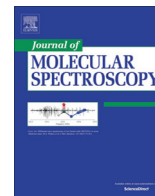




Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: [www.elsevier.com/locate/jms](http://www.elsevier.com/locate/jms)

# Fourier transformation microwave spectroscopy of the methyl glycolate–H<sub>2</sub>O complex

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## ARTICLE INFO

## Article history:

Received 14 May 2017

In revised form 17 September 2017

Accepted 21 September 2017

Available online xxxxx

## Keywords:

Methyl glycolate–H<sub>2</sub>O complex

Rotational spectroscopy

Methyl internal rotation

Ring-inversion

Conformational flexibility

## ABSTRACT

The rotational spectrum of one conformer of the methyl glycolate–H<sub>2</sub>O complex has been measured by means of the pulsed jet Fourier transform microwave spectrometer. The observed *a*- and *b*-type transitions exhibit doublet splittings due to the internal rotation of the methyl group. On the other hand, most of the *c*-type transitions exhibit quartet splittings arising from the methyl internal rotation and the inversion motion between two equivalent conformations. The spectrum was analyzed using parameterized expressions of the Hamiltonian matrix elements derived by applying the tunneling matrix formalism. Based on the results obtained from *ab initio* calculation, the observed complex of methyl glycolate–H<sub>2</sub>O was assigned to the most stable conformer of the insertion complex, in which a non-planar seven membered-ring structure is formed by the intermolecular hydrogen bonds between methyl glycolate and H<sub>2</sub>O subunits. The inversion motion observed in the *c*-type transitions is therefore a kind of ring-inversion motion between two equivalent conformations. Conformational flexibility, which corresponds to the ring-inversion between two equivalent conformations and to the isomerization between two possible conformers of the insertion complex, was investigated with the help of the *ab initio* calculation.

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## 1. Introduction

A number of hydrogen-bonded complexes between hydrophilic molecules and water have been studied extensively, because they might serve to understand various phenomena in liquids at the molecular level. Molecules having the intramolecular hydrogen bond are generally expected to form addition and insertion complexes with the water molecules. In the case of the addition complex, the water molecule forms a hydrogen bond to one of the available sites of the target molecule as a simple H-donor or H-acceptor, without breaking the existing intramolecular hydrogen bond. In the generation process of the insertion complex, a disruption of the intramolecular hydrogen bond and a construction of the intermolecular hydrogen bond network caused by the H<sub>2</sub>O insertion need to occur simultaneously. Usually, the insertion complexes are more stable in energy compared to the addition complexes. However the molecular structure or the properties of the inserted molecule may change considerably from that of the monomer.

Methyl glycolate (MG), CH<sub>3</sub>O–C(=O)–CH<sub>2</sub>–OH, is a member of the  $\alpha$ -hydroxyester's family, and possesses both a hydrogen bond

donor group (OH) and an acceptor groups (C=O/COC/COH) to form intramolecular hydrogen bond. MG has three different internal rotation axes (CC–OH, OC–C(=O) and (O=)C–OC) that can give rise to conformational isomers in addition to the methyl group internal rotation (O–CH<sub>3</sub>). The interconversions between the conformers are allowed by the internal rotations hindered by relatively low potential barrier heights. The most stable conformer of MG is the *Ss* form in which the three CCOH, OCC=O and O=COC dihedral angles are close to 0° and being stabilized into the five-membered ring arrangement by an intramolecular OH...O=C hydrogen bond [1]. The intramolecular hydrogen bond makes the O–H stretching vibrational frequency significantly lower than that in the related aliphatic alcohols and also makes the CC–OH torsional frequency higher [2]. This conformer has three low-frequency torsional modes. The microwave spectra of this conformer in the vibrational ground state [3] and the torsionally excited states [4] have already been investigated. Analysis of the A–E methyl internal rotation splittings observed in the microwave spectra yielded different effective *V*<sub>3</sub> barriers to the methyl internal rotation for the vibrational ground state and the torsionally excited states [3,4]. Meyer et al. [5] analyzed combined data from microwave and far-infrared spectroscopy by a flexible model accounting for the methyl and two skeletal torsional modes. They suggested that the C–C torsion induces a change in the electronic structure

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of the carboxyl group to influence the methyl torsion through the intramolecular hydrogen bond. Six different conformers of MG were predicted by *ab initio* calculation and the two most stable conformers of MG were observed and characterized by vibrational spectroscopy [6].

Meanwhile, another  $\alpha$ -hydroxyester, methyl lactate (ML) was investigated recently by free jet millimeter-wave absorption and molecular beam Fourier-transform microwave spectroscopy [7,8]. The analysis of the spectrum was made to determine the rotational constants and the barrier height  $V_3$  to the internal rotation of the  $\text{CH}_3\text{—O}$  methyl group in the vibrational ground state for the most stable conformer SsC. The SsC conformer forms the same five-membered ring structure as MG Ss due to the intramolecular hydrogen bond and also has similar torsional flexibility. Thomas et al. reported the rotational spectroscopic and *ab initio* theoretical studies on two kinds of the hydrogen bond clusters of ML,  $\text{ML—NH}_3$  [9] and  $\text{ML—(H}_2\text{O)}_{1,2}$  [10]. For both kinds of cluster, only the insertion type complexes, in which the ring structures are formed by the intermolecular hydrogen bonds, were identified. In the case of  $\text{ML—NH}_3$ , the  $\text{NH}_3$  internal rotation was observed as well as the  $\text{CH}_3\text{—O}$  internal rotation, although the  $\text{NH}_3$  subunit forms a  $\text{OH}\cdots\text{NH}\cdots\text{O}=\text{C}$  intermolecular hydrogen bond with ML. The internal rotation barrier height of the  $\text{CH}_3\text{—O}$  methyl group was found to be close to that of the ML monomer. In the case of  $\text{ML—H}_2\text{O}$ , the authors determined its conformation completely from four candidates with similar structure by combining the extensive isotopic studies. The wagging motion of the free H atom of  $\text{H}_2\text{O}$  subunit in  $\text{ML—H}_2\text{O}$  was investigated based on *ab initio* calculation, and the conversion barrier corresponding to the isomerization between the two most stable conformers was estimated to be low. The methyl internal rotation barrier height of ML increases considerably upon hydration.

In this study, we report the rotational spectrum of a  $\text{MG—H}_2\text{O}$  complex by means of pulsed jet Fourier transform microwave spectroscopy. The  $\text{MG—H}_2\text{O}$  complex is expected to form the hydrogen bond network of the seven membered ring in the most stable insertion type conformation as well as the  $\text{ML—H}_2\text{O}$  complex. However, because of the high symmetry of MG, the  $\text{MG—H}_2\text{O}$  complex has a feasible large amplitude motion between two equivalent mirror images belonging to the same conformer, in addition to the methyl internal rotation. Parameterized expressions of the Hamiltonian matrix elements suitable for the analysis of the rotational spectrum of  $\text{MG—H}_2\text{O}$  were derived by applying the tunneling matrix formalism developed by Hougen [11]. The tunneling matrix formalism is extremely useful for the analysis of the molecular spectrum in which tunneling splittings caused by more than two kinds of the large amplitude vibrational motions appear. The conformational structure of the observed conformer was assigned by comparing the spectroscopic constants determined experimentally with those obtained by *ab initio* calculation. Conformational flexibility, which gives rise to the large amplitude motion between two equivalent conformations and to the isomerization between two possible conformers of the insertion complex of  $\text{MG—H}_2\text{O}$ , was investigated with the help of *ab initio* calculation.

## 2. Experimental

Rotational spectra of the MG monomer and the  $\text{MG—H}_2\text{O}$  complex were observed in the 8–26 GHz region by means of the pulsed supersonic jet Fourier-transform microwave (FTMW) spectrometer which has been described elsewhere [12]. A commercial sample of MG (Sigma-Aldrich) was used without further purification. The liquid sample of MG was put into a reservoir nozzle and maintained the temperature around 50 °C by electrical heating in order to increase the concentration of MG in the supersonic jet. Pure neon

gas (Takachiho Trading Co., Ltd.) was used as a carrier gas at a stagnation pressure of about 800 kPa. For the observation of  $\text{MG—H}_2\text{O}$  complexes, the neon carrier gas was seeded with water vapor by passing through a liquid water reservoir which was inserted between the inlet of the nozzle and the carrier gas line, and kept at room temperature. The  $\text{MG/Ne}$  or  $\text{MG/H}_2\text{O/Ne}$  mixture was then injected into a vacuum chamber by a pulsed solenoid valve ( $\sim 0.8$  mm orifice diameter) at a repetition rate of  $\sim 2$  Hz to create supersonic beam. The molecules in the beam were polarized with 0.5–2.0  $\mu\text{s}$  microwave pulses and subsequent free-induction decay (FID) time-domain signal from the molecules was digitized for 4096 or 8192 points at an 8 MHz clock rate. Depending on the signal intensity, 300–20,000 FID signals were averaged in order to get a sufficient signal-to-noise ratio. The averaged FID data were then Fourier transformed to obtain the frequency-domain power spectrum. Since the supersonic jet beam axis and the Fabry–Pérot resonator axis were arranged coaxially, each transition was observed as a doublet due to the Doppler-effect. The transition frequency was thus determined by averaging the peak frequencies of the two Doppler components. The estimated accuracy of the frequency measured is better than 2 kHz for the unblended lines.

## 3. Theoretical calculation—*ab-initio* quantum chemistry calculation

We carried out *ab initio* calculations on the MG monomer and the  $\text{MG—H}_2\text{O}$  complexes to predict the molecular properties relevant to the interpretation of the rotational spectra of the possible conformers, such as rotational constants, electric dipole moments and methyl internal rotation parameters as well as relative energies and harmonic vibrational frequencies. All calculations were performed using the Gaussian 09 W program package [13].

For the MG monomer, only the most dominant conformer (Ss) was optimized at the MP2/aug-cc-pVTZ level of theory and the spectroscopic parameters were estimated.

The six most stable conformers of  $\text{MG—H}_2\text{O}$  optimized at the MP2/aug-cc-pVTZ level of theory are shown in Fig. 1, and the energies and spectroscopic properties for each conformer are given in Table 1. The label of each atom in MG and  $\text{H}_2\text{O}$  distinguished by a number is shown in Fig. 1, where the hydrogen groups {H(10), H(11), H(12)} and {H(5), H(8)} correspond to the methyl group and the methylene group of MG, respectively. For  $\text{H}_2\text{O}$ , a hydrogen bonding H atom is labeled as H(14) and another H atom which is free from the hydrogen bonding is H(15). These conformers were derived from the most dominant conformation of MG monomer (Ss). Two conformers named as “In- a” and “In-b” are the insertion complexes, and “a” and “b” classify the direction of the hydrogen-bond free H(15) atom of  $\text{H}_2\text{O}$ . Remaining conformers, “Ad(Z)” or “Ad(Z)-X” (Z = OH, O=C, COC and X =  $\text{CH}_2$  or Me), are the addition complexes where “Z” specifies the oxygen atom of the hydration site in MG which accepts a proton of  $\text{H}_2\text{O}$  to form the intermolecular hydrogen bond. In the case of Ad(COC), the orientation of  $\text{H}_2\text{O}$  is also distinguished by the index X. The In-a conformer is the most stable one and is similar to the “i-I” conformer of methyl lactate- $\text{H}_2\text{O}$  complex reported by Thomas et al. [10]. Optimized structural parameters for the two most stable conformers, In-a and In-b, of  $\text{MG—H}_2\text{O}$  are available as Supplementary material (Table S1 in the Supplementary material).

For the insertion type conformers of  $\text{MG—H}_2\text{O}$ , counterpoise corrections [14,15] were also computed, but this correction yield no significant changes to the relative energy and the optimized structure.

Especially in the case of the insertion type complex, hydration distorts the structure of the MG subunit significantly from the equilibrium structure of the MG monomer. We calculated the

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