Near-Infrared Laser-Induced Generation of Three Rare Conformers of Glycolic Acid

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ABSTRACT: Structural transformations were induced in conformers of glycolic acid by selective excitation with monochromatic tunable near-infrared laser light. For the compound isolated in Ar matrices, near-IR excitation led to generation of two higher-energy conformers (GAC; AAT) differing from the most stable SSC form by 180° rotation around the C–C bond. A detailed investigation of this transformation revealed that one conformer (GAC) is produced directly from the near-IR-excited most stable conformer. The other higher-energy conformer (AAT) was effectively generated only upon excitation of the primary photoproduct (GAC) with another near-IR photon. Once these higher-energy conformers of glycolic acid were generated in an Ar matrix, they could be subsequently transformed into one another upon selective near-IR excitations. Interestingly, no repopulation of the initial most stable SSC conformer occurred upon near-IR excitation of the higher-energy forms of the compound isolated in solid Ar. A dramatically different picture of near-IR-induced conformational transformations was observed for glycolic acid isolated in N₂ matrices. In this case, upon near-IR excitation, the most stable SSC form converted solely into a new conformer (SST), where the acid OH group is rotated by 180°. This conformational transformation was found to be photoirreversible. Moreover, SST conformer, photoproduced in the N₂ matrix, spontaneously converted to the most stable SSC form of glycolic acid, when the matrix was kept at cryogenic temperature and in the dark.

1. INTRODUCTION

Glycolic acid (GA or hydroxyacetic acid) is the smallest of the α-hydroxy carboxylic acids. All theoretical calculations carried out so far on this molecule predicted the SSC structure (see Chart 1) to be the lowest-energy form. 1,2 Other conformations differ from SSC by the values of the O₂=C−C=O, H−O₂=C−C, and/or H−O₁=C=O dihedral angles (where O₁ denotes the oxygen atom of the carboxyl OH group and O₂ denotes the oxygen atom of the alcohol OH group). Energies theoretically calculated at the MP2 level for GAC and AAT conformers (see Chart 1) are higher by about 10 and 13 kJ mol⁻¹ with respect to that of SSC, whereas the energies of other forms are significantly higher; e.g., the energy difference between SST and SSC was predicted 3,4 as 20 kJ mol⁻¹.

For glycolic acid in a free jet expansion, SSC conformer was found by microwave spectroscopy to be the most populated form of the compound. 5 Alongside the most abundant SSC form, only small amounts of AAT were detected in these experiments. SSC conformer was also found to be the most populated in solid matrices, prepared by trapping vapor of glycolic acid (together with a large excess of argon) on a low-temperature substrate. 4,5 Together with the dominating SSC form, small amounts of rare GAC and AAT conformers were trapped from the gas phase into Ar matrices and detected by FTIR spectroscopy. 5

In earlier matrix-isolation experiments, 3,6 conversion of SSC into the higher-energy GAC and AAT forms was found to occur upon excitation of glycolic acid monomers with broadband near-IR/mid-IR light. Application of modern tunable laser sources allows much more detailed investigation of such processes. In particular, narrowband excitation at spectral position of specific near-IR absorptions of individual isomers permits a significantly better control of the light-induced conformational conversions. Moreover, using this technique, the relative populations of the conformers can be better manipulated, and generation of new conformers can be attempted.

It often happens that conformers generated in Ar matrices upon near-IR excitation are not stable enough to be detected by stationary spectroscopic techniques. However, the lifetime of such photogenerated species can be extended by using solid nitrogen as the matrix host, instead of a solid noble gas. This effect has been demonstrated for several matrix-isolated molecules. 7–12

In the current work, we used narrowband near-IR tunable sources (a tunable diode laser and an optical parametric oscillator) to manipulate the conformational composition of
GA isolated in low-temperature Ar and N₂ matrices. For the compound isolated in solid nitrogen, we successfully attempted to generate a new conformer that has never been reported so far. We also demonstrate the dramatic differences between the near-IR-induced conformational transformations occurring for GA isolated in Ar and N₂ matrices.

2. EXPERIMENTAL SECTION

The sample of glycolic acid (purity 98%) used in the present study was a commercial product supplied by Sigma-Aldrich. Prior to matrix-isolation experiments, the solid compound, known for its hygroscopicity, was put in a glass tube and purged with a flux of dry nitrogen. This approach permitted removal of the bound water. The tube with dry GA crystals was then connected through a needle valve to the vacuum chamber of a helium-cooled cryostat. In the matrix-isolation experiments (fwhm <1 MHz, 40 mW). The wavelengths of the near-IR light were measured with a HighFinesse WS-S wavelength meter. During experiments on spontaneous conformational transformations, the spectra were recorded with a long-pass filter transmitting light only with wavenumbers lower than 1700 cm⁻¹ (see the transmission curve in Figure S4 in the Supporting Information). The filter was placed between the spectrometer source and the matrix sample. This filter protected isolated glycolic acid molecules from excitations at energies higher than 20 kJ mol⁻¹ (equivalent to the cutoff of the filter at ~1700 cm⁻¹).

3. COMPUTATIONAL SECTION

The geometries of glycolic acid conformers were fully optimized at the DFT(B3LYP),¹³–¹⁵ MP2,¹⁶ and QCISD¹⁷ levels of theory. These geometries are collected in Tables S2 and S3 in the Supporting Information. The relative energies of the conformers were calculated using the QCISD method at geometries optimized at this level. The harmonic vibrational frequencies calculated at the same QCISD level (Table S4, Supporting Information) were used to account for the zero-point vibrational corrections (Table S1, Supporting Information). The harmonic (Table S5, Supporting Information) and anharmonic (Table S6, Supporting Information) vibrational frequencies and IR intensities were calculated using the DFT(B3LYP) method. The harmonic DFT frequencies were scaled by a single factor equal to 0.98.

The two-dimensional potential energy surfaces (PES) of glycolic acid were computationally probed (at the MP2/aug-cc-pvDz level) by carrying out numerous restricted geometry optimizations. The performed PES scans consist of 324 points each. For each of these points, values of two conformationally relevant dihedral angles (OA−C−C−O, H−O−C−C−O, or H−O−C−C−O) were fixed and all the remaining geometric parameters were optimized. The electronic energy of the GA molecule at partially optimized geometry was presented as a function of the values of two fixed dihedral angles.

All quantum-mechanical computations were carried out using the Gaussian 09 program¹⁸ and the standard Dunning aug-cc-pvDz basis set as defined in this package.

4. RESULTS AND DISCUSSION


The molecule of glycolic acid has three conformationally relevant degrees of freedom, related with the internal rotation around the O₁−C−C−O and C−C−O single bonds. In the current work we carried out a detailed investigation of the PES of GA in order to locate the minima and to characterize the barriers separating them. The structures and energies of all obtained minima, calculated at the QCISD level of theory, are provided in Table S1 in the Supporting Information. Table 1 and Chart 1 summarize the most important data.

As it is known for many organic acids, also in GA, the OH group in the carboxylic O=O−H fragment can adopt either a cis or trans orientation. Considering these two orientations, relaxed PES scans were performed on two-dimensional (2D) grids of points as a function of two dihedral angles, H−O−C−C−O and O−C−C−O, which were

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Chart 1. Structures of Glycolic Acid Conformers Observed in the Current Work

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure optimized at the QCISD/aug-cc-pvDz level</th>
<th>Torsional angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC</td>
<td><img src="image1" alt="SSC structure" /></td>
<td>r₁ 0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₂ 0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₃ 0°</td>
</tr>
<tr>
<td>C₁</td>
<td><img src="image2" alt="C₁ structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td><img src="image3" alt="GAC structure" /></td>
<td>r₁ -51.0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₂ -154.7°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₃ 0.4°</td>
</tr>
<tr>
<td>AAT</td>
<td><img src="image4" alt="AAT structure" /></td>
<td>r₁ 180°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₂ 180°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₃ 180°</td>
</tr>
<tr>
<td>SST</td>
<td><img src="image5" alt="SST structure" /></td>
<td>r₁ 0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₂ 0°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>r₃ 180°</td>
</tr>
</tbody>
</table>

In the SSC, GAC, AAT, and SST symbolic names, S, G, A, C, and T stand for syn, gauche, anti, cis, and trans. The first letter describes the orientation of the H−O alcohol group (syn, anti, or gauche, around the H−O−C−C torsional angle, r₁); the second letter describes the syn or anti orientation of the alcohol and carboxyl groups, around the O−C−C−O torsional angle, r₂; the third letter describes the orientation of the H−O carboxyl group (cis or trans, around the O−C−C−O−H torsional angle, r₃).

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[^1]: dx.doi.org/10.1021/jp5051589 J. Phys. Chem. A 2014, 118, 5626–5635
Table 1. Relative Electronic Energies (ΔE_e) and Relative Electronic Energies Corrected for Zero-Point Vibrational Energy (ΔE_{total} = ΔE_e + ΔZPE) of Glycolic Acid Conformers Observed in Ar and/or N\textsubscript{2} Low-Temperature Matrixes\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th>SSC</th>
<th>GAC</th>
<th>AAT</th>
<th>SST</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE_e  (kJ mol\textsuperscript{-1})</td>
<td>0.0</td>
<td>9.18</td>
<td>12.86</td>
<td>19.38</td>
</tr>
<tr>
<td>ΔE_{total} (kJ mol\textsuperscript{-1})</td>
<td>0.0</td>
<td>9.54</td>
<td>12.54</td>
<td>18.97</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All energies were calculated using the QCISD/aug-cc-pvDz method at geometries optimized at the same level.

incrementally fixed with a step of 20°, and used as reaction coordinates. The remaining geometric parameters were fully optimized. The resulting 2D surfaces are presented in Figure 1a and b. Among the optimized geometry coordinates, the initial value of the O=C=O—H dihedral angle was close to 0° (Figure 1a) or 180° (Figure 1b), which correspond to the cis and trans orientation of the carboxyl fragment, respectively. Although the O=C=O—H dihedral coordinate was subject to optimization (was not fixed), the energy-minimization procedure did not lead (at any point) to its change from cis to trans (Figure 1a) or from trans to cis (Figure 1b) orientation. The orientations of this important dihedral angle (which we designate “parameter”, as opposite to “reaction coordinate”) are specified on top of each frame in Figure 1.

From these two surfaces, it is possible to identify seven different minima: SSC, GAC, ASC, and AAC (Figure 1a) and AAT, SST, and AST (Figure 1b). The structures of SSC, GAC, AAT, and SST are presented in Chart 1, whereas the structures of ASC, AAC, and AST are given in Table S1 in the Supporting Information. In agreement with the previous findings\textsuperscript{3,6} six conformers belong to the C\textsubscript{1} symmetry point group, with 0 or 180° values of all conformationally relevant dihedral angles. The only exception is the GAC form, belonging to the C\textsubscript{2v} point group and having a symmetry-equivalent mirror-image counterpart, designated in Figure 1a as G'AC. Note that the structure, which according to the adopted naming system might be called SAT (see Table S1 in the Supporting Information), is not an energy minimum but a second-order transition state. Its geometry is marked with a yellow symbol “+” in Figure 1b.

Two more 2D surfaces were calculated for the GA monomer. In these additional surfaces, the O\textsubscript{A}—C—C==O was chosen as a parameter, initially adopting syn or anti configurations. The dihedral angles H—O\textsubscript{A}—C—C and O==C—O==H, defining orientations of the two OH groups, were incrementally changed with a step of 20°, in all possible combinations. For the starting syn orientation of the O\textsubscript{A}—C—C==O heavy atom backbone, at any chosen combination of the fixed values of the H—O\textsubscript{A}—C—C and O==C—O==H dihedral angles, optimization did not change the O\textsubscript{A}—C—C==O orientation from syn to anti. The corresponding 2D relaxed PES is shown in Figure 1c. However, for the starting anti O\textsubscript{A}—C—C==O configuration, a significant deviation from the original orientation of this coordinate occurred upon geometry optimization around the SAT configuration, where the two OH groups are oriented toward each other and the region between them is overcrowded with hydrogen atoms. To get a better insight into this surface, the anti O\textsubscript{A}—C—C==O configuration was enforced and the corresponding dihedral angle was fixed at 180°. The 2D PES presented in Figure 1d is in fact a rigid PES. The seven minima found on surfaces c and d are the same as those found on surfaces a and b but showing alternative barriers separating conformers SSC, GAC, AAT, SST, ASC, AAC, and AST (Figure 1). It is important to mention here that the particular interest of calculating the rigid PES (Figure 1d) was to find the lowest energy path connecting the GAC and SAT minima. This lowest-energy path goes through a point designated with a blue symbol “x”. This geometry was subsequently fully optimized, and was found to be a first order saddle point conserving the anti configuration around the O\textsubscript{A}—C—C==O dihedral angle. The existence of this path will be deemed important later, when discussing the experimentally observed direct transformation between GAC and AAT.

Each of the calculated 2D surfaces was constructed on a grid consisting of 18 x 18 = 324 points. For four surfaces, it makes up to 1296 individual geometry optimizations. In order to make these calculations feasible within a reasonable time, the calculation level for the 2D PES was chosen to be MP2/aug-cc-pvDz. The energies of all the minima and saddle points calculated in the direction from the “starting form” (named in the first column) toward the form specified in the headline. Structures of all the GA conformers are presented in Tables S1—S3 (in the Supporting Information).\textsuperscript{7} All the calculated stationary points (given in the E_{barr} section) were characterized by vibrational calculations as the first-order saddle point conserving the anti conformation.

### Table 2. Relative Electronic Energies (E_{barr}) of Glycolic Acid Conformers and Heights of the Torsional Barriers (E_{barr}) between the Conformers\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>starting form\textsuperscript{b}</th>
<th>E_{min}</th>
<th>SSC</th>
<th>GAC</th>
<th>ASC</th>
<th>AAT</th>
<th>SST</th>
<th>AST</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC</td>
<td>0.0</td>
<td>18.6</td>
<td>19.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td>9.2</td>
<td>9.4</td>
<td>11.5</td>
<td>48.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASC</td>
<td>17.0</td>
<td>2.4</td>
<td>8.7</td>
<td>50.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AAC</td>
<td>18.7</td>
<td>2.0</td>
<td>6.9</td>
<td>47.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AAT</td>
<td>12.4</td>
<td>44.9</td>
<td>53.4</td>
<td>23.6</td>
<td>36.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SST</td>
<td>19.5</td>
<td>30.6</td>
<td>16.5</td>
<td>24.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AST</td>
<td>41.6</td>
<td></td>
<td>25.4</td>
<td>7.3</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}All energies are in kJ mol\textsuperscript{-1}, and were calculated using the MP2/aug-cc-pvDz method at geometries optimized at the same level. \textsuperscript{b}The height of the barrier E_{barr} is given relatively to the energy E_{min}, and is calculated in the direction from the “starting form” (named in the first column) toward the form specified in the headline. Structures of all the GA conformers are presented in Tables S1—S3 (in the Supporting Information).\textsuperscript{7} All the calculated stationary points (given in the E_{barr} section) were characterized by vibrational calculations as the first-order transition states. There are two different transition states connecting the symmetry-identical GAC and G'AC forms with SSC (see colored crosses in Figure 1a). This table shows only the value of the lowest energy barrier in the [SSC, GAC] pair. The other barrier is higher by 4 kJ mol\textsuperscript{-1}.
to them by excitation, would easily undergo ASC → SSC (Figure 1a and c), AAC → GAC (Figure 1a and d), and AST → SST (Figure 1b and c) conversions to lower-energy, more stable forms. Moreover, these transformations should be significantly facilitated by proton tunneling, since all of them concern only rotation of the HOA group around the OA−C single bond and the only particle displaced in these processes is a light hydrogen atom.

Of the forms SSC, GAC, AAT, and SST, corresponding to the minima deep enough to permit stabilization at low temperature, the SSC, GAC, and AAT conformers have been already experimentally observed in argon,3,5 krypton,3 and xenon5 matrixes. However, no experimental observation of the SST form has been reported hitherto. This conformer is located in a relatively deep potential well. It is separated by a barrier of 16.5 kJ mol⁻¹ from AAT (Figure 1b, Table 2) and by a barrier of 30.6 kJ mol⁻¹ from SSC (Figure 1c, Table 2). Hence, such energy barriers make the SST structure a potential candidate for experimental detection.

4.2. Near-IR-Induced Transformations of Glycolic Acid Isolated in Ar Matrixes. 4.2.1. Generation of GAC and AAT Conformers from SSC. The mid-IR spectrum of glycolic acid isolated in an Ar matrix is presented in Figure 2. The IR absorptions due to the stretching vibrations of the two OH groups in the molecule overlap in the experimental spectrum, appearing as a single band at 3561 cm⁻¹. The band due to the
νC=O stretching vibration was found at 1773 cm$^{-1}$. The experimental spectrum of GA isolated in solid argon is well reproduced by the spectrum theoretically calculated for the lowest-energy SSC conformer (Figure 2). The spectral positions of all intense IR experimental bands (all assigned to SSC) are the same as previously reported.$^{3-5}$ In the near-IR region of the experimental spectrum (Figure 3), the bands due to 2νOH overtones do not overlap (as is the case for νOH fundamentals) and appear as separate absorptions at 6954 and 6938 cm$^{-1}$ (Figure 3a). These wavenumbers are lower (by a usual matrix shift) than 6995 cm$^{-1}$, where the 2ν-OH overtone band was detected for GA in the gas phase.$^{19}$

GA isolated in the Ar matrix was irradiated with monochromatic near-IR light at 6954 cm$^{-1}$, where the peak of the more intense 2νOH overtone band was found in the absorption spectrum. This irradiation resulted in a decrease of the initial IR spectrum of SSC conformer and in a growth of the spectra of photoproduced species. The spectra recorded before and after irradiation at 6954 cm$^{-1}$ are presented in Figure 4 (mid-IR range) and in Figure 3 (near-IR range). The increasing mid-IR bands of the products coincide well with those growing

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**Figure 2.** Infrared spectra of glycolic acid isolated in N$_2$ (lower panel) and Ar (middle panel) matrixes compared with the theoretical spectrum of SSC conformer calculated within the harmonic approximation at the DFT(B3LYP)/aug-cc-pvDz level (top). The theoretical wavenumbers were scaled by a single factor of 0.98.

**Figure 3.** Fragments of the near-IR spectra of glycolic acid isolated in an Ar matrix: (a) recorded before any irradiation; (b) recorded after 1 h of irradiation at 6954 cm$^{-1}$; (c) difference spectrum: trace b minus trace a; (d) the anharmonic overtone wavenumbers calculated at the DFT(B3LYP)/aug-cc-pvDz level for SSC (blue), GAC (red), and AAT (green) conformers.

**Figure 4.** Fragments of the mid-IR spectra of glycolic acid isolated in an Ar matrix: (a) recorded before any irradiation; (b) recorded after 1 h of irradiation at 6954 cm$^{-1}$; (c) difference spectrum: trace b minus trace a; (d) the anharmonic fundamental wavenumbers calculated at the DFT(B3LYP)/aug-cc-pvDz level for SSC (blue), GAC (red), and AAT (green) conformers.
in the spectra of matrix-isolated GA upon broadband mid-IR/near-IR irradiation.\textsuperscript{3,6} These bands were previously\textsuperscript{3,6} identified as belonging to the spectra of GAC and AAT conformers of glycolic acid. In the current experiment, upon irradiation at 6954 cm\textsuperscript{-1}, the \(\nu\)-OH bands of AAT grow at 3670 and 3473 cm\textsuperscript{-1}, whereas the \(\nu\)-OH bands of GAC grow at 3648 and 3563 cm\textsuperscript{-1} (Figure 4). The band at 3563 cm\textsuperscript{-1} partially overlaps with the band at 3561 cm\textsuperscript{-1} in the initial spectrum of SSC. Similarly, in the \(2\nu\)-OH overtone region, the growing band centered at 6958 cm\textsuperscript{-1} (due to GAC) partially overlaps with the band centered at 6954 cm\textsuperscript{-1} in the spectrum of SSC (Figure 3). A close vicinity of the frequencies of the \(2\nu\)-OH overtones due to the acid OH groups of glycolic acid in SSC and GAC forms was earlier theoretically predicted by Havey et al.\textsuperscript{20} and is also confirmed by our anharmonic calculations (Figure 3d). Hence, irradiation at 6954 cm\textsuperscript{-1} leads not only to excitation of the initially present SSC form, but it can also excite the photogenerated GAC conformer. A priori, there are two possible mechanisms of formation of GAC and AAT conformers upon 6954 cm\textsuperscript{-1} irradiation: (i) both conformers are produced directly from near-IR-excited SSC or (ii) SSC converts into GAC as the sole primary product, which can be subsequently transformed into AAT upon absorption of another photon.

In a second experiment, glycolic acid isolated in an Ar matrix was irradiated at 6938 cm\textsuperscript{-1}, where the weaker \(2\nu\)-OH absorption was detected in the near-IR spectrum of the initial SSC form. No near-IR band was found in this range of the spectra of photogenerated GAC or AAT forms (Figure 3). As a result of SSC irradiation at 6938 cm\textsuperscript{-1}, GAC conformer was generated nearly exclusively, whereas production of AAT was very low (see Figure 5, right panel). This result differs considerably from the effects induced by the previous irradiation at 6954 cm\textsuperscript{-1} (Figure 5, left panel). It may suggest that SSC excited at 6954 cm\textsuperscript{-1} is mostly transformed into GAC which subsequently, upon absorption of another photon, is converted into AAT. In other words, the observations resulting from both irradiations (at 6954 and 6938 cm\textsuperscript{-1}) point to strong domination of mechanism (ii), implying GAC as the only primary product of SSC photocrystallization, over mechanism (i) where GAC and AAT would be concomitantly produced from near-IR excited SSC.

This conclusion is also supported by kinetic data; the observation of the progress of the conformational transformations induced by 6954 and 6938 cm\textsuperscript{-1} irradiations is presented in Figure 5, bottom panels. At the initial stage of the process induced by irradiation at 6954 cm\textsuperscript{-1}, photoproduction of GAC clearly dominates, whereas, at later stages, the growth of the population of GAC is significantly slower, while the amount of AAT increases almost linearly. This clearly contradicts the domination of mechanism (i). Would mechanism (i) be dominating, then the kinetics of the growth of AAT (in time of irradiation at 6954 cm\textsuperscript{-1}) should be analogous to the kinetics of the growth of GAC. Data presented in Figure 5, left panel, show that it is evidently not the case. Also, the results of irradiation at 6938 cm\textsuperscript{-1} support domination of mechanism (ii). With no photoexcitation of GAC, near-IR-induced conversion of SSC into GAC is nearly the sole observed process and dominates very strongly over generation of tiny amounts of AAT (Figure 5, right panel).

Mechanistically, transformation of SSC into GAC (and subsequently into AAT) must involve rotation of heavy-atom fragments of the molecule around the C–C bond. The fact that such reorganization occurs upon near-IR excitation of the \(2\nu\)-OH vibrations implies intramolecular redistribution of vibrational energy. The energy gained by absorption of a near-IR photon must be transferred from the initially excited OH stretching vibrations to torsions of the heavy-atom backbone of the molecule. It should be noted that this type of near-IR-induced conformational transformation was previously observed for hydroxyacetone, glyicine, and propionic acid isolated in Ar matrices.\textsuperscript{21–23}

In Ar matrices deposited within the current work, some small amounts of GAC and AAT conformers were found already before any irradiation. This indicates that a small amount of these forms was already present in the gas phase prior to matrix deposition and that they can be efficiently trapped in the low-temperature matrices without noticeable conversion (by conformational cooling)\textsuperscript{24} into the most stable SSC form. Small amounts of GAC and AAT forms in freshly deposited matrices were observed also in previous studies on GA conformers.\textsuperscript{5,5}

4.2.2. Near-IR-Induced GAC ↔ AAT Interconversion. Once GAC and AAT conformers could be successfully generated in

![Figure 5. Near-IR-induced conformational transformation of the most stable SSC form of glycolic acid into GAC and AAT products, occurring in Ar matrices upon monochromatic irradiation at 6954 cm\textsuperscript{-1} (left panel) and at 6938 cm\textsuperscript{-1} (right panel). Spectra recorded: (a) before any irradiation and (b) after 10 min, (c) after 20 min, and (d) after 30 min of irradiation. The bottom panels show the progress of the conformational transformations induced by 6954 and 6938 cm\textsuperscript{-1} radiation. Squares, the absorbance measured at 1773 cm\textsuperscript{-1}; triangles, the absorbance measured at 1783 cm\textsuperscript{-1}; asterisks, the absorbance measured at 1806 cm\textsuperscript{-1}.](Image 360x414 to 528x749)
in a series of narrowband near-IR irradiations, we were able to transform several times GAC and AAT conformers into one another, as shown in Figures S1–S3 in the Supporting Information. Interestingly, no detectable changes in the population of SSC accompanied the near-IR-induced conversions of GAC into AAT and AAT into GAC (see the difference spectra in Figure 6). This indicates that excitation of GAC or AAT to their 2ν\(\text{OH}\) overtones does not lead to transformation of these conformers to the most stable SSC form.

Argon matrices with considerable amounts of higher-energy GAC and AAT conformers (photoproduced by narrowband near-IR irradiation as described above) were kept for 10 h in the dark and at cryogenic temperatures (3.5 or 15 K). The matrixes were periodically monitored by recording their mid-IR spectra in the 1700–450 cm\(^{-1}\) range. Along these experiments, when no spectra were recorded, the spectrometer beams were completely blocked. During collection of spectra, the matrix was protected from radiation with wavenumbers higher than 1700 cm\(^{-1}\) by a long-pass filter placed between the spectrometer source and the cryostat (see Figure S4 in the Supporting Information). No detectable changes of the populations of the GAC and AAT conformers were found over the period of 10 h, neither at 3.5 K nor at 15 K. This indicates that in the low-temperature Ar matrixes the spontaneous conversion of these forms into the most stable SSC conformer is either extremely slow or does not occur at all. Also, the spontaneous conversion of AAT into GAC or GAC into AAT must be very, very slow.

As pointed out before, there is a direct pathway for the interconversion between AAT and GAC (see Figure 1d).

According to the theoretical calculations, this pathway has a high energy barrier (predicted MP2 values, depending on the direction, are 44.9 or 48.1 kJ mol\(^{-1}\), see Table 2). Moreover, tunneling through such a barrier would be significantly hindered by the necessity of concerted displacement of two hydrogen atoms (hence 2 times higher mass). This should explain a drastic difference between the very slow spontaneous GAC \(\rightarrow\) AAT or AAT \(\rightarrow\) GAC conversion and the much faster tunneling processes concerning displacement of a single hydrogen atom, which were previously observed for a number of compounds bearing OH groups.\(^{25-27}\)

On the other hand, for the GAC \(\rightarrow\) SSC transformation, the predicted barrier is less than 10 kJ mol\(^{-1}\) (see Figure 1a, Table 2). However, the GAC \(\rightarrow\) SSC conversion implies considerable displacements of oxygen atoms within the heavy-atom backbone of the molecule. This does not allow a significant role of tunneling in the case of the GAC \(\rightarrow\) SSC transformation. Note that such a transformation did not occur (\textit{vide supra}) for glycolic acid molecules excited with near-IR light providing an excess energy of 80 kJ mol\(^{-1}\). Hence, the spontaneous GAC \(\rightarrow\) SSC conversion is not supposed to occur either.

### 4.3. Near-IR-Induced and Spontaneous Transformations of Glycolic Acid Isolated in \(\text{N}_2\) Matrixes

Monomers of glycolic acid were also trapped in \(\text{N}_2\) matrixes at 15 K. Contrarily to what was observed in the case of GA in Ar matrixes, in the mid-IR spectra recorded after deposition of an \(\text{N}_2\) matrix (Figure 2), the \(\nu\text{OH}\) bands (due to the two OH groups of the dominating SSC conformer) do not overlap. They were found at well separated frequencies, 3574 and 3540 cm\(^{-1}\). Also in the 2\(\nu\text{OH}\) overtone region, two well-separated absorptions were detected at 6965 and 6909 cm\(^{-1}\) (Figure 7).

Upon near-IR irradiation at 6909 or 6965 cm\(^{-1}\), the bands in the IR spectrum of the initially most abundant SSC form decreased, whereas a new spectrum of a photogenerated species emerged. In the new spectrum, relatively strong bands were found at 3580, 1798, 1295, 1099, and 510 cm\(^{-1}\) (Figure 8). No low-intensity bands were detected in the spectrum recorded

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**Figure 6.** Near-IR-induced transformations of GAC into AAT (left panel) and of AAT into GAC (right panel): (a, black) the spectrum recorded after irradiation of GA isolated in an Ar matrix at 6954 cm\(^{-1}\); (b, red) the spectrum recorded after subsequent irradiation at 7126 cm\(^{-1}\); (c, blue) the spectrum recorded after subsequent irradiation at 7174 cm\(^{-1}\); (d) difference spectrum: trace b minus trace a; (e) difference spectrum: trace c minus trace b. We observe no change of the SSC population upon irradiations at 7126 and 7174 cm\(^{-1}\).

**Figure 7.** Fragments of the near-IR spectra of glycolic acid isolated in an \(\text{N}_2\) matrix: (a) the spectrum recorded before any irradiation; (b) the spectrum recorded after 30 min of near-IR irradiation at 6909 cm\(^{-1}\); (c) difference spectrum: trace b minus trace a, compared with (d) the anharmonic wavenumbers calculated at the DFT(B3LYP)/aug-cc-pVdz level for SSC and SST conformers.
before any irradiation at the spectral positions where these new bands appeared. This shows that the photoproduced form was not present in the freshly deposited N₂ matrix. Hence, the near-IR-generated form is, most probably, a conformer of glycolic acid with energy substantially higher than that of SSC (and higher than those of GAC and AAT). The pattern of bands in the mid-IR spectrum of the species generated upon irradiation of an N₂ matrix at 6909 or 6965 cm⁻¹ does not resemble the spectra of GAC or AAT, which were photoproduced in Ar matrices. This observation indicates that transformation of SSC into GAC or AAT, that would involve substantial displacements of heavy atoms in the backbone of the glycolic acid molecule, does not occur for the compound isolated in solid nitrogen.

The spectrum of the new photoproduction generated in solid N₂ is well reproduced by the theoretical spectrum calculated for the SST conformer of GA (Figure 9). The similarity strongly suggests that this new form of GA has the SST structure. In the 1900–400 cm⁻¹ range of the theoretical spectrum, only four bands have a calculated intensity higher than 100 km mol⁻¹ (see Tables S4 and S5, Supporting Information). Experimental counterparts of these bands were found in the spectrum of the new form appearing upon irradiation at 6909 or 6965 cm⁻¹. Theoretical intensities of all other IR bands of SST, appearing in the 1900–400 cm⁻¹ range, are very low (see Figure 9). In agreement with this prediction, no more than four bands were observed in the corresponding range of the experimental spectrum.

It was already demonstrated for several cases that nitrogen matrixes stabilize the near-IR-generated, higher-energy conformers with carboxyl groups in trans orientation around the O==C—O—H dihedral angle. Because the SSC → SST transformation occurs for SSC conformer excited at the energies of 2νOH vibration of any of its OH groups (6909 or 6965 cm⁻¹), there must exist an effective transport of vibrational energy from the excited OH alcohol group to the isomerizing OH group of the carboxyl moiety. Analogous photoproduction of SST can probably occur also for glycolic acid isolated in Ar matrixes. However, in solid Ar, where the rotation of the OH group is not hindered, unlike in a solid nitrogen environment, the SST product is, with all probability, converting spontaneously to the most stable SSC form so fast that it hardly can be detected using stationary spectroscopic techniques.

In the overtone region of the spectrum of the near-IR-generated SST, a new band was observed at 6988 cm⁻¹ (Figure 7). Irradiation of the N₂ matrixes at this wavenumber led to depopulation of SST and repopulation of SSC (Figure 8). The SST → SSC conversion occurred also spontaneously in a nitrogen matrix kept in the dark (see Figure 10) at either 3.5 or 15 K.
Scheme 1. Near-IR-Induced Conformational Transformations Observed for Glycolic Acid Isolated in Low-Temperature Ar and N₂ Matrixes

![Scheme 1](https://example.com/scheme1.png)

15 K. This process was observed for N₂ matrices where the SST form has been previously populated by near-IR excitation of SSC. The IR light of the spectrometer source was blocked over the whole experiment, except for monitoring the progress of the conversion by recording mid-IR spectra (where the 1700 cm⁻¹ long-pass filter was placed between the spectrometer source and the matrix). The barrier for the SST → SSC conversion was theoretically estimated as 30.6 kJ mol⁻¹ (see Figure 1c, Table 2), and the transformation involves only reorientation of a light particle (single hydrogen atom). Therefore, tunneling must play a crucial and rate-determining role in the spontaneous SST → SSC transformation. At both temperatures considered (3.5 and 15 K), the rate of the spontaneous SST → SSC conversion was similar, with the estimated half-lifetime of the process being 200–220 min (Figure 10).

5. CONCLUSIONS

The most stable SSC conformer of glycolic acid was trapped from the gas phase into low-temperature matrixes. Together with this most populated form, low amounts of higher-energy GAC and AAT conformers were detected in freshly deposited matrixes.

For glycolic acid isolated in Ar matrixes, GAC and AAT forms were photoproduced upon monochromatic near-IR excitation of SSC at 6954 or 6938 cm⁻¹. The experiments carried out in the present work indicate that GAC is produced directly from near-IR-excited SSC, whereas transformation of SSC into AAT occurs (at least in most part) stepwise. In the first step, SSC is photoconverted to GAC, which needs excitation with another near-IR photon to be transformed into AAT.

Upon selective near-IR excitations, the GAC and AAT higher-energy conformers were successfully transformed into one another. Transformation of GAC into AAT occurred upon excitation of GAC to any of its two 2νOH overtones. Similarly, excitation to any of the two 2νOH overtones of AAT led to transformation of this form into GAC. The GAC → AAT and AAT → GAC phototransformations were not accompanied by any discernible repopulation of the most stable SSC form.

For glycolic acid isolated in N₂ matrixes, the GAC or AAT conformers were not produced from near-IR-excited SSC. The only form photogenerated from SSC in solid nitrogen was the SST conformer, differing from its precursor just in rotation of the carboxyl OH group by 180°. Generation of SST as a sole product of near-IR excitation of GA in N₂ matrixes shows that rotation around the central C–C bond (necessary for SSC conversion into GAC and AAT) does not occur for the vibrationally excited compound isolated in a solid nitrogen environment.

The detailed study of the structural transformations observed for GA isolated in low-temperature matrices (Scheme 1) was possible thanks to selective excitation of particular conformers with monochromatic, tunable near-IR light. Two different sources of such light were applied in the current work: (i) a pulsed, nanosecond optical parametric oscillator and (ii) a continuous-wave tunable diode laser. The conformational conversions induced by near-IR light emitted by each of these sources were qualitatively the same. The only noticeable difference concerned the higher speed of the transformations induced by the light of the applied optical parametric oscillator, which was more powerful (100 mW mean power) than the diode laser used (40 mW).

ASSOCIATED CONTENT

Supporting Information

Figures S1, S2, and S3, showing the effects of the sequences of monochromatic near-IR excitations to the 2νOH overtone absorptions of SSC, GAC, and AAT conformers of glycolic acid. Figure S4, showing the transmission range of the long-pass filter used in the present work. Table S1, collecting structures and energies of all glycolic acid conformers. Tables S2 and S3, presenting optimized geometries of all glycolic acid conformers. Tables S4 and S5, presenting harmonic vibrational data for all glycolic acid conformers. Table S6, presenting anharmonic vibrational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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