Conformers of Kojic Acid and Their Near-IR-Induced Conversions: Long-Range Intramolecular Vibrational Energy Transfer

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Supporting Information

ABSTRACT: Conformational transformations were investigated for molecules of kojic acid trapped in low-temperature argon and nitrogen matrices. Two conformers, differing from each other by 120° rotation of the hydroxymethyl (−CH2OH) moiety, were found to be populated in freshly deposited matrices, prior to any irradiation. Matrices containing isolated monomers of kojic acid were irradiated with narrow-band, tunable near-infrared (near-IR) laser light. Excitations at wavenumbers corresponding to the overtone of the stretching vibration of the OH bond of the hydroxymethyl group led to conversion of one of the observed conformers into another. The direction of this conformational transformation depended on the wavenumber (within the 7126−7115 cm⁻¹ range) used for irradiation. The same conformational photoconversion was also observed to occur upon narrowband irradiation at much lower wavenumbers (from the 6468−6447 cm⁻¹ range). Near-IR light from this range selectively excites overtone vibrations of the OH group directly attached to the heterocyclic ring. Such an observation provides a convincing evidence of a long-range vibrational energy transfer from the initially excited OH group (directly attached to the ring) to the remote hydroxymethyl fragment which changes its orientation. Structural changes, occurring in matrix-isolated molecules of kojic acid upon near-IR excitation, were monitored by FTIR spectroscopy.

1. INTRODUCTION

Kojic acid is a common name for 2-(hydroxymethyl)-5-hydroxy-γ-pyrone. The wide range of its applications, starting from preventing oxidative browning of food,¹,² ending with depigmenting properties,³ makes the compound important for food and cosmetics industry. The compound in its solid state and in aqueous solutions has been studied by spectroscopic³,⁴ and crystallographic methods⁵. However, as far as we are aware, there are no reported experimental investigations on the conformational structures of kojic acid monomers, nor on their temperature-induced or light-induced conformational conversions.

Matrix isolation is an experimental technique well-suited to study the structure of conformers, conformational equilibria and conformational transformations. This method is especially powerful when combined with excitation of matrix-isolated species with narrowband, tunable near-infrared (near-IR) laser light. Upon selective near-IR excitation, molecules can change their conformation. Hence, the population ratio of conformers trapped in a matrix can be manipulated.

In the majority of cases reported so far, rotation of the hydroxyl (OH) group around the C–OH bond was induced by excitation of the 2ν-OH overtone stretching vibration of the same OH group (Scheme 1). Such conversions were observed not only for a number of compounds bearing a carboxylic COOH group⁶–¹³ but also for such species as squaric acid¹⁴ and cytosine.¹⁵ Only for a very limited number of the reported cases, the photoinduced conformational transformations concerned rotations of heavy-atom groups around a C–C bond in the α position with respect to the OH or NH₂ groups, which were vibrationally excited to the 2ν-OH or 2ν-NH₂ states (Scheme 2).⁸,¹⁶–¹⁸

Very recently, experimental evidence was found for long-range intramolecular vibrational energy redistribution from the initially excited vibration of a group of atoms to a remote (separated by several chemical bonds) fragment that changes its orientation. The first of the reported cases concerned matrix-isolated 2-thiocytosine molecules,¹⁹ where the long-range intramolecular vibrational energy transfer was detected as a change of the SH group orientation, induced by near-IR excitation of the overtone or combination vibrations of the remote NH₂...
A very convincing example of a long-distance redistribution of vibrational energy was observed for 6-methoxyindole,20 where the near-IR excitation of the N−H stretching overtone vibration resulted in a change of orientation of the remote methoxyl fragment.

In the current work, excitation with narrowband tunable near-IR laser light was used to manipulate the ratio of conformers of kojic acid isolated in low-temperature matrixes. Special attention was devoted to experimental demonstration that the change of the conformational structure of kojic acid (by 120° rotation of the hydroxymethyl moiety) occurs upon near-IR excitation of the 2νOH overtone vibration of the OH group belonging to this hydroxymethyl fragment as well as upon near-IR excitation of the 2νOH overtone vibration of the remote OH group directly attached to the γ-pyrone ring.

2. EXPERIMENTAL SECTION

The sample of kojic acid (purity 98%) used in the present study was a commercial product supplied by Sigma-Aldrich. In the matrix-isolation experiments carried out within the present work, the solid compound evaporated from a miniature glass oven heated to 370 K. The vapors of kojic acid were codeposited with a large excess of argon or nitrogen onto a CsI window, cooled to 5 or 15 K. Two types of closed-cycle refrigerators were used: APD Cryogenics DE-202A (able to cool down to 10 K) and Sumitomo SRDK-408D2 (able to cool down to 3.3 K). Mid-infrared (mid-IR) spectra were recorded with 0.5 cm−1 resolution using a Thermo Nicolet 6700 FTIR spectrometer equipped with a KBr beam splitter and MCT-B or DTGS detectors. Near-IR spectra were recorded with 1 cm−1 resolution using the same spectrometer but equipped with a CaF2 beam splitter and an MCT-B detector. Monomers of kojic acid isolated in low-temperature matrixes were irradiated with tunable, narrowband near-IR light of the idler beam generated in a Quanta-Ray MOPO-SL pulsed (pulse energy 10 mJ, fwhm 0.2 cm−1) optical parametric oscillator pumped with a pulsed Nd:YAG laser (pulse duration 10 ns, repetition rate 10 Hz).

3. COMPUTATIONAL SECTION

The relative energies of the conformers were calculated using the DFT(B3LYP),21−23 QCISD,24 and CCSD25 methods, at geometries fully optimized at the same DFT, QCISD, or CCSD levels. Cartesian coordinates optimized for two most stable forms are given in Tables S1 and S2 in the Supporting Information. The harmonic vibrational frequencies and infrared intensities were calculated at the DFT(B3LYP) level of theory. For the two lowest-energy conformers, anharmonic vibrational frequencies and infrared intensities were also calculated, using the procedures implemented in the Gaussian 09 set of programs (Tables S3 and S4 in the Supporting Information).26

The potential energy surface (PES) of kojic acid was computationally probed by carrying out a two-dimensional relaxed scan.

![Scheme 2. Near-IR-Induced Conformational Conversion by Rotation around the C−C Bond in the α Position with Respect to the Initially Excited OH Group](image_url)

![Chart 1. Numbering of Heavy Atoms in the Molecule of Kojic Acid](image_url)

![Figure 1. Two-dimensional relaxed potential energy surface calculated for the molecule of kojic acid, at the B3LYP/6-31++G(d,p) level of theory, as the function of O1−C2−C7−O8 and C2−C7−O8−H dihedral angles. Each of the dihedral angles was incremented with a step of 10° and all other geometric parameters were fully optimized. The color bar at the top designates the relative energy scale. The electronic energy of the G′g−(equivalent of G−g′) conformer was chosen as the relative zero. The color palette changes with a step of 0.5 kJ mol−1. The continuous black isoenergy lines are traced with an interval of 2 kJ mol−1. An additional (dashed) isoenergy line is added at 6.5 kJ mol−1 (to show the pair of shallow G−t and G+t minima). The white dots specify positions of the local minima. Values of the O1−C2−C7−O8 dihedral angle are designated by capital letters (G, Gauche; T, Trans), and values of the C2−C7−O8−H dihedral angle are shown by small letters (g, gauche; t, trans). Superscripts “+” and “−” (at G and g) indicate clockwise or anticlockwise Gauche (gauche) orientation. At each point of the scan, the hydrogen atom of the OH group directly attached to the ring is oriented toward the vicinal C=O fragment.](image_url)
consisting of 1296 points. For each of these points, values of two conformationally relevant dihedral angles (O1−C2−C7−O8 and C2−C7−O8−H, see Chart 1 for atom numbering) were fixed and all the remaining geometric parameters were optimized at the DFT(B3LYP)/6-31+G(d,p) level. At each partially optimized geometry, electronic energy was calculated as a function of the values of two fixed O1−C2−C7−O8 and C2−C7−O8−H dihedral angles. For both O1−C2−C7−O8 and C2−C7−O8−H dihedral angles, the performed two-dimensional scan covered, with a step of 10°, the full 0°–360° range.

One-dimensional relaxed potential energy scans were computed at the DFT(B3LYP)/6-311++G(3df,3pd) level. These scans were carried out along the O1−C2−C7−O8 or along the C2−C7−O8−H torsional coordinate. At each step, the value of the O1−C2−C7−O8 or C2−C7−O8−H dihedral angle was fixed and all remaining coordinates describing the geometry of the molecule were optimized. All quantum-mechanical computations were carried out with the Gaussian 09 program using the 6-31+G(d,p) or 6-311++G(3df,3pd) basis sets.

4. RESULTS AND DISCUSSION

4.1. Low-Energy Structures of Kojic Acid. In the molecule of kojic acid, there are three conformationally relevant degrees of freedom. One of them concerns rotation of the O10−H group directly attached to the ring. The structures with the hydroxymethyl group of this atom directed toward the C4−O9 moiety are stabilized by the intramolecular hydrogen-bond-like C4−O9−H−O10 interaction. Such conformers are substantially more stable (by more than 40 kJ mol⁻¹) than those with the O10−H group rotated by ca. 180°. The forms with the C4−O9−H−O10 interaction absent and relative energy as high as 40 kJ mol⁻¹ can be expected to have negligible populations in the gas phase. Hence, only the conformers stabilized by the intramolecular C4−O9−H−O10 interaction should be relevant to the further discussion.

Two other conformational degrees of freedom concern (i) rotation of the whole hydroxymethyl group with respect to the ring, measured by the value of the O1−C2−C7−O8 dihedral angle, and (ii) rotation of the O8−H group within the hydroxymethyl fragment, measured by the value of the C2−C7−O8−H dihedral angle. A two-dimensional relaxed scan of the potential energy surface (PES) of kojic acid has been computed at the DFT(B3LYP)/6-31+G(d,p) level, as described in the Computational Section. On the obtained potential energy map, shown in Figure 1, nine minima can be identified. In the structures corresponding to these minima (see Table 1 and Table S5 in the Supporting Information), the hydroxymethyl group adopts either the trans orientation (T, with the O1−C2−C7−O8 dihedral angle approximately equal to 180°) or one of the gauche orientations (G+ or G−, with the O1−C2−C7−O8 dihedral angle approximately equal to +60° or −60°, respectively). For each of the T, G+, and G− orientations of the hydroxymethyl group, the O8−H fragment within it can adopt either the trans orientation (t, with the C2−C7−O8−H dihedral angle approximately equal to 180°) or one of the gauche orientations (g+ or g−, with the C2−C7−O8−H dihedral angle approximately equal to +60° or −60°, respectively). Among the conformers corresponding to the minima found on the PES map shown in Figure 1, there are four pairs of structures identical by symmetry: [(G+g+ and G−g−), (G+g− and G−g+), (Tg+ and Tg−)]. Hence, there are five conformers nonidentical by symmetry: the four pairs listed above and the Tt form (see the structures presented in Table 1 and Table S5 in the Supporting Information).

The minima on the potential energy surface of kojic acid and the barriers separating them were also analyzed by carrying out one-dimensional scans computed at the DFT(B3LYP)/6-311+ +G(3df,3pd) level. In three of the scans, shown in Figure 2a, the energy was computed as a function of fixed values of the O1−C2−C7−O8 dihedral angle with conserved trans (t) or gauche (g+ or g−) orientation of the O8−H group (though the

### Table 1. Relative Electronic Energies (ΔEel/kJ mol⁻¹) of Kojic Acid Conformers Computed at Three Levels of Theory

<table>
<thead>
<tr>
<th></th>
<th>ΔEel</th>
<th>ΔE_total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg</td>
<td>172.7°</td>
<td>172.7°</td>
</tr>
<tr>
<td>G+g−</td>
<td>61.9°</td>
<td>61.9°</td>
</tr>
<tr>
<td>Tt</td>
<td>180.0°</td>
<td>180.0°</td>
</tr>
<tr>
<td>G+g+</td>
<td>64.1°</td>
<td>64.1°</td>
</tr>
<tr>
<td>G−g−</td>
<td>−165.4°</td>
<td>−165.4°</td>
</tr>
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</table>

The optimized structures are presented graphically and numerical values are given for dihedral angles defining orientation of the hydroxymethyl group. The hydrogen atoms attached to carbon atoms are not shown. The structures of other conformers Tg−, G−g−, G−g+, G−t are mirror images of structures Tg+, G+g−, G+g+, G−t presented above (see Table S5 in the Supporting Information). ΔE_total relative electronic energies corrected for zero-point vibrational energy (ΔE_total = ΔEel + ΔZPVE).
value of the C2–C7–O8–H dihedral angle was not fixed). In the scans displayed in Figure 2b, the energy was computed as a function of fixed values of the C2–C7–O8–H dihedral angle with conserved trans (T) or gauche (G− or G+) orientation of the hydroxymethyl fragment (though the value of the O1–C2–C7–O8 dihedral angle was not fixed).

Electronic energies of the conformers of kojic acid were computed using the DFT(B3LYP)/6-311++G(3df,3pd) level of theory. In three scans (panel a) the energy was computed as a function of fixed values of the O1–C2–C7–O8 dihedral angle. In three other scans (panel b) the energy was computed as a function of fixed values of the C2–C7–O8–H dihedral angle. The electronic energy of the conformer Tg− (or its mirror image Tg+) was chosen as the relative zero. At each point of the scans, the hydrogen atom of the OH group directly attached to the ring is oriented toward the vicinal C=O fragment. Structures corresponding to the minima on the scans are presented in Table 1 and in Table S5 in the Supporting Information.

Among the structures with trans (T) orientation of the hydroxymethyl group, the higher-energy Tt conformer is separated by a very low energy barrier (~1.3 kJ mol−1, Figure 2b) from the more stable form Tg− (or Tg+). Therefore, the Tt conformer is expected to convert to Tg− (or Tg+) during formation of the matrixes.

The calculated barrier for the rotation of the whole hydroxymethyl group, changing the orientation from G to T (or vice versa), is not higher than 5.6 kJ mol−1 (Figure 2a). However, its crossing in a rigid matrix (that would result in Tg− ↔ G− or G+ ↔ G+′ conversion) may be difficult. Such a transformation involves the torsional movement of a large hydroxymethyl group, which includes a heavy oxygen atom and three hydrogen atoms. Indeed, it has been previously observed that a barrier of 3.5 kJ mol−1 (related to reorientations of heavy atoms) is sufficient to trap in cryogenic matrixes minor conformers of cyanoacetic acid and methyl cyanoacetate.29–31

The performed computations suggest that only two forms of kojic acid: Tg− (or Tg+) and G− or G+ (or G+′), differing in T or G orientation of the whole hydroxymethyl group, should be present in low-temperature matrixes. The calculated energies of these two forms (Table 1) are very close to each other and the computations do not give a clear prediction which of them should be more stable. The conclusive answer to this question was obtained in the experimental work described below.

4.2. Monomers of Kojic Acid Isolated in Low-Temperature Argon and Nitrogen Matrixes. 4.2.1. Thermally-Induced Conformational Conversions; Conformational Cooling. Low-temperature Ar and N2 matrixes containing monomers of kojic acid were deposited onto a CsI substrate cooled to 15 or 5 K. Fragments of the mid-IR spectra recorded after deposition of N2 and Ar matrixes at 15 K are presented in Figure 3a,b. Comparison of these spectra with the results of the theoretical simulations (Figure 3c), carried out for conformer T (Tg− or Tg+) and for conformer G (G− or G+), shows that the most intense experimental bands have their counterparts in the spectra calculated for structure T. Alongside the experimental bands that can be ascribed to conformer T, some weaker bands [such as those at 1662, 1224, 1043, 898 cm−1 (Ar)] appear at spectral positions corresponding to the theoretical bands predicted for G. This suggests that in low-temperature Ar or N2 matrixes at 15 K, the major part of kojic acid molecules adopts structure T, whereas some minor part is trapped in form G.

The spectra of Ar matrixes recorded after deposition on CsI substrate at 5 K (Figure 4d) differ from those recorded after deposition at 15 K (Figure 4c). Dissimilarities are particularly visible in the 1250–1150 cm−1 range, where the bands at 1224 (assigned to G) and 1204 cm−1 (assigned to T) have considerably different relative intensities in the spectra of Ar matrixes deposited at 5 and 15 K. In the spectrum of the matrix deposited at 15 K, the relative intensity of the band at 1224 cm−1 (characteristic of G) is lower than that in the spectrum of the matrix deposited at 5 K. This indicates a lower relative population of G in the matrix deposited at 15 K, in comparison to that prepared with CsI substrate kept at 5 K. Spectral signatures of different relative populations of T and G, trapped in matrixes deposited at 15 or 5 K, were also observed in other regions of the spectrum, e.g., for the bands at 932 and 898 cm−1, shown in Figure 4. This observation is a clear indication of the occurrence of conformational cooling.32,33 If the freezing process

Figure 2. One-dimensional relaxed potential energy scans, calculated for the molecule of kojic acid at the DFT(B3LYP)/6-311++G(3df,3pd) level of theory. In three scans (panel a) the energy was computed as a function of fixed values of the O1–C2–C7–O8 dihedral angle. In three other scans (panel b) the energy was computed as a function of fixed values of the C2–C7–O8–H dihedral angle. The electronic energy of the conformer Tg− (or its mirror image Tg+) was chosen as the relative zero. At each point of the scans, the hydrogen atom of the OH group directly attached to the ring is oriented toward the vicinal C=O fragment. Structures corresponding to the minima on the scans are presented in Table 1 and in Table S5 in the Supporting Information.
is not very rapid (e.g., by matrix formation at 15 K), then higher-energy conformers may convert by conformational cooling to lower-energy forms. In the present case, conformational cooling shifts the population ratio of \( G \) and \( T \) from that corresponding to thermal conformational equilibrium in the gas phase at 370 K toward the cryogenic-temperature equilibrium, where the lowest-energy form should strongly dominate. Conformational cooling led to substantial effects when matrixes were prepared with the substrate at 15 K, whereas for \( \text{Ar} \) matrixes prepared at 5 or 9 K (see Figures S1 and S2 in the Supporting Information) rapid freezing results in significantly less pronounced effects of conformational cooling. Moreover, the ratios of \( T \) and \( G \) conformers trapped in \( \text{Ar} \) matrixes deposited at 5 and 9 K are virtually the same. This suggests that at temperatures as low as 5–9 K the conformational cooling can be considered negligible. Conformational cooling, similar to that observed in the current work for kojic acid, was previously reported for other compounds, such as cyanoacetic acid, methyl cyanoacetate,31 1,2-butandiol,32 and furfuryl alcohol.33

The current experimental results demonstrate that the form with the trans (\( T \)) orientation of the hydroxymethyl moiety, where the hydrogen-bond-like \( \text{O8}--\text{H}--\text{O1} \) interaction is absent, has a lower energy than the form with the gauche (\( G \)) orientation of this group, which might be stabilized by the \( \text{O8}--\text{H}--\text{O1} \) interaction. Moreover, the crystal structure examinations, carried out by Lokaj et al., resulted in identification of structure \( T \) of kojic acid as the main conformation adopted by molecules of kojic acid in the crystalline state.

Thermal conformational transformations in matrix-isolated monomers of kojic acid were also induced by annealing of \( \text{Ar} \) or \( \text{N}_2 \) matrixes. In these experiments, matrixes were deposited at 5 K, and then the temperature of the CsI substrate was gradually increased up to 25 K. Upon an increase of temperature, the population of the less stable form \( G \) was diminishing, while the population of the more stable form \( T \) was growing (Figure 5). The observation of the thermally induced \( G \rightarrow T \) conversion provides a further proof that \( G \) has higher energy than \( T \).

4.2.2. Near-IR-Induced Conformational Conversions; Long Range Vibrational Energy Transfer. The spectra of kojic acid isolated in low-temperature \( \text{Ar} \) matrixes were also recorded in the near-IR range. In the 7500–6000 cm\(^{-1}\) spectral region, two absorptions were detected. A sharp band at 7119 cm\(^{-1}\) (Figure 6c) should be assigned to the \( 2\nu\text{OH} \) stretching vibration of the \( \text{O8}--\text{H}--\text{O1} \) group in the hydroxymethyl fragment, whereas the broad band at 6490–6430 cm\(^{-1}\) should be due to the \( 2\nu\text{OH} \) stretching vibration of the \( \text{O10}--\text{H} \) group directly attached to the ring. These two near-IR bands are due to...
ovetone transitions corresponding to the fundamental $\nu$OH bands observed at 3646 and 3377 cm$^{-1}$ (Figure 6b). The 2$\nu$OH and $\nu$OH bands at 7119 and 3646 cm$^{-1}$ appear at spectral positions typical of overtone and fundamental transitions due to stretching O—H vibrations in hydroxymethyl groups not involved in intramolecular hydrogen-bond-like interactions.5 Much lower wavenumbers and broadening of the 2$\nu$OH and $\nu$OH bands at 6490—6430 and 3377 cm$^{-1}$ are the spectral indications of the involvement of the other O10—H group (directly attached to the ring) in the intramolecular interaction with the vicinal C4==O9 fragment.11

Monomers of kojic acid isolated in Ar matrices were irradiated with monochromatic near-IR light at 7119 cm$^{-1}$. Upon such irradiation, the bands due to the most populated form T decreased in intensity, whereas intensities of the bands due to the G conformer increased (Figure 7a). The correctness of the assignment of structures T and G to the conformers of kojic acid, which populations decreased and increased, respectively, upon irradiation at 7119 cm$^{-1}$, is confirmed by the comparison of the experimental difference spectrum with the spectra theoretically predicted for T and for G (Figure 7ac). See also the agreement between the separated experimental spectra of T and G and the theoretical spectra predicted for these conformers presented in Figures S4 and S5 and in Table S6 in the Supporting Information.

Figure 5. Fragments of mid-IR spectra of kojic acid isolated in argon and nitrogen matrices: (a) recorded after deposition at 5 K, (b)–(d) subsequently recorded after matrix annealing up to 25 K (for an Ar matrix) and up to 21 K (for an N$_2$ matrix). The spectra theoretically computed for two lowest-energy conformers T (Tg$^-$ or Tg$^+$) and G (G$^g$ or G$^g'$) are presented in (e). Calculations were carried out within the harmonic approximation at the DFT(B3LYP)/6-31+G(d,p) level. The theoretical wavenumbers were scaled by a single factor of 0.98.

Argon matrices containing monomers of kojic acid were also irradiated at various wavenumbers within the profile of the absorption band with peak intensity at 7119 cm$^{-1}$ (Figures 7 and 8). After each such irradiation, the changes in the relative populations of forms T and G were monitored by recording an FTIR spectrum. Irradiation at 7123 cm$^{-1}$ resulted in a decreasing G population accompanied by increasing T population (Figure 7b). Hence, the direction of the conversion (G $\rightarrow$ T) induced by excitation at 7123 cm$^{-1}$ was opposite to the direction (T $\rightarrow$ G) of the conformational transformation induced by excitation at 7119 cm$^{-1}$ (Figures 7 and 8). This result is in agreement with the higher wavenumber theoretically predicted for the 2$\nu$OH overtone band in the spectrum of G, in comparison to the spectral position calculated for the 2$\nu$OH overtone band in the spectrum of T (Figure 6d).

Monomers of kojic acid isolated in Ar matrices were also excited at wavenumbers from the 6490—6430 cm$^{-1}$ range. Such irradiations should excite the 2$\nu$OH overtone stretching vibration of the O10—H group directly attached to the ring. Excitation at 6467 cm$^{-1}$ resulted in a decrease of the mid-IR bands of conformer T accompanied by increase of the bands due to conformer G (Figure 9b). Upon this irradiation no new bands, which might indicate generation of other conformers of kojic acid, appeared in the mid-IR and near-IR spectrum (Figure S6 in the Supporting Information). The changes in the mid-IR spectrum induced by irradiation at 6467 cm$^{-1}$ were the same as those induced by exposure of the matrix to the near-IR light with wavenumber 7119 cm$^{-1}$ (Figure 9a). The experimental observation of the (T $\rightarrow$ G) conformational conversion, occurring upon excitation with monochromatic 6467 cm$^{-1}$ near-IR light, provides a clear proof of long-range
vibrational energy transfer from the initially excited 2νO10H stretching vibration of the O10−H group directly attached to the ring to the remote hydroxymethyl fragment that undergoes internal rotation by ca. 120°.

Near-IR excitations of monomers of kojic acid isolated in N2 matrices resulted only in extremely small changes in relative populations of T and G conformers of the compound. Evidently, a more interacting solid nitrogen environment hinders near-IR-induced rotations of molecular fragments, such as the hydroxymethyl group. An analogous effect was observed in the previous study of near-IR induced conformational transformations in glycolic acid.

Figure 6. Fragments of mid-IR (b) and near-IR (c) spectra of kojic acid isolated in an argon matrix, compared with the theoretical spectra (a, d) obtained in anharmonic calculations carried out at the DFT(B3LYP)/6-31+G(d,p) level for two lowest-energy T (Tg− or Tg+) and G (Gg− or Gg+) conformers of the compound.

5. CONCLUSIONS

Structures of conformers and conformational transformations were investigated for monomers of kojic acid isolated in solid argon or solid nitrogen. The two lowest energy forms (T and G) of the compound, differing by 120° rotation of the hydroxymethyl (−CH2OH) group, were trapped from the gas phase into the low-temperature matrices. In matrices deposited at 15 K, the relative population of the G conformer was significantly lower than in matrices deposited at 5 K. This demonstrates that a temperature-induced conformational transformation of form G into form T occurred during deposition of Ar and N2 matrices at 15 K. Temperature-induced transformation of form G into conformer T was also observed for Ar and N2 matrices deposited at 5 K and then annealed up to 25 K. The G → T direction of the conformational changes, occurring by virtue of conformational cooling or by matrix annealing, provides an experimental evidence that structure T is the lowest-energy conformer of kojic acid.

Changes of conformational structure, transforming form G into T or vice versa, were also induced by selective excitation of kojic acid monomers isolated in solid Ar with narrowband near-IR laser light (Scheme 3). It has been experimentally verified that the conformational transformations are induced by narrowband laser radiation and not by exposure to the spectrometer beam during collection of the spectra (Figure S7 in the Supporting Information). Narrowband irradiations at wavenumbers corresponding to the 2νOH overtone excitation of the OH group belonging to the hydroxymethyl (−CH2OH) moiety resulted in changes of the conformational structure. These near-IR-induced conformational transformations were photoreversible: upon excitation at 7119 cm−1 form T converted into G, whereas upon excitation at 7123 cm−1 form G converted into T. It is worth mentioning that such T → G or G → T structural changes induced by irradiation at 7119 and 7123 cm−1 require an intramolecular vibrational energy transfer from the initially excited 2νO8H stretching vibration to the torsional movement around the C2−C7 bond.

Furthermore, a conformational transformation converting T into G was induced by irradiation at 6467 cm−1. Near-IR light with this wavenumber should excite the 2νO10H overtone vibration of the O10−H group directly attached to the γ-pyrone

Scheme 3. Conformational Transformation Induced in Isolated Molecules of Kojic Acid by Irradiations with Narrowband near-IR Light

Near-IR selective excitations of the overtone stretching vibrations of any of the OH groups (that belonging to the hydroxymethyl group or that directly attached to the ring) resulted in the conformational transformation.
The large difference between the spectral positions of the 2\(\nu_{\text{OH}}\) overtone transitions of the O8\(\cdot\)H and O10\(\cdot\)H hydroxyl groups (7119 and 6467 cm\(^{-1}\), respectively, Figure 6) leaves no doubt that irradiation at 6467 cm\(^{-1}\) excites just the 2\(\nu_{\text{OH}}\) overtone stretching vibration of the O10\(\cdot\)H group. The occurrence of the T \(\rightarrow\) G structural change upon irradiation at 6467 cm\(^{-1}\) requires an intramolecular vibrational energy transfer for a very long distance, from the initially excited 2\(\nu_{\text{OH}}\) overtone stretching vibration of the O10\(\cdot\)H group to the torsional motion around the C2\(\rightarrow\)C7 bond, located at the remote, opposite side of the molecule. Experimental observation of the T \(\rightarrow\) G conformational conversion occurring upon irradiation at 6467 cm\(^{-1}\) provides a direct proof of long-range intramolecular vibrational energy redistribution in monomers of kojic acid.

So far, only two examples of a long-range intramolecular vibrational energy transfer were reported. These very recent observations concern reorientation of the SH group in 2-thiocytosine induced by near-IR excitation of the remote NH\(_2\) fragment\(^{19}\) and reorientation of the methoxyl group in 6-methoxyindole\(^{20}\) induced by excitation of the distant N\(\rightarrow\)H moiety. The results obtained in the present work for monomers of kojic acid confirm that mechanisms of long-range vibrational energy transfer, from a fragment initially excited by absorption of a near-IR photon to a remote group that changes its orientation, are operational in molecules of various structures. A theoretical model, which would prove its adequacy by correct predictions of long-range vibrational energy redistribution, is still not available. The reports on experimental observations of long-range vibrational energy transfer suggest that it may be possible to proceed with further computational studies in order to confirm the adequacy of the theoretical model of long-range vibrational energy transfer.
transfer (current work and refs 19 and 20) challenge the theoreticians to create such a model.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b01275.

Figures S1 and S2, showing the mid-IR spectra of kojic acid isolated in Ar matrixes deposited at 15, 9, and 5 K; Figure S3, presenting the mid-IR spectra of kojic acid isolated in N2 matrixes deposited at 15 and 5 K; Figures S4 and S5, showing the comparison of separated spectra of conformers T and G with the spectra theoretically predicted; Figure S6 demonstrating that no conformers other than T and G are involved in the transformation induced by irradiation at 6467 cm−1; Figure S7, showing the changes in the mid-IR spectra of kojic acid induced by annealing of an Ar matrix and by near-IR irradiation. Chart S1, showing the atom numbering. Tables S1 and S2 with Cartesian coordinates for conformers G and T optimized at different levels of theory; Tables S3 and S4 with harmonic and anharmonic infrared spectra of forms G and T calculated at the DFT(B3LYP)/6-31++G(d,p) level; Table S5 showing structures of nine conformers of kojic acid optimized at the QCISD/6-31++G(d,p) level; Table S6 with band positions of the IR absorptions of kojic acid optimized at the QCISD/6-31++G(d,p) level; Table S7 showing structures of nine conformers of kojic acid isolated in N2 matrixes deposited at 15, 9, and 5 K; Figures S8 and S9, presenting the mid-IR spectra of kojic acid isolated in Ar matrixes deposited at 15 K with monochromatic near-IR light at 7119 and 6467 cm−1. The experimental spectra are compared with the theoretical spectra of conformers G (Gg+ or Gg−, presented as positive bands) and T (Tg+ or Tg−, presented as negative bands). Calculations were carried out within the harmonic approximation at the DFT(B3LYP)/6-31+G(d,p) level. The theoretical wavenumbers were scaled by a single factor of 0.98. The two strongest bands in the experimental spectra were truncated.

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REFERENCES


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(9) Halasa, A.; Lapinski, L.; Rostkowski, H.; Reva, I.; Nowak, M. J.

(10) Mačkas, E. M. S.; Fausto, R.; Pettersson, M.; Khriachtchev, L.; Räsänen, M.

(11) Reva, I.; Nunes, C. M.; Biczysko, M.; Fausto, R.

(12) Gerbig, D.; Schreiner, P. R.

(13) Olbert-Majkut, A.; Lundell, J.; Wierzejewska, M.

(14) Lapinski, L.; Reva, I.; Rostkowski, H.; Fausto, R.; Nowak, M. J.

(15) Lapinski, L.; Nowak, M. J.; Reva, I.; Rostkowski, H.; Fausto, R.

(16) Bazso, G.; Magyarfalvi, G.; Tarczy, G.

(17) Sharma, A.; Reva, I.; Fausto, R.

(18) Mačkas, E. M. S.; Khriachtchev, L.; Pettersson, M.; Fausto, R.; Räsänen, M.

(19) Halasa, A.; Lapinski, L.; Rostkowski, H.; Nowak, M. J.

(20) Lopes Jesus, A. J.; Reva, I. D.; Araujo-Andrade, C.; Fausto, R.

(21) Becke, A. D.

(22) Lee, C. T.; Yang, W. T.; Parr, R. G.

(23) Vosko, S. H.; Wilk, L.; Nussair, M.

(24) Pople, J. A.; Head-Gordon, M.; Raghavachari, K.

(25) Purvis, G. D., III; Bartlett, R. J.

Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(27) Benderskii, V. A.; Goldanskii, V. I.; Jortner, J., Eds.

(28) Miyazaki, T., Ed.

(29) Reva, I. D.; Stepanian, S. G.; Adamowicz, L.; Fausto, R.