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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

## Anharmonic calculations of frequencies and intensities of O—H stretching vibrations of (*R*)-1,3-butanediol conformers in the fundamentals and first overtones by density functional theory

Yoshisuke Futami<sup>a,\*</sup>, Chihiro Minamoto<sup>b</sup>, Satoshi Kudoh<sup>c</sup><sup>a</sup> Department of Biological and Chemical Systems Engineering, National Institute of Technology, Kumamoto College, Yatsushiro, Kumamoto 866-8501, Japan<sup>b</sup> Department of Applied Chemistry and Biotechnology, National Institute of Technology, Niihama College, Niihama, Ehime 792-8580, Japan<sup>c</sup> College of Engineering, Shibaura Institute of Technology, Saitama, Saitama 337-8570, Japan

## ARTICLE INFO

## Article history:

Received 30 November 2017

Received in revised form 5 February 2018

Accepted 7 February 2018

Available online xxxxx

## Keywords:

Hydrogen bonding

OH stretching vibration

Overtone

Conformer

Anharmonic frequency analysis

## ABSTRACT

The frequencies and absorption intensities of the five kinds of conformers of 1,3-butanediol with the same carbon skeleton (GG') were calculated by anharmonic calculation for the fundamentals and first overtones of OH stretching vibrations. The four kinds of conformers form intramolecular hydrogen bonds and one conformer did not. Intramolecular hydrogen bond formation shifted the frequency of fundamental and first overtone of H-bonding OH stretching vibration to the lower frequency. The absorption intensities of the fundamentals as well as the vibrational anharmonicities increased upon hydrogen bond formation, while the intensities of first overtones decreased. The differences of conformers were clearly seen in the frequencies of the first overtones of free OH.

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## 1. Introduction

Near-infrared (NIR) spectroscopy has been used in various scenes of basic sciences and applications. It is used for the studies of vibrational potentials and anharmonicities of molecular vibrations in basic sciences and non-destructive analysis of foods and medicines using chemometrics in applications. NIR spectroscopy covers the spectral region of 12,500–4000 cm<sup>-1</sup> (800–2500 nm in wavelength), where bands due to overtones and combination modes of XH stretching vibrations (X = N, O) are mainly observed. The frequencies and absorption intensities of XH stretching vibrations are both sensitive to hydrogen bond formation. This has been known for more than 50 years. For this reason, NIR spectroscopy has also been used for the study of hydrogen bond formation, which attracts attentions as one of the factors of physical properties of materials and specificity of biomolecules [1–6]. The importance of the absorption intensities of overtones has been pointed out in the studies of intermolecular interaction in these days. Generally, the changes in the absorption intensities of overtones are different from those of the fundamentals [7–16].

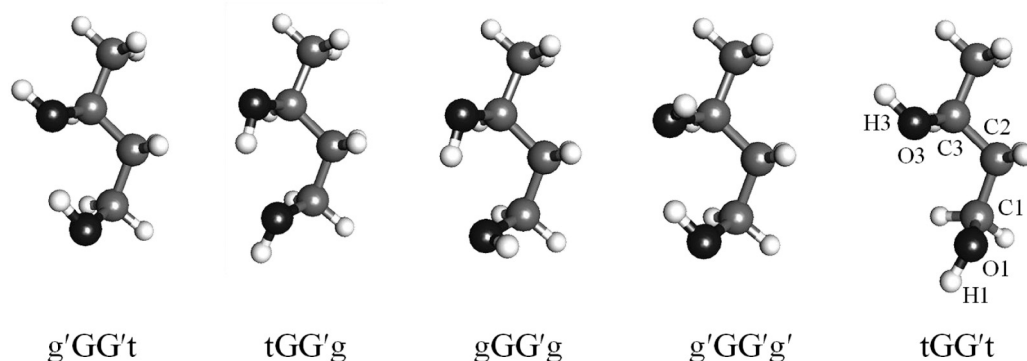
Diols are well known to form intermolecular and intramolecular hydrogen bonds by two OH groups in the molecule. And formation of an intramolecular hydrogen bond is known to stabilize the specific

conformation within many conformations [17–19]. The infrared (IR) and NIR spectra of many diols have been examined for the frequencies and absorption intensities of OH stretching vibrations on the formation of intramolecular hydrogen bond. By the hydrogen-bond formation, the absorption intensities of the fundamentals are reported to increase, while those of the first overtones decrease [20]. Absorption intensities of overtones are zero for a harmonic oscillator, so it is necessary to consider the anharmonicity of the oscillator in the analyses of overtones. In local-mode model, stable conformers of glycol (EG), 1,3-propanediol (PD) and 1,4-butanediol (BD) are examined with QCISD/6-311++G(2d, 2p) and the frequencies and absorption intensities of OH stretching vibrations were calculated with anharmonic vibrational potentials; the changes in the absorption intensities of the fundamentals and first overtones on hydrogen bond formation are theoretically reproduced. In addition, it is reported that broadening of the absorption peaks due to hydrogen bond formation makes it more difficult to observe the overtones [21]. There is little information on the relationship between NIR spectra and conformation of diols.

The structure of 1,3-butanediol was calculated at B3LYP/6-311++G\*\* level and 1,3-butanediol was reported to have four particularly stable conformers [22]. The structure of 1,3-butanediol was also investigated at MP2/6-311++G(d,p) level and 73 stable conformers, six of which were observed in IR absorption spectra in argon matrix, were found [23]. However, the IR absorption spectra in the carbon tetrachloride solvent did not distinguish the conformers although

\* Corresponding author.

E-mail address: [futami@kumamoto-nct.ac.jp](mailto:futami@kumamoto-nct.ac.jp) (Y. Futami).



**Fig. 1.** Optimized structures of the five stable conformations of (*R*)-1,3-butanediol calculated at the DFT//B3LYP/6-311++G(3df,3pd) level. The conformers are named by the rule of Jesus et al. [22], that is, “the conformations are defined according to the following rules: *trans* ( $180 \pm 30^\circ$ ), *gauche* clockwise ( $60 \pm 30^\circ$ ), and *gauche* anticlockwise ( $-60 \pm 30^\circ$ ), abbreviated *t* or *T*, *g* or *G*, and *g'* or *G'*, respectively. The capital letters refer to the backbone dihedrals while the minuscule ones refer to the dihedrals which contain the OH groups.” The dihedral angles and the zero point vibration-corrected relative energies for the five conformers are shown in Table 1. Atom numbering scheme is presented in the conformer tGG't.

free OH and H-bonding OH were observed [24]. The conformers are expected to be distinguished by the NIR absorption spectra, which prominently exhibit anharmonicities of molecular vibrations.

In this study we have investigated the relationship between the conformation of 1,3-butanediol and the vibration frequency and the absorption intensity of OH stretching vibration by the VPT 2 method. In recent years, a vibrational calculation method considering anharmonicity of molecular vibration has been developed by second order vibrational perturbation theory (VPT 2) [25–30].

## 2. Computational Methods

The Gaussian09 program [31] with the 6-311++G(3df,3pd) basis set was used for the DFT calculations. Becke's three-parameter hybrid density function in combination with the Lee-Yang-Parr correlation functional (B3LYP) was employed for the optimization of geometrical structures and the computation of anharmonic frequencies, IR intensities and zero-point energies [32,33]. The calculation conditions for Gaussian09 were tight convergence in the SCF and standard grid in DFT.

We selected five conformers of (*R*)-1,3-butanediol from the reported ones [23]. Their conformations of (*R*)-1,3-butanediol were optimized as shown in Fig. 1. Here, the carbon skeleton of the conformers was chosen as GG', which was reported to give particularly stable conformers [22,23]. The dihedral angles and relative energies were calculated as listed in Table 1. The conformations and energies were almost identical to the reported values [22,23]. It was reported that four conformers (*g'*GG't, tGG'g, gGG'g, *g'*GG'g') formed intramolecular hydrogen bonds, while one conformer (tGG't) formed no hydrogen bonds [22,23]. Anharmonic calculations of frequencies and intensities of these five conformers were performed.

**Table 1**  
The dihedral angles and the zero point vibration-corrected relative energies for the five conformers of (*R*)-1,3-butanediol.<sup>a</sup>

Conformer	Dihedral angles/ $^\circ$				O–H...O–H	$\Delta E/\text{kJ mol}^{-1}$
	1st	2nd	3rd	4th		
<i>g'</i> GG't	–46	73	–59	177	120	0.00
tGG'g	–174	63	–70	42	125	0.16
gGG'g	71	61	–66	46	96	0.66
<i>g'</i> GG'g'	–49	68	–58	–74	93	1.23
tGG't	–170	94	–59	180	–	20.38

<sup>a</sup> Conformations of (*R*)-1,3-butanediol are due to the four flexible coordinates associated with rotation around the C–O and C–C bonds in the molecule. These coordinates correspond to the four dihedral angles H1–O1–C1–C2 (1st), O1–C1–C2–C3 (2nd), C1–C2–C3–O3 (3rd) and C2–C3–O3–H3 (4th) [22]. The atomic numbering scheme is shown in Fig. 1.

## 3. Results and Discussion

Table 2 shows the frequencies and absorption intensities of fundamentals ( $\nu_1$  and  $I_1$ ) and first overtones ( $\nu_2$  and  $I_2$ ) of the OH stretching vibrations with their anharmonicities ( $\chi = 0.5\nu_2 - \nu_1$ ). The  $\nu_1$  and  $\nu_2$  values of the two OH stretching vibrations of tGG't are  $\nu_1 = 3649 \text{ cm}^{-1}$  and  $3640 \text{ cm}^{-1}$ ,  $\nu_2 = 7117 \text{ cm}^{-1}$  and  $7099 \text{ cm}^{-1}$ . Each higher frequency corresponds to the OH stretching vibration of the OH group bound to the first carbon atom. The differences in frequencies of the two OH vibrations in the fundamental and in the first overtone are about  $10 \text{ cm}^{-1}$  and about  $20 \text{ cm}^{-1}$ , respectively. The anharmonicities of the two OH stretching vibrations are the same ( $-90 \text{ cm}^{-1}$ ); the two free OH groups of tGG't have nearly equal frequencies and anharmonicities.

In contrast, the two OH (free OH and H-bonding OH) groups of the other four kinds of conformers (*g'*GG't, tGG'g, gGG'g, *g'*GG'g') have significantly different frequencies and anharmonicities. The frequencies of fundamentals of free OH of *g'*GG't, tGG'g, gGG'g and *g'*GG'g' are  $3665 \text{ cm}^{-1}$ ,  $3683 \text{ cm}^{-1}$ ,  $3630 \text{ cm}^{-1}$  and  $3624 \text{ cm}^{-1}$ , respectively, which are in the range of  $3654 \pm 30 \text{ cm}^{-1}$ . In the same way, the frequencies of first overtones of free OH are in the range of  $7138 \pm 60 \text{ cm}^{-1}$ . The width of the frequencies range of the first overtones is about twice as large as those of fundamentals as expected. These frequency ranges are close to the frequencies of free OH vibrations of tGG't. For butyl alcohols, it has been reported that the experimental positions of the fundamentals and the first overtones of the free OH depend on OH group conformation and do not depend on the chain conformation [34]. The result of this work is consistent with the results of the butyl alcohols.

On the other hand, the frequencies of fundamentals of H-bonding OH of *g'*GG't, tGG'g, gGG'g and *g'*GG'g' are in the range of  $3562 \pm 16 \text{ cm}^{-1}$ . The frequencies of first overtone of H-bonding OH of *g'*GG't, tGG'g, gGG'g and *g'*GG'g' are in the range of  $6925 \pm 35 \text{ cm}^{-1}$ . The centers of frequency ranges of H-bonding OH are clearly reduced from those of free OH by  $92 \text{ cm}^{-1}$  in the fundamentals and by  $213 \text{ cm}^{-1}$  in the first overtones. The reduction of the OH vibrational frequency on H-bond formation is generally observed [1–5,7–9,20,21], and the reduction is also reported in fundamentals of (*R*)-1,3-butanediol OH vibration [23,24].

It should be noted here that the half widths of the ranges of H-bonding OH ( $16$  and  $35 \text{ cm}^{-1}$  for fundamental and first overtone, respectively) are narrower than those of free OH ( $30$  and  $60 \text{ cm}^{-1}$ , respectively), suggesting that the Hydrogen bond formation determines the frequencies dominantly rather than the variations of conformers.

The frequencies of fundamentals of H-bonding OH of *g'*GG't and tGG'g in argon matrix were reported to be  $3579$  and  $3569 \text{ cm}^{-1}$  (The frequencies of tGG't, gGG'g and *g'*GG'g' were not reported) [23]. Our

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