to the T_{cL} isomer and used for $T_{cL} \rightarrow T_{tL}$ isomerization decreasing the isomerization quantum yield of $T_{cT} \rightarrow T_{tT}$ process. However, we still believe that the

differences between the photoisomerization efficiency in tight and loose site mainly originate from sterical constraints as well as from the lattice-phonon-assisted energy relaxation pathway related to local matrix morphology within the same host.

The comparison of the glyoxylic acid isomerization processes in argon matrix [2] with the ones observed in xenon matrix shows that in a latter environment the process is significantly faster than in argon. The optimized exponential time constant (τ) is 36 min for the isomerization in argon matrix at 15 K [2] while for the process in xenon it is equal to 19.9 and 12.7 min for tight and loose sites, respectively, at the same temperature. This is because of the fact that the solid host compensates the energy mismatch between the intramolecular energy levels involved in the energy relaxation by converting the excess internal energy of the guest molecule into

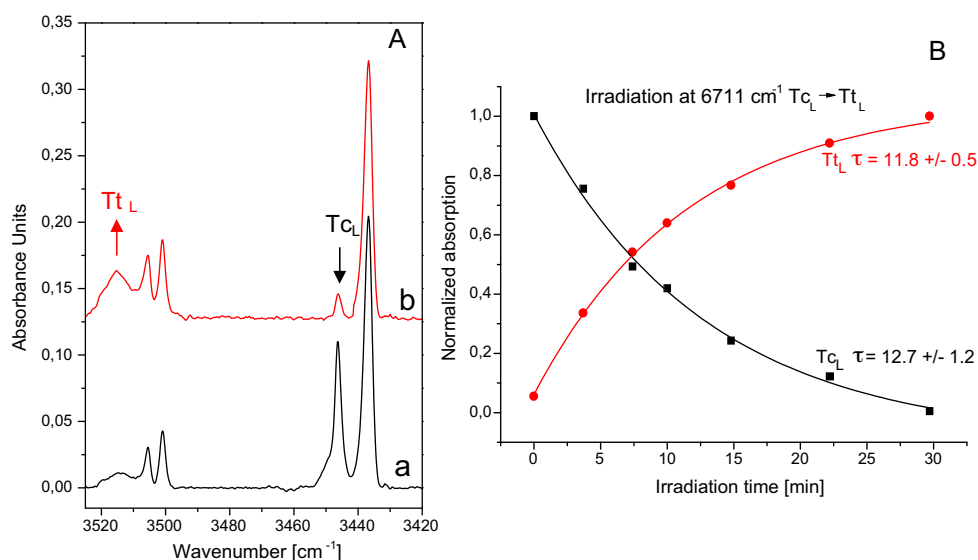


Figure 4. The $T_c \rightarrow T_t$ isomerization in the loose site upon irradiation at 6711 cm^{-1} . (A) The spectra of the GA/Xe matrix before (a) and after (b) NIR-irradiation. (B) The evolution of the abundances of T_{cL} (black squares) and T_{tL} (red dots) conformers with time upon irradiation by 6711 cm^{-1} . Solid lines represent the best fits using first order decay kinetics formula $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 12.7 min for T_{cL} band decay and 11.8 for T_{tL} band's growth. Matrix temperature during the measurements and irradiation processes was 15 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

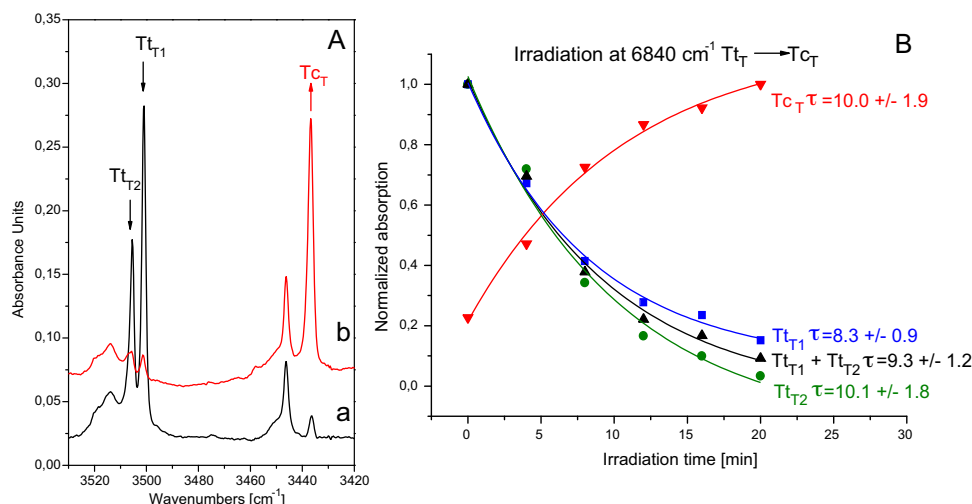


Figure 5. The Tt \rightarrow Tc isomerization in the tight site upon irradiation at 6840 cm^{-1} . (A) The spectra of the GA/Xe matrix before (a) and after (b) NIR-irradiation. (B) The evolution of the abundances of Tt_{T1} (blue squares) and Tt_{T2} (green squares) and the sum of Tt_{T1} and Tt_{T2} (black triangles) as well as Tc_T (red triangles) conformers with time upon irradiation by 6840 cm^{-1} . Solid lines represent the best fits using first order decay kinetics formula $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 10.0 min for Tc_T band's growth and 9.3 for Tt_{T1} + Tt_{T2} band decay. Matrix temperature during the measurements and irradiation processes was 15 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

lattice phonons [4]. It is worth to note that the Debye frequency for Ar is equal to 93 cm^{-1} while for Xe it equals 64 cm^{-1} [15]. Therefore, the coupling between vibrational levels of GA and matrix phonon is stronger for argon host.

3.2.2. Tt \rightarrow Tc isomerization

Analogically to the intramolecular hydrogen bond opening process, Tc \rightarrow Tt isomerization, the conversion of the Tt isomer into Tc was induced in two sites, separately. As can be seen in Figure 5 the 6840 cm^{-1} line was used to induce this process in tight site. It is important to note that it was not possible to find two different laser lines for selective isomerization of the systems represented by Tt_{T1} and Tt_{T2}. This is due to the fact that both absorptions are separated by only ca 4 cm^{-1} being slightly beyond the spectral width of the used laser. Nevertheless, while looking for the most optimal energy to induce the Tt_T \rightarrow Tc_T isomerization we were examining the highest quantum yield of the Tc_T formation process. The line 6840 cm^{-1} appeared to be the most effective one.

As can be seen in Figure 5A, the irradiation at the chosen laser line results in decrease of the bands due to the Tt isomer in a tight site (Tt_{T1} and Tt_{T2}) and simultaneous increase of the intensity of the band due to the Tc conformer isolated in tight site (Tc_T). According to the kinetic profile prepared for the 6840 cm^{-1} -induced reaction at the chosen laser line the decrease of Tt_{T2} band is slightly slower as compared with Tt_{T1} feature. Nevertheless, if we look at the decrease of the integrated sum of Tt_{T2} and Tt_{T1} absorptions, we see that the optimized exponential time constant (τ) for it perfectly matches the τ value determined for increase of Tc conformer in tight site (9.3 min versus 10.0 min, respectively). It means that using 6840 cm^{-1} line we were able to induce simultaneous isomerization of Tt conformer isolated in both tight sites.

The Tt \rightarrow Tc isomerization process taking place in a loose site was induced by using 6863 cm^{-1} laser line. Upon irradiation the intensity of the band at 3514.0 cm^{-1} (Tt_L) belonging to Tt isomer isolated in the loose site decreases while the absorption due to the Tc molecule embedded in loose site (Tc_L) at 3446 cm^{-1} increases (see Figure 6A).

Unlike the kinetic profiles presented before there are some discrepancies between the intensity growth of the Tc_L band and the absorption decay of the Tt_L band (see Figure 6). The optimized exponential time constant is equal to 6.2 min for Tt_L while 7.6 min for

Tc_L. The disagreement between these two kinetic values might originate from the error caused during the band integration procedure in the spectra. As it was discussed before, the band due to the Tt isomer in a loose site is a very broad one and as we mentioned before the exact structure of the band cannot be precisely determined. We checked the changes of all bands due to the Tc and Tt conformers trapped in loose site in other spectral regions but the one presented in Figure 6 seems to be the most representative one. Nevertheless, from the optimized time values we can conclude that upon the irradiation at 6863 cm^{-1} the Tt isomer embedded in a loose site can be converted into the Tc isomer in the same matrix cage and that it is represented by the 1:1 stoichiometry.

Comparing the kinetics of the Tt \rightarrow Tc process in both tight and loose matrix traps we can see the same pattern as observed for the reverse reaction. The process in a loose site is faster than in the tight site. It is because of the same reasons we already discussed for Tc \rightarrow Tt isomerization.

Taking into account the optimized exponential time constants determined before for GA in an argon matrix [2] we clearly see that also for Tt \rightarrow Tc process the xenon matrix speeds up the isomerization. For the experiments in argon matrix the exponential time constant for Tt conformer decay was equal to 20 min while for xenon matrix it equals 6.2 and 9.3 min for loose and tight sites, respectively. As discussed before for the Tc \rightarrow Tt process, this effect must be again due to the repulsive part of the intermolecular potential which is dominant in the relaxation mechanism. The distance between a guest molecule and rare gas atoms is longer for xenon than for argon matrix leading to a decrease of the interactions. This allows to conclude that the decrease of the quantum yield by the coupling through the host low-frequency modes in xenon is less efficient than in argon.

The comparison of the kinetic parameters determined for the Tc \rightarrow Tt and Tt \rightarrow Tc isomerization shows that the latter process is almost twice faster than the former one, regardless the matrix site (loose or tight). Similar results we obtained for the experiments in argon matrix [2]. This was explained based on the energy dissipation which for the Tc conformer is 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. The proposed reason for it was the IVR (Intramolecular Vibrational Energy Redistribution) processes

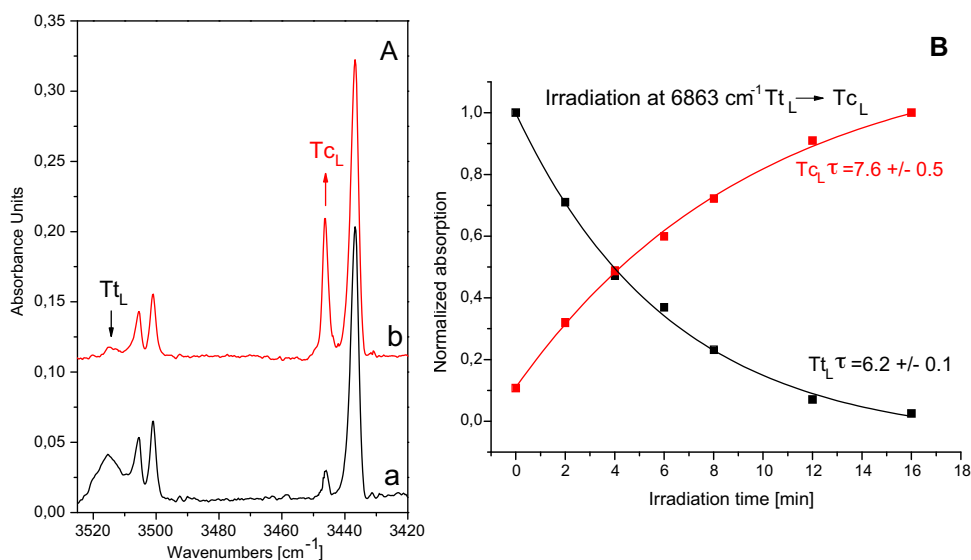


Figure 6. The Tt → Tc isomerization in the loose site upon irradiation at 6863 cm⁻¹. (A) The spectra of the GA/Xe matrix before (a) and after (b) NIR-irradiation. (B) The evolution of the abundances of Tt_L (black squares) and Tc_L (red squares) conformers with time upon irradiation. Solid lines represent the best fits using first order decay kinetics formula $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 6.2 min for Tt_L band decay and 7.6 min for Tc_L band growth. Matrix temperature during the measurements and irradiation processes were 15 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

connected with the intramolecular hydrogen bond in Tc conformer that could be treated as an additional channel for energy dissipation. We suggested that for Tc 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 [2]. In fact, the experiments performed in the xenon matrix nicely confines with our previous interpretation.

3.3. Glyoxylic acid–water complex isomerization

In our previous letters [1,2], it was reported that GA forms a hydrogen bonded complex with a single water molecule and four different structures have been experimentally identified in low temperature matrix (see Ref. [2]). Alike the argon matrix experiments the most abundant complex structure observed in xenon matrix is the one with the water molecule interacting with C=O moiety of the aldehyde group and OH group of carboxylic group (see Figure 1). The bands positions identified for all four GA complexes observed in xenon matrix are included in Table 2. As can be seen, in the case of complexes we do not distinguish loose or tight matrix site. All the complexes seem to be embedded in one kind matrix site and unlike the GA monomers every mode is represented by one band. The values of the bands shifts upon complexation observed for argon matrix [2] are very close to the frequency shifts in the xenon experiments determined with reference to the bands of GA monomers trapped in loose matrix site. Therefore we assume that in xenon the surrounding of the GA-H₂O complex is comparable with the one that GA monomers encounter in the loose site.

By analogy to our argon experiment [2], we wanted to study the intramolecular hydrogen bond opening and closing process for the described complexes. The irradiation at 6671 cm⁻¹, which is in resonance with the first overtone of $\nu(\text{OH})$ of Tc conformer of glyoxylic acid in water complex results in the decrease of the bands belonging to the Tc-H₂O complex (see Figure 7A).

Unfortunately, in the region of $\nu(\text{OH})$ we could not to identify any band due to the $\nu(\text{OH})$ mode of Tt isomer in the complex with water molecule. The decrease of the bands due to the Tc-H₂O system is accompanied by the increase of Tt-H₂O bands in all spectral regions except for OH stretching modes regions. It is probably due to the fact that the $\nu(\text{OH})$ feature of the discussed complex might overlap

with the doublet structure of the Tt monomer in the tight site. The lack of the visible feature of the $\nu(\text{OH})$ motion in Tt-H₂O complex makes impossible to estimate the wavenumber of the irradiation that could be used to induce Tt-H₂O → Tc-H₂O reaction. Therefore,

Table 2

Experimental vibrational spectra (in cm⁻¹) of Tc-H₂O and Tt-H₂O complexes in xenon matrix.

| Ar matrix ^a | | Xe matrix | | |
|------------------------|-------------|---------------|--------|------------------------|
| Tc A | Tc B | Tc A | Tc B | |
| 3140–3130 | 3455.0 | ~3163 (broad) | 3431.5 | ν O–H |
| – | 2918.0 | 2842.5 | 2902.0 | ν C–H |
| 1780.0 | 1792.5 | 1780.0 | 1785.5 | ν C=O carb |
| 1759.7 | 1738.0 | 1758.0 | 1743.0 | ν C=O ald |
| – | – | 1325.0 | 1323.0 | δ COH/ ν CO |
| 1354.9 | 1348.2 | – | 1343.0 | δ C–H |
| 1209.0 | 1173.0 | – | 1166.0 | ν CO/ δ COH |
| – | 1007.0 | – | 1001.8 | γ C–H |
| – | 880.0/876.0 | 881.0 | 873.0 | ν C–C |
| – | 681.5 | – | 656.5 | δ C–C=O ald |
| – | 662.4 | – | 646.0 | γ OH |
| – | 572.7 | – | 569.0 | γ skel |
| – | 506.0 | – | – | δ C–C=O carb |
| – | – | – | – | δ skel |
| – | – | – | – | γ CC |

| Ar matrix ^a | | Xe matrix | | |
|------------------------|---------------|-----------|--------|-----------------------------|
| Tt A | Tt B | Tt A | Tt B | |
| 3108.0 | 3543.5 | – | – | ν O–H |
| – | 2893.0 | – | 2861.0 | ν C–H |
| 1750.5 | 1765.0 | 1747.0 | 1762.0 | ν C=O carb |
| 1737.0 | 1738.5 | – | 1735.5 | ν C=O ald |
| – | – | – | – | δ COH/ ν CO |
| – | 1391.0 | – | 1373.0 | δ C–H |
| 1235.0 | 1139.0/1129.0 | 1215.5 | – | ν CO/ δ COH |
| – | – | – | – | γ C–H |
| – | – | – | – | ν C–C |
| 883.0 | – | – | – | γ skel + γ OH |
| 687.5 | 646.0 | – | 649.0 | δ C–C=O ald |
| – | – | – | – | γ OH + γ skel |
| – | – | – | – | δ C–C=O carb |
| – | – | – | – | δ skel |
| – | – | – | – | γ CC |

^a Taken from Ref. [2] TcA, TcB, TtA and TtB correspond to the different structure of the complexes presented in Fig. 2 in Ref [2].

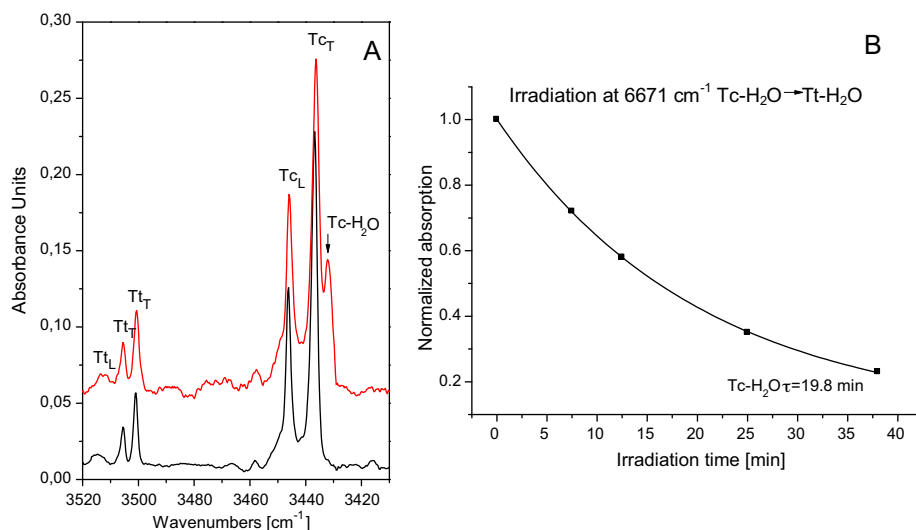


Figure 7. The $\text{Tc-H}_2\text{O} \rightarrow \text{Tt-H}_2\text{O}$ isomerization in xenon matrix upon irradiation at 6671 cm^{-1} . (A) the spectra of the GA/ H_2O /Xe matrix before (a) and after (b) NIR-irradiation. (B) The evolution of the abundance of Tc- H_2O complex with time upon irradiation. Solid line represent the best fit using first order decay kinetics formula $A = \exp(-t/\tau)$. The optimized exponential time constant (τ) is 19.8 min for Tc- H_2O band decay. Matrix temperature during the measurements and irradiation processes was 15 K.

further we will discuss solely the $\text{Tc-H}_2\text{O} \rightarrow \text{Tt-H}_2\text{O}$ process in view of the analogous reaction observed for the Tc monomer.

As it is presented in Figure 7B, the optimized time constant for the exponential decay for the $\text{Tc-H}_2\text{O} \rightarrow \text{Tt-H}_2\text{O}$ isomerization in xenon matrix is equal to 19.8 min. For Tc- H_2O trapped in argon environment the τ value of the process was estimated to be equal to be 57 min. It is ca 2.8 times slower than for xenon matrix. Exactly the same factor was determined for the Tc monomer in loose site in xenon (this work) and in argon matrix [2] (12.8 min versus 37 min, respectively) as well as for Tt decay in loose xenon site and in argon matrix [2] (6.8 min versus 12 min, respectively). It indicates that the observed faster isomerization in a xenon matrix as compared with argon environment is purely because of the interactions with the host. Neither intramolecular nor intermolecular hydrogen bonds do affect it. In turn, it also means that for glyoxylic acid monomer the loose site in xenon matrix corresponds to a similar environment that it experienced in argon environment.

The comparison of the time constant determined for the Tc- H_2O decay with the one observed for Tc monomer in the loose site shows that the isomerization process of GA complex with water molecule is ca 1.5 time slower than Tc monomer embedded in loose site (19.8 versus 12.7). The experiment in argon matrix shows exactly the same effect with the τ value equal to 39.5 min for Tc- H_2O complex and 25 min for the Tc monomer [2]. This comparison nicely confirms our previous explanation that slower isomerization of the Tc conformer in water complex as compared with hydrogen-bond opening reaction in Tc monomer is due to the energy dissipation via intramolecular hydrogen bond to the aldehyde moiety, and further to water molecule via intermolecular hydrogen bond. Moreover, one can see that here the coupling with the lattice phonons resulting in energy transfer in the supermolecular system seems not to be a competing energy dissipation channel with respect to the intramolecular IVR process.

4. Conclusions

The isomerization kinetics has been followed for Tc and Tt monomers upon NIR irradiation in xenon matrix. It is shown that xenon environment produces two types of matrix sites (loose and tight) for GA monomer. It is shown that the $\text{Tc} \rightarrow \text{Tt}$ transition in

tight site is by a factor of ca 2 slower than in the loose site. This observation is connected to the sterical constraints as well as to the lattice-phonon-assisted energy relaxation pathway related to local matrix morphology within the same host.

The $\text{Tt} \rightarrow \text{Tc}$ process in both loose and tight site appeared to be twice faster than the $\text{Tc} \rightarrow \text{Tt}$ conversion into Tt regardless the matrix site (loose or tight). This is explained by the contribution of the intramolecular hydrogen bond present in the Tc conformer to the vibrational energy dissipation in the system. The comparison with the results obtained for argon matrix [2] indicates that the described energy distribution is not affected by the environment.

The studies of the GA- H_2O system in xenon show that the complex structure is embedded in the matrix site with the geometry corresponding to the loose site for the GA monomer.

The kinetic profile obtained for the $\text{Tc-H}_2\text{O} \rightarrow \text{Tt-H}_2\text{O}$ isomerization suggests that the interaction with water decreases the efficiency of the isomerization process of the Tc conformer by factor of 1.5. That is in agreement with the isomerization in argon [2] and confirms that the vibrational energy deposited in the system can be transferred via both inter- and intramolecular hydrogen bonds. Analogically to the monomer isomerization this process is not affected by the environment.

References

- [1] J. Lundell, A. Olbert-Majkut, *Spectrochim. Acta A* (2013), <http://dx.doi.org/10.1016/j.saa.2013.08.120> (in press).
- [2] A. Olbert-Majkut, J. Lundell, M. Wierzejewska, *J. Phys. Chem. A* 118 (2014) 350.
- [3] E. Knözinger, W. Schuller, W. Lange, *Faraday Discuss. Chem. Soc.* 86 (1988) 285.
- [4] P.M. Agrawal, D.L. Thompson, L.M. Raff, *J. Chem. Phys.* 101 (1994) 9937.
- [5] A. Aspö, J. Murto, P. Sten, *Chem. Phys.* 106 (1986) 399.
- [6] P.M. Agrawal, D.L. Thompson, L.M. Raff, *J. Chem. Phys.* 102 (1995) 7000.
- [7] R.L. Redington, C.-K. Liang, *J. Mol. Spectrosc.* 104 (1984) 25.
- [8] H.E. Hallam, *Vibrational Spectroscopy of Trapped Species*, Wiley & Sons, 1973.
- [9] P. van Eijck, F.B. van Duijneveldt, *J. Mol. Struct.* 39 (1977) 157.
- [10] C. Chen, S.F. Shyu, *J. Mol. Struct. Theorchem.* 503 (2000) 201.
- [11] A.J. Barnes, *J. Mol. Struct.* 113 (1984) 161.
- [12] K.L. Plath, J.L. Axson, G.C. Nelson, K. Takahashi, R.T. Skodje, V. Vaida, *React. Kinet. Catal. Lett.* 96 (2009) 209.
- [13] F. Legay, in: B. Moore (Ed.), *Chemical and Biochemical Applications of Lasers*, vol. II, Academic, New York, 1977, V.E. Bondybey, M. Räsänen, A. Lammers, Annu.
- [14] V.E. Bondybey, *Annu. Rev. Phys. Chem.* 35 (1984) 591.
- [15] H.J. Jodl, in: L. Andrews, M. Moskovits (Eds.), *Chemistry and Physics of Matrix-Isolated Species*, North-Holland, Amsterdam, 1989.