



IR induced photochemistry of glycolaldehyde in nitrogen matrix



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ABSTRACT

The conformational equilibria and IR isomerisation processes of glycolaldehyde (HOCH₂CHO) conformers have been studied at low temperature in nitrogen cryogenic matrix. The effects of selective IR irradiation, in the ν_{OH} and ν_{CH} domains, have been followed by FTIR spectroscopy. After deposition the main form is the most stable one, CC (*Cis-Cis*), which features an intramolecular hydrogen bond. Upon selective IR irradiation, this latter form is able to interconvert into two open forms, those called TT (*Trans-Trans*), and TG (*Trans-Gauche*). From TT and TG forms, no recovering (by tunneling, dark process, irradiation, annealing, etc.) of the initial state (i.e. CC regeneration) has been observed. However, a TT \rightleftharpoons TG thermal equilibrium is observed with a standard reaction enthalpy about 0.37 kJ mol⁻¹.

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1. Introduction

Infrared (IR) spectroscopy combined with matrix isolation technique is widely accepted as a powerful tool for studying various phenomena in molecular systems. Studies in matrices reveal great advantages of such technique for studying molecular complexes, as well as examining unstable intermediate species such as high energy isomers, radicals, etc. Indeed, these media exhibit weak interactions with the isolated species within the matrix cages although some perturbation on the guest still exists. This technique can lead, when combined with IR irradiation, to isomerisation and thus is fully appropriate to study high energy conformers at low temperature [1–12]. Since the first observation of infrared-induced cis–trans isomerisation of nitrous acid by Pimentel and co-workers [1], several other compounds have also been found to isomerise in low temperature matrices under irradiation of infrared light [13,2–5,14,15,6–12]. The excitation energy is transferred from the initially excited vibrational mode to the mode involved in the reaction coordinate at energies higher than the reaction barrier [2]. However, isomerisation processes can also compete with other possible energy relaxation channels although the guest–guest energy transfer is reduced due to the isolation of the guest molecules in diluted matrices. For example, it has been shown that energy relaxation may involve the transfer of excitation energy to the lattice vibrational modes [16]. The relaxation rates are then expected to be dependent on the number of phonons involved and on the temperature of the phonon bath.

Glycolaldehyde, HOCH₂CHO (hereafter referred as GA) is an isomer of acetic acid and methyl formate. It possesses both hydroxyl and aldehyde groups (Fig. 1). Because it is one of the largest organic molecules ever detected in interstellar media [18,19], it has been subject to many studies in order to identify the chemical routes to form complex organic species in interstellar molecular clouds [20–23]. The potential energy surface of GA has four minima (Fig. 1), the so-called CC, TT, TG, and CT conformers (C, T, and G, respectively, refer to cis-, trans-, and gauche conformations around the C–C and C–O bonds) [17,24]. The global minimum is the CC form [17,24]; it is stabilized by an internal H-bond (Fig. 1) and is so far the only conformer detected in the interstellar medium [18,25,19]. The other conformers are “open” structures and display no H-bonds. Gas phase experiments also report on only the CC form being observed [26–30]. IR studies in cryogenic matrices refer to CC, TT, TG forms but only the most stable CC species is detected in the as-deposited matrices, while TT and TG conformers are observed only when irradiating matrices with IR/UV sources [31,32]. GA has been also widely studied from theoretical point of view and full vibrational assignments including combination and overtones have been previously reported [33,14].

The main goal of this paper is to obtain as much information as possible related to structural, spectral, and isomerisation properties. For that purpose, the infrared photochemistry of GA upon infrared laser irradiation is investigated in nitrogen matrix. The hydrogen-bonded CC form is transformed mainly into open forms TT and TG. We report for the first time CC \rightarrow TG isomerisation reaction induced from selective infrared irradiation. In addition a thermal equilibrium is observed between TG and TT.

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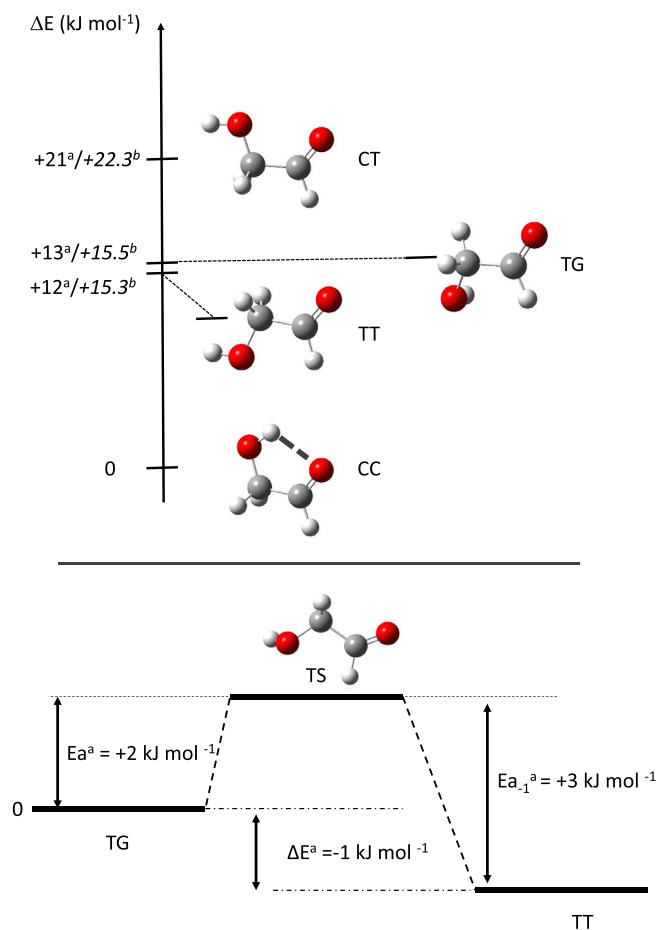


Fig. 1. The four stable conformers of GA: CC, TT, TG, and CT. TS is the transition state which connects TG and TT conformers. Relative energies are given in kJ mol^{-1} . ^aThis work, calculated at B3LYP/6-311+G(d) level of theory. ^bCalculated at MP4 (SDTQ)/cc-pVQZ//MP2/cc-pVQZ level of theory [17].

2. Experimental and theoretical methods

Glycolaldehyde (hereafter denoted GA) was purchased as a dimer respectively from Sigma Aldrich (99.95 % of purity) and heated under vacuum to about 80°C to produce gas-phase monomer. Samples were produced as follows: 180 mbar of purified GA and nitrogen (Air Liquide grade N50) in a 1/1000 molecular ratio were sprayed during 10 s onto a highly polished gold-plated copper cube maintained at 17 K by a closed-cycle He cryogenerator (Cryomech PT-405). FTIR spectra have been recorded with a Bruker IFS 66/S spectrometer in the transmission-reflection mode using a MCT detector at a resolution of 0.12 cm^{-1} . Each spectrum was averaged over 50 scans (2 min), except for the background averaged over one hundred scans. Since IR photons induce rotamerisation of GA [31], the exposure of the sample to the global source was kept as short as possible during acquisition, otherwise the matrix was kept in the dark (*i.e.* protected from the global source) at all times. We have checked the global and the black body photons effects. We left the sample during tens of hours in the global beam and also protected from the global beam (*i.e.* uniquely irradiated by the black body photons at 4.5 K). We observed weak effects compared with conformational changes induced by IR laser that we can neglect conformational changes induced by the global source of the spectrometer during spectra recording (2 min). Indeed, the selective irradiation experiments together with the back reaction observation experiments lengthened two hours. It is perfectly known that each measure affects the sample but we

compare in this work uniquely series of experiments recorded exactly in the same conditions. Knowing that at our experiment timescale there is no relevance of the global or the black body effects, there was no need to work with IR filters.

Selective infrared irradiations on infrared absorption bands related to OH or CH stretching modes were carried out using an IR OPO Laserspec setup (average power 20 mW in the ν_{OH} domain, average power 5 mW in the ν_{CH} domain, FWHM 1.5 cm^{-1}) pumped at 10 Hz by a pulsed Nd:YAG Quantel Brilliant B laser (1064 nm , pulse duration 6 ns). We assign the photo-effects on the basis of difference spectra (after irradiation minus before irradiation). Calculations on the fully optimized conformers of GA (Fig. 1) were carried out in the framework of DFT theory using the GAUSSIAN 09 pack of programs and the basis set 6-311 + G(d) [34–36]. Becke's three-parameter functional was used [37,38], including the gradient-dependent correction and the nonlocal correlation function [39]. Torsional barrier between the TT and TG conformers was calculated along the minimum energy paths and agree within 2 kJ mol^{-1} with the value obtained with more sophisticated methods [32,33,17]. The vibrational assignments of CC, TT, and TG conformers are based on previous experimental works in N_2 and rare gas matrices [31,32] but also on full vibrational assignments for GA conformers obtained from theoretical works [33,14].

3. Results and discussion

3.1. Infrared spectroscopy as deposited sample

IR spectrum of GA in N_2 matrix is displayed in Fig. 2 where it is compared with the CC theoretical one. After deposition, the infrared spectrum is mainly that of the H-bonded CC conformer - the most stable conformer - in agreement with previous experimental studies in rare gas, nitrogen and para- H_2 ($p\text{H}_2$) matrices [31,32,40], vapor phase [27,14] and theoretical calculations [33]. Experimental frequencies in N_2 are listed in Table 1 and compared with harmonic and anharmonic frequencies. Due to the intramolecular H-bond, the OH stretching mode (ν_{OH}) of the CC conformer is red-shifted (3532 cm^{-1}) compared to the value of "free" OH group (around 3650 cm^{-1}). In addition, site effects can be seen as multiplets in N_2 . The most intense band of this conformer is observed at 1754 cm^{-1} (C=O stretching mode) while this band is observed at

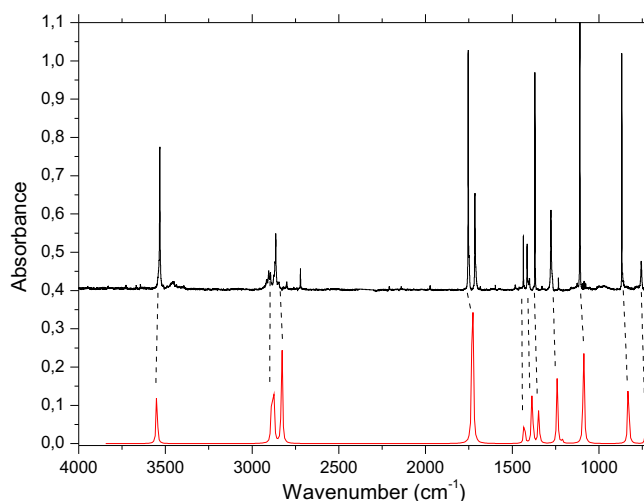


Fig. 2. Matrix infrared spectrum of GA (top spectrum) in N_2 matrix at 4 K. This spectrum is compared with B3LYP/6-311+G(d) calculated spectrum (bottom spectrum) for CC conformer. Calculated harmonic frequencies were scaled with a factor of 0.963. Small bands around $3300\text{--}3500\text{ cm}^{-1}$ may be assigned to dimers (tentative).

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