

Mono, di, tri and tetraethylene glycol: Spectroscopic characterization using density functional method and experiment

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ABSTRACT

We report infrared and electronic absorption spectra of mono, di, tri and tetra ethylene glycol (EG) in gas phase, their cation and anion and in water solvent using density functional theory calculations at B3LYP/TZVP level. Structural parameters, rotational and centrifugal distortional constants and dipole moments are also reported. A significant shifts in vibrational frequencies and peaks in electronic absorption spectra have been observed upon ionization of mono, di, tri and tetra ethylene glycols. We have also obtained experimental vibrational spectrum of monoethylene glycol. Vibrational frequencies of mono ethylene glycol from theory and experiment are compared. We have used integral equation formalism polarizable continuum model (IEFPCM) model to study the influence of water solvent on vibrational frequencies of neutral mono, di, tri and tetra ethylene glycol. Electronic absorption spectra for these molecules have been obtained using Time dependent density functional theory (TDDFT).

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1. Introduction

Ethylene glycol (HOCH₂-CH₂OH) is a di alcohol and asymmetric top molecule. It is non rigid molecule having three internal degrees of freedom. Some efforts have been made to detect ethylene glycol in space [1–3]. According to Hudson et al. ethylene glycol (EG) and glycolaldehyde (GA) are interconvertible and they claimed presence of glycolaldehyde in interstellar medium [4]. They also reported low temperature mid IR spectra, selected band strengths and positions for ethylene glycol and glycolaldehyde. Butscher et al. have studied formation of ethylene glycol and glycolaldehyde in interstellar grains at low temperature theoretically and experimentally [5]. Fedoseev et al. have studied formation of EG and GA using Monte Carlo model [6].

Several theoretical [7–15] as well as experimental [16–29] studies have been performed to study ethylene glycol. Its interaction with water molecule has been studied using many-body interaction through ethylene glycol-(water)_n (n = 1–3) complexes [30]. Buckley and Giguere have performed first experimental analysis of ethylene glycol molecule and confirmed that the trans isomers are less stable than the gauche [31]. Ha et al. have experimentally proposed that there is only gauche conformer

of ethylene glycol and it has only one internal hydrogen bond [32]. Frei et al. have performed a detailed study of conformer analysis of ethylene glycol and reported two slightly different conformers whose nuclear configurations lie in a neighborhood of the r_{e1} structure [33]. Müller et al. have reported only two conformers of ethylene glycol viz. anti and gauche and showed that gauche is the lowest energy conformer [34]. Hollis et al. have designated g'Ga form as the lowest energy conformer of ethylene glycol [1]. Conformational analysis of ethylene glycol has been carried out by Radom et al. have using theoretical calculations at LCAO SCF level [35]. Gauche (aGg') ethylene glycol has been detected in Orion KL by Brouillet [36].

Ethylene glycol is the simplest possible aldehyde sugar [37]. The structural rearrangement of C–C and C–O bonds decides different conformers of ethylene glycol [38,39]. It has twenty seven stable different conformers. The uncertainty in its equilibrium conformation has been resolved from experimental and theoretical work. The ethylene glycol may exist either as a gauche conformer or anti conformer depending on the energy difference. To our knowledge, no systematic study on comparative infrared and electronic absorption spectra of mono, di, tri and tetra ethylene glycol, their cation, anion and in water ice has been carried out yet. The aim of this paper is to present comparative spectra of mono, di, tri and tetra ethylene glycol using electronic structure calculations. The computational details are given in the next section. The infrared and electronic absorption spectra of

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mono, di, tri and tetra ethylene glycol, their ions and in water ice are presented and compared in the third section. Conclusions are drawn in the last section.

2. Computational details

The geometry of gauche mono ethylene glycol is optimized with B3LYP functional [40–42] of density functional theory with six different basis sets. The gauche mono ethylene glycol has minimum energy at B3LYP/TZVP level. This method and basis set further used for optimization of neutral, di, tri and tetra ethylene glycol and their ions. The infrared and electronic absorption spectra have also been calculated at B3LYP/TZVP level. To study neutral mono, di, tri and tetra ethylene glycol in water solvent, we optimized geometries at B3LYP/TZVP level of theory using IEFFCM model [43–45]. We have used dielectric constant 78.5 water to calculate vibrational frequencies. As it is lower than that of ice, the calculated vibrational frequencies not for ice but close to those in ice. The scaling factor of 0.965 has been used for the vibrational frequencies [46]. Time dependent density functional theory (TDDFT) [47–52] have been used to obtain excited states of neutral, cation, anion and in water ice of mono, di, tri and tetra ethylene glycol at the same level of theory. The % contribution from each transition was obtained using the SWizard program [53]. Gaussian 03 program package has been used to perform all the calculations [54]. Ethylene glycol of AR grade (assay \geq 99.5%) was purchased from S. D. Fine Chem. Ltd. and used without any further purification. An infrared spectrum of pure ethylene glycol has been recorded using Perkin-Elmer Spectrum two IR spectrometer.

3. Result and discussion

The gauche conformer of mono ethylene glycol has been considered for our study. The optimized structures of mono, di, tri and tetra ethylene glycol are shown in Fig. 1. The relative energy of ethylene glycol using B3LYP method with 6-311G, 6-311+G, 6-311++G, 6-311++G*, SDD and TZVP basis sets is summarized in

Table 1

Relative energy (kcal mol⁻¹) of ethylene glycol with B3LYP method and different basis sets.

Basis set	Relative energy (kcal mol ⁻¹)
6-311G	65.169
6-311+G	58.11
6-311++G	57.886
6-311++G*	19.334
SDD	74.967
TZVP	0

Table 1. The C₁ is the symmetry of these molecules in gas phase which does not change for the ions and in water solvent. The mono, di, tri and tetra EG are lower in energy in water solvent by 5.313, 13.409, 7.595 and 10.78 kcal mol⁻¹ respectively than that of gas phase. **Table 2** summarizes bond lengths, bond angles and dihedral angles of neutral mono, di, tri and tetra ethylene glycol in gas phase and in water ice with available experimental values [55] of mono ethylene glycol in gas phase. The experimental values of mono ethylene glycol are in well agreement with our theoretical calculations. The dipole moment of mono ethylene glycol is in agreement with the available experimental value. There is no large difference in the structural parameters of neutral glycols in water solvent and gas phase. The highest change in dihedral angle of di EG by 9.43° is observed from gas phase to water solvent.

3.1. Infrared spectra

The vibrational spectra (4000–200 cm⁻¹) of neutral mono, di, tri and tetra ethylene glycol (EG) with experimental spectrum for mono EG are shown in Fig. 2. The vibrational spectrum is studied broadly for the major modes viz. OH stretching, CH stretching, CH₂ bending, OH out of plane stretching and CC stretching modes. The CH stretching includes symmetric and asymmetric stretching modes and CH₂ bending modes include scissoring, twisting, wagging and rocking modes. The mono ethylene glycol (C₂H₆O₂) has 24 vibrational modes two for OH stretching, four for CH stretching, eight for bending modes and ten for the

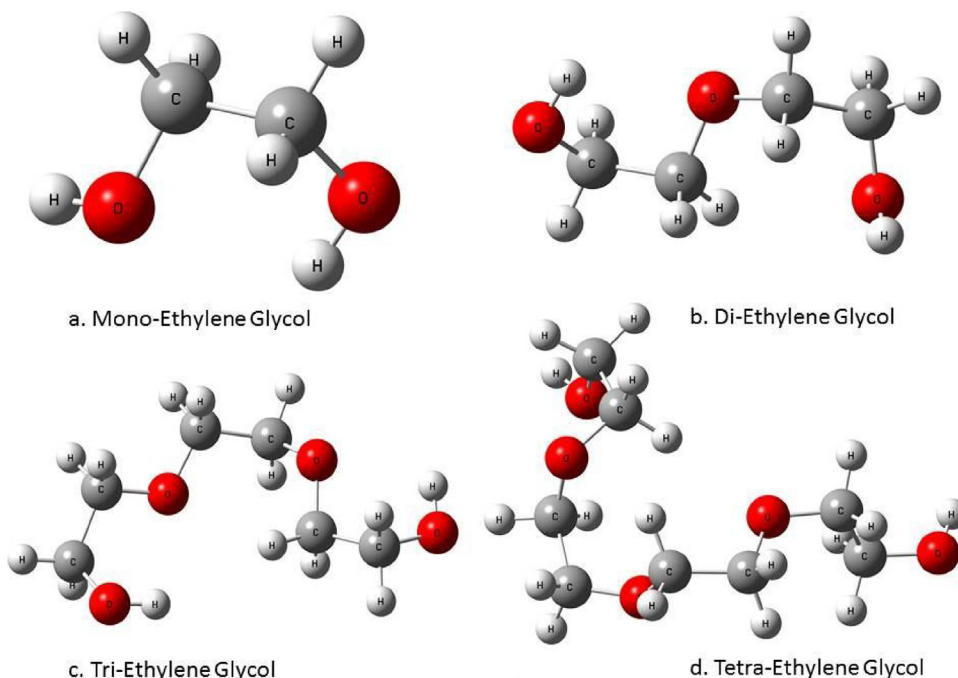


Fig. 1. Optimized geometries of mono, di, tri and tetra ethylene glycol at B3LYP/TZVP level of theory.

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