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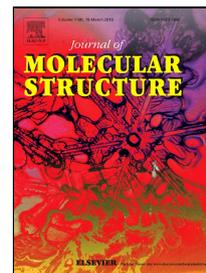
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Raman spectroscopy of glycolic acid complexes with N₂

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Abstract

High overtone excitation induced conformational isomerization of glycolic acid – nitrogen complex in an argon matrix was investigated by Raman spectroscopy. The interaction between glycolic acid and nitrogen change the green light (532 nm) induced isomerization processes compared to non-complexed glycolic acid. The 180 degree rotation around of the C-C bond and stabilization of carboxyl O=C-O-H dihedral angle to *trans* position were the main conformational changes observed in the complex of the lowest energy conformer and nitrogen. Interestingly, only one stable light-induced conformational product was observed, which isomerises back to the lowest energy conformer upon prolonged irradiation at 532 nm. The vibrational Raman spectrum of glycolic acid – nitrogen complex and the analysis of the isomerization kinetics are presented.

Keywords: Matrix isolation; Raman spectroscopy; High overtone excitation; isomerization; molecular complex

Introduction

High overtone excitations are considered vibrational transitions where molecular vibrational modes are excited to high vibrational states on their ground electronic potential energy surface. An interesting focus area of high overtone excitations are the transitions where the O-H stretching modes are excited to states with a vibrational quantum number of 3-6. These

transitions can be initiated by direct single photon absorption with photon energies ranging from near-infrared to visible light. Even though many atmospheric reactions are initiated by electronic excitations of molecules, the high overtone excitations with much weaker absorption cross-sections can play important role in atmospheric chemistry in certain conditions when high energy, i.e. ultraviolet, photons are lacking or the electronic states are not accessible.[1,2] The laboratory experiment can expand our understanding how the intramolecular vibrational energy redistribution [3] takes place in molecules after high overtone excitation and what kind of chemistry it may result to.

Glycolic acid, a smallest α -hydroxy acid, is a good prototype molecule to investigate high overtone induced chemistry of small organic molecules. Two functional OH groups, alcohol and carboxyl, provide two different channels to access high overtone states of the O-H stretching vibrations in the molecule. Moreover, the high overtone transitions of the O-H stretching vibrations typically possess larger cross-section than the C—H, S—H, and N—H stretching vibrations.[4–6] Thus, the high overtone excitations are more easily accessible for the O-H stretching modes. The vibrational fundamental and the first overtone excitation induced isomerization of glycolic acid has been investigated in argon and nitrogen matrices.[7–9] Three different structural conformers of glycolic acid has been found to be stable in an argon matrix after near-infrared excitation induced isomerization reactions, and the fourth conformer have only been found in a nitrogen matrix, where the first overtone excitation yields completely different products than in an argon matrix.[9] The experimentally observed conformers and their observed overtone excitation induced reaction paths are shown in Figure 1.

Recently, we have shown that the high overtone induced isomerization of glycolic acid in an argon matrix [10] follows different pathways than the isomerization initiated by the first overtone excitations [9]. The same isomerization products can be obtained in an argon matrix by both excitation approaches, but near-infrared excitation yields completely different isomerization reactions in a nitrogen matrix.[9,10] The appearance of the SST conformer only in a nitrogen matrix [9] has been proposed to happen because of stabilization of carboxyl O=C-O-H angle to *trans* position [11–15] and slower tunneling reaction[11–13] back to the *cis* position. These observations demonstrate how interaction with surrounding environment can affect the intramolecular vibrational energy distribution of overtone excited molecules, and hence different products can appear depending on the nature of surrounding environment.

In the present investigation, we have used a visible light excitation combined with matrix isolation Raman spectroscopy to study high overtone induced conformational isomerization processes of glycolic acid in an argon matrix when nitrogen molecules are brought in the close vicinity of glycolic acid. The method of high overtone excitations combined with the matrix isolation Raman spectroscopy has been successfully used to investigate high overtone and combination mode excitation induced isomerization and chemistry of matrix isolated carboxylic acids.[10,16–18] Here, the presence of molecular nitrogen affects the glycolic acid conformational isomerization processes by directing the conformational interconversion and its rate.

Experimental

Commercially available glycolic acid (Sigma-Aldrich, Reagent Plus®, 99 %) was used in the present study. Atmospheric gases including water were removed from the acid in a high vacuum line. The matrix samples were prepared by passing high purity mixture of nitrogen (Aga, Scientific Nitrogen, 6.0) and argon (Aga, Scientific Argon 6.0 B) gases over solid glycolic acid. The relative amounts of nitrogen and argon in the gas mixture were controlled by partial pressures using capacitance manometers (MKS Baratron). The relatively low vapor pressure of glycolic acid was increased by heating solid substance to ca. 30 – 44 °C. The gas flow was controlled by a needle valve (Leybold, Typ: EV 016 DOS AV). Typical flow rate for gas was below 0.8 mmol/min and the total amount of deposited gas was 10 – 15 mmol. The gas mixture was deposited onto ca. 200 µm thick sapphire substrate kept at 15 – 22 K in a closed cycle helium cryostat (APD Cryogenic DE 202A) equipped with MgF₂ windows. The cryostat was equipped with a silicon diode thermometer and a resistive heater, which were controlled with a temperature controller (LakeShore 330). All measurements were performed at 10 K.

A back-scattering Raman spectroscopy setup was used to record the Raman spectra as described in Ref. [17]. A solid-state diode pumped laser (Verdi, Coherent) with the operating wavelength of 532 nm was used as an excitation light source. Laser power up to 400 mW at the sample was used. An achromatic lens with 12 cm focal length was used to focus the excitation laser on a sample and to collect scattered light from a sample. The Rayleigh scattering was attenuated with an ultrasteep long-pass edge filter (Semrock, RazorEdge®). An achromatic lens with 15 cm focal length was used to collect Raman scattering to spectrograph's

slit. Typical slit width in the experiments was 50 μm . A 50 cm focal length spectrograph (Action Research Corporation, Spectra Pro 2500i) equipped with 600 grooves/mm ruled grating was used to disperse the Raman scattering. The Raman spectra were recorded with a CCD camera (Andor Technology, Newton) mounted on the spectrograph.

Results and discussion

Figure 2 shows the Raman spectrum of the C=O and the O-H stretching regions of glycolic acid in argon and nitrogen-argon ($\text{N}_2/\text{Ar} \approx 1/1000$) matrices. The observed bands of the SSC conformer of glycolic acid in an argon matrix appear at 3566 cm^{-1} and 1777 cm^{-1} for the O-H and the C=O stretching vibrations.[10] Adding nitrogen to the matrix yield a blue shift of the bands in the O-H and the C=O stretching regions. New bands appear at 3545, 3554 and 3562 cm^{-1} for the O-H stretching vibrations and at 1775 cm^{-1} for the C=O stretching vibrations in a nitrogen-argon matrix. The absence of the glycolic acid monomer bands in the O-H stretching region in a mixed nitrogen-argon matrix is a strong evidence of the complex formation between glycolic acid and nitrogen.

The appearance of three bands in the O-H stretching region might partly be explained by divergence of the O-H stretching vibrations of the carboxyl and alcohol OH groups due to the complexation. In the case of the 1:1 complex between glycolic acid and nitrogen, either the carboxyl or the alcohol O-H chromophore is the most probable site for nitrogen molecule. Thus, different shifts in the vibrational wavenumbers is expected for the two O-H chromophores. The appearance of the third O-H band could originate from a different trapping site or from a complex with more than one nitrogen molecules interacting with the carboxylic acid. However, the spectral resolution in the present experiments is too low to scrutinize the complex band structure in the O-H stretching region. The sample was annealed to 33 K after deposition without significant change in the O-H band structure, so all the trapping sites are substantially stable. The observed band with a blue-shifted shoulder at 1775 cm^{-1} supports the existence of different trapping sites of the complex structures.

Irradiation of glycolic acid in a mixed nitrogen-argon matrix by visible light (532 nm) decrease the intensity of the bands observed prior to the irradiation while new bands appear at 3474, 3480, 3486, 3567, 3669 and 3673 (shoulder) cm^{-1} in the O-H stretching region and at 1787 and 1810 cm^{-1} in the C=O stretching region. Similarly, the bands of the most stable conformer SSC

conformer found after deposition in an argon matrix decrease and the bands of the GAC and AAT conformers appear upon irradiation at 532 nm.[10] Annealing the nitrogen-argon matrix to 33 K after the irradiation (Figure 3) decrease in the intensity at 3480, 3567 and 3673 cm^{-1} , and the band at 3487 cm^{-1} blue-shifted *ca.* 1 cm^{-1} . The intensity of the bands at 3474 and 3669 cm^{-1} and the broader band at 3550 cm^{-1} increase upon annealing. Other changes in the band structures in the O-H stretching region were minor. Simultaneously, the decrease in the intensity was observed in the C=O stretching region at 1777 and 1787 cm^{-1} . The bands at 1770 and 1810 cm^{-1} are found to become slightly narrower and to gain intensity upon annealing.

According to their annealing behavior, it is plausible that the bands at 3480, 3567 and 3673 cm^{-1} in the O-H stretching region are due to unstable or unrelaxed photoproducts. It can be assumed that the observed bands of the unstable or unrelaxed photoproducts overlap in the C=O stretching region. For example, the peak at 1777 cm^{-1} appears after deposition and decreases upon irradiation and subsequent annealing. Thus, it is evident that the bands of a precursor and a product overlap at 1777 cm^{-1} . Similarly, the stable and unstable photoproducts overlap at 1787 cm^{-1} . After annealing the most stable observed bands appear at 1775, 1787, 1810, 3474, 3486, 3545, 3554, 3562 and 3669 cm^{-1} .

The three bands observed in the C=O stretching region resemble the band pattern of the monomeric glycolic acid in an argon matrix.[10] The band at 1775 cm^{-1} is blue-shifted 2 cm^{-1} from the monomer band of the SSC conformer at 1777 cm^{-1} and the bands at 1787 and 1810 cm^{-1} appear close to wavenumbers of the bands of the GAC and AAT conformers at 1788 and 1810 cm^{-1} in argon matrix, respectively. Thus, tentatively these bands at 1775, 1787 and 1810 cm^{-1} are assigned to the SSC \cdots N₂, GAC \cdots N₂ and AAT \cdots N₂ complexes, respectively. However, there is no clear evidence of the GAC \cdots N₂ complex in the O-H stretching region. The observed bands of the GAC conformer in an argon matrix appear at 3568 and 3652 cm^{-1} , but only one stable photoproduct band was observed in nitrogen-argon matrix at 3669 cm^{-1} . All stable bands between 3540 and 3570 cm^{-1} seem to belong to the precursor species. This leads to an assumption that only one type of photoproduct appear in the O-H stretching region of the Raman spectrum. Two bands at 3474 and 3486 cm^{-1} in nitrogen-argon matrix appear close to the position of the carboxyl O-H stretching of the AAT conformer in argon matrix. Two carboxyl O-H stretching bands could possibly arise from different complex structures of glycolic acid nitrogen-complex. If only one stable photoproduct would exist in nitrogen-argon matrix, it would mean that the high overtone excitation induced isomerization of glycolic acid

is greatly influenced by the interaction with nitrogen. Further analysis is therefore needed for better understanding of the spectral observations.

A spectral simulation was used to separate different peaks from the band structures for more detailed kinetic analysis. Lorentzian functions were successfully used to simulate experimental spectra. Figure 4 shows the result of the fit of Lorentzian functions to the experimental spectrum in the O-H stretching region. Altogether, nine Raman-observed peaks in the O-H stretching region and four peaks in the C=O stretching region were identified to be involved in the high overtone induced processes. These Raman-induced peaks are collected in Table 1.

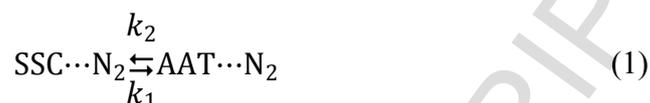
The kinetic curves of each peak in the C=O and the O-H stretching region were obtained by the spectral simulation of the entire data set. Figure 5 shows the decay and growth curves of the peaks, which were divided into three categories according to their behavior upon irradiation and subsequent annealing. The peaks originating from precursors, which appeared after deposition of the matrix formed the first category. Interestingly, they did not show the same kinetics. The peak at 3553 cm^{-1} show faster and the peak at 1777 cm^{-1} slower decay than the remaining peaks in this category. The slower kinetic of the 1777 cm^{-1} peak might be explained by the overlap of the peaks of precursor and unstable photoproduct.

The second category of peaks identified are the unstable photoproducts, which show monotonic growth during irradiation but which disappear almost completely upon subsequent annealing. An acceptable simulation result was only obtained for the strongest peak in this category at 3672 cm^{-1} , while the other peaks were too weak to yield reliable result in simulations. The growth curve of the 3672 cm^{-1} was qualitatively similar to the ones found in the third category. This third category consists of stable photoproducts and the growth curves show very similar trends for all peaks. The simulated Raman spectra of each category is shown in Figure 6.

At this point, the existence of a stable $\text{GAC}\cdots\text{N}_2$ photoproduct is becoming unlikely. The band pattern of the stable photoproducts resemble more the Raman spectrum of the AAT conformer in the O-H stretching region. Two peaks separated by *ca.* 13 cm^{-1} in the carboxyl O-H stretching region of the AAT could originate from the different interactions geometries between the carboxyl O-H group and nitrogen. However, this does not explain the two peaks with even larger separation (23 cm^{-1}) in the C=O stretching region.

The relative abundance of the SSC conformer is *ca.* 95 % at room temperature[19], so it is supposed to be the most abundant conformer in the spectrum after deposition. Thus, we assign all peaks, which show decay upon irradiation to $\text{SSC}\cdots\text{N}_2$ complexes. The general trend of the

decay and the growth curves suggest equilibrium between the precursors and photoproducts upon 532 nm irradiation. Recently, we have shown visible light induced equilibrium reactions $\text{SSC} \rightleftharpoons \text{GAC}$ and $\text{SSC} \rightleftharpoons \text{AAT}$ upon irradiation of glycolic acid in an argon matrix at 532 nm.[10] As the existence $\text{GAC} \cdots \text{N}_2$ in the present investigation seem to be uncertain, the photo-induced processes are bound to happen between $\text{SSC} \cdots \text{N}_2$ and $\text{AAT} \cdots \text{N}_2$. This can be written with rate constants as follows:



where k_i ($i = 1, 2$) is reaction (isomerization) rate constant. Reactions in equation (1) are unimolecular isomerization reactions, so the rate law can be written as

$$\frac{d[\text{SSC} \cdots \text{N}_2]}{dt} = -k_1[\text{SSC} \cdots \text{N}_2] + k_2[\text{AAT} \cdots \text{N}_2] \quad (2)$$

$$\frac{d[\text{AAT} \cdots \text{N}_2]}{dt} = -k_2[\text{AAT} \cdots \text{N}_2] + k_1[\text{SSC} \cdots \text{N}_2] \quad (3)$$

Analytical solutions for the kinetic equations were obtained by Mathematica software[20] and the resulting functions were then fitted to experimental decay and growth curves. An example of the fit of the model is shown in Figure 7. The peaks at 1774 ($\text{SSC} \cdots \text{N}_2$) and 3669 ($\text{AAT} \cdots \text{N}_2$) cm^{-1} were chosen to represent the irradiation kinetics (see Figure 7). The obtained rate constants are $k_1 = 0.0026$ 1/min and $k_2 = 0.0014$ 1/min. Similarly, a good fit result was obtained when the band position at 1810 cm^{-1} was chosen to represent the growth of the photoproduct. The decay kinetics of the Raman intensity of the 3545 cm^{-1} peak match very well with the growth of the intensity of the peaks at 1810 and 3669 cm^{-1} . Thus, the peaks at 1774 and 3545 cm^{-1} belong to the same species as do the peaks at 1810 and 3669 cm^{-1} belong to the same photoproduct. We could not fit the kinetic data of the remaining peaks with the same accuracy, because of weaker intensity of the peaks or their strong overlapping with each other. However, according to their similar behavior it is possible to assign all peaks which appeared after deposition to $\text{SSC} \cdots \text{N}_2$ in different trapping sites or with different number of complexed nitrogen molecules. The same trend in the growth of the photoproducts leads us to believe that only one type of stable photoproduct, namely $\text{AAT} \cdots \text{N}_2$, exist in the present experiment. The origin of the peak at 1787 cm^{-1} is still unclear. The present experimental data does not give full explanation for the appearance of the peak. We hope that forthcoming

experimental and computational experiments will shed more light on the problem and that a solid assignment can be done in near future.

Conclusions

Matrix isolation Raman spectroscopy has been employed to study glycolic acid complexed with a nitrogen molecule in an argon matrix. The presence of molecular nitrogen affects the glycolic acid conformational isomerization processes by directing the conformational interconversion and its rate. Experimental findings indicate that in the experimental conditions used, the glycolic acid is complexed with one nitrogen molecule. However, a minor amount of complexes with two nitrogen molecules is found, as well as higher-energy unstable site structures of the 1:1 complexes.

High overtone induced visible light (532 nm) processes have been observed during the experiments, and they can be connected with conformational isomerization of glycolic acid in their nitrogen complexed entities. The disappearance of the most stable SSC conformer is analogous with the previous experiments of isolated glycolic acid in solid argon matrix.[10] On the contrary, for glycolic acid – nitrogen complexes only AAT-N₂ complexes were found after irradiation, whereas for isolated glycolic acid both GAC and AAT conformers were present. Moreover, there was no evidence for the production of SST-N₂ in analogous to the photoinduced reactions of glycolic acid in solid nitrogen matrix.[9] A kinetic model developed is able to explain the experimental findings by identifying the most likely photolysis process to be SSC-N₂ → AAT-N₂ in an argon matrix upon high overtone excitation of the precursor OH stretching modes.

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Table 1. The observed Raman peaks obtained by spectral simulation of the C=O and O-H stretching region of glycolic acid in a nitrogen-argon matrix.

Monomer[10]	Conformer	Complex	Conformer/Complex
3675	AAT	3672 ^u 3669	AAT...N ₂ AAT...N ₂
3652	GAC		
3568	GAC		
3566/3566*	SSC/SSC	3567 ^u 3562 3554 3545 3487 ^u /3486 3479 ^u	SSC...N ₂ SSC...N ₂ SSC...N ₂ AAT...N ₂ AAT...N ₂
3473	AAT	3473	AAT...N ₂
1810	AAT	1810	AAT...N ₂
1788	GAC	1787 1777	SSC...N ₂
1777	SSC	1774	SSC...N ₂

u stands for unstable site identified upon annealing the irradiated matrix.

* Two O-H stretching vibrations of the SSC conformer are degenerate in argon matrix.

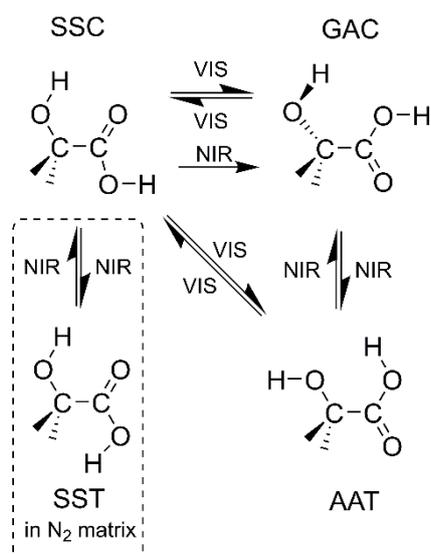


Figure 1. Visible [10] and near-infrared [9] light induced conformational isomerization processes observed for glycolic acid conformers in low temperature argon and nitrogen matrices. The conformer abbreviations are according to Halasa et al.[9] In the SSC, GAC, AAT, and SST symbolic names, S, G, A, C, and T stand for *syn*, *gauche*, *anti*, *cis*, and *trans*, respectively. The first letter describes the orientation of the H-O alcohol group (*syn*, *anti*, or *gauche*, around the H-O-C-C torsional angle); the second letter describes the *syn* or *anti* orientation of the alcohol and carboxyl groups, around the O-C-C=O torsional angle); the third letter describes the orientation of the H-O carboxyl group (*cis* or *trans*, around the O=C-O-H torsional angle).

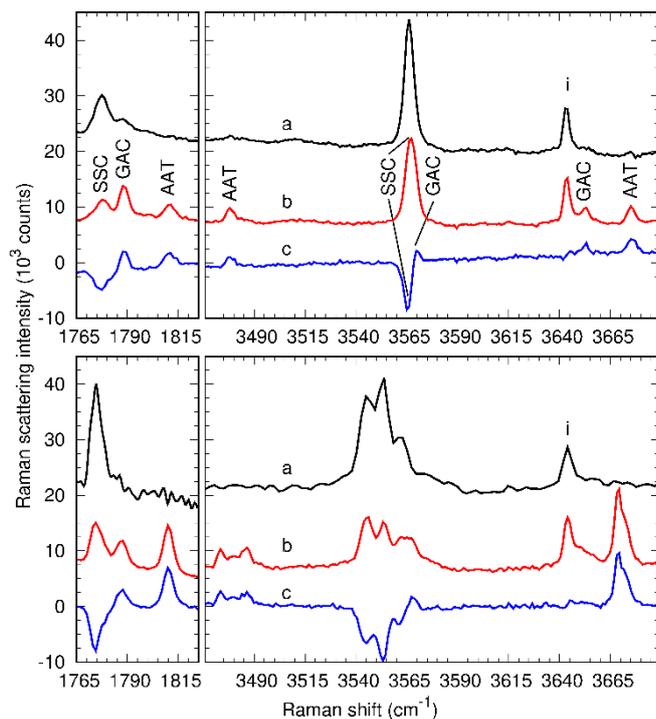


Figure 2. The Raman spectra of the C=O and OH stretching regions of glycolic acid in an argon (upper frames) and in a nitrogen-argon ($N_2/Ar = 1/1000$) matrix (lower frames). a) Before irradiation; b) After irradiation at 532 nm; c) Difference spectrum (b-a). The Raman bands of the SSC, GAC and AAT monomers in argon matrix are labelled in the upper spectra. An impurity band is labelled with i.

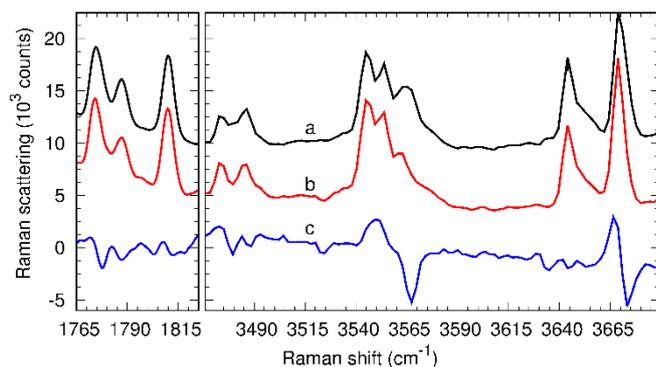


Figure 3. Raman spectrum of the C=O and the O-H stretching regions of irradiated (532 nm) glycolic acid in mixed nitrogen-argon matrix. a) After irradiation, b) after annealing at 33 K and c) difference spectrum (b – a) multiplied by 2.

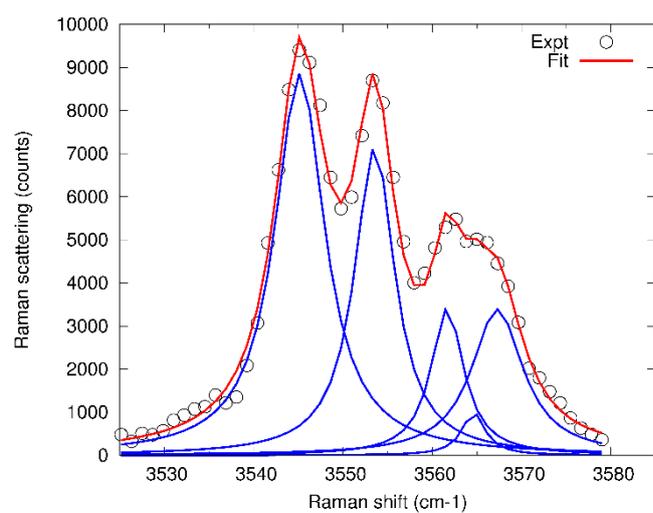


Figure 4. The fit of Lorentzian functions to the experimental Raman spectrum of glycolic acid in nitrogen-argon matrix.

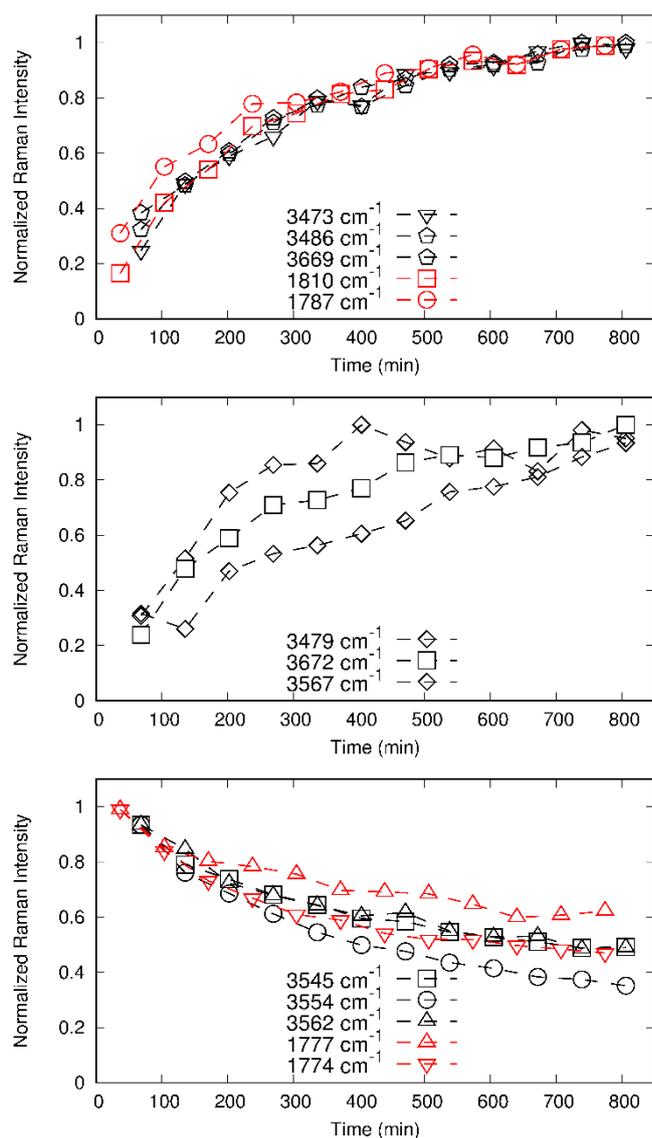


Figure 5. The normalized Raman scattering peak intensities in the C=O and O-H stretching regions upon irradiation at 532 nm. Top frame: the decay curves of the precursor species; middle frame: the growth of the unstable photoproducts; top frame: the growth of the stable photoproducts.

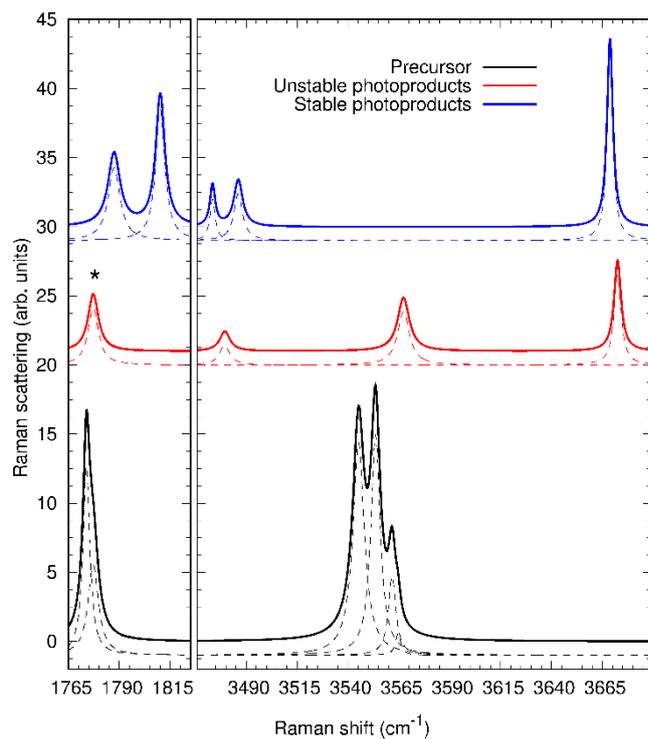


Figure 6. The simulated spectra of the different categories. The peak marked with an asterisk can not be unambiguously assigned to the unstable photoproducts due to its overlap with the precursor peak.

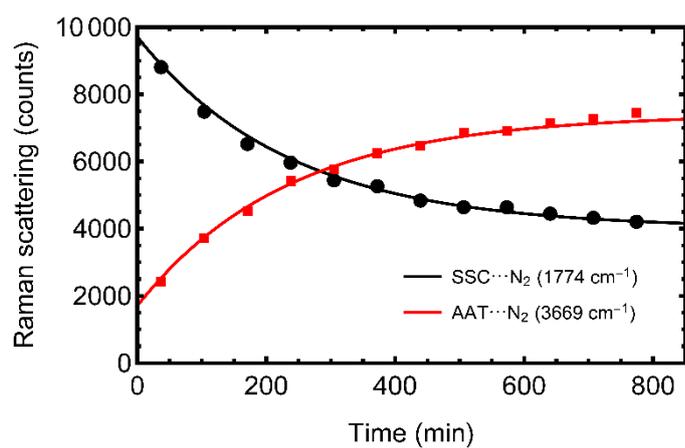


Figure 7. The fit of the kinetic model to the experimental data. Symbols represent experimental values and solid lines represent the fit results ($R^2 = 0.999$).

Highlights

- The photon energy at 532 nm (visible light) is sufficient to excite high overtone states of glycolic acid on the ground electronic states.
- High overtone excitation of the molecular complexes of glycolic acid with nitrogen induce conformational isomerization.
- The interacting nitrogen molecule significantly affects the high overtone induced isomerization reactions of glycolic acid compared to the monomeric glycolic acid.

