



A Raman spectroscopic study of the conformations of 1,4-dioxane in the pure liquid, methanol, and aqueous solution



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ABSTRACT

The conformational equilibria of 1,4-dioxane in organic solvents and aqueous solution have been investigated by Raman spectroscopy with the aid of density functional theory calculations. The proportions of the conformers of 1,4-dioxane in the liquid phase has been a controversial issue. We determined that the proportions of the 2,5-twisted-boat and 1,4-twisted-boat conformers are 12% and 9%, respectively. We also determined the conformational thermodynamics in the pure liquid, methanol, and water. Finally, we demonstrated that the hydration structure outside the first shell plays a crucial role in the conformational thermodynamics in aqueous solution.

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1. Introduction

1,4-Dioxane, which is commonly used as a solvent, is a six-membered ring compound. Six-membered rings containing oxygen atoms are commonly found in organic and biomolecules. 1,4-Dioxane is useful as an experimental model to investigate the conformation of cyclic molecules because of its high solubility. In addition, 1,4-dioxane is also a simple model molecule to investigate the relationship between the conformation and hydration of polyethers that have OCCO unit segments in common with 1,4-dioxane, such as poly(oxyethylene) and crown-ether.

It is known that six-membered ring compounds such as cyclohexane can form chair and twisted-boat conformers [1]. In fact, in the gas phase, cyclohexane mainly forms the chair conformer according to a quantum chemical calculation [2] and electron diffraction measurement [3]. 1,4-Dioxane could form one chair conformer and two twisted-boat conformers (2,5-twisted boat (2,5-TB) and 1,4-twisted boat (1,4-TB)). In the gas phase, 1,4-dioxane mainly forms the chair conformer, as is the case with cyclohexane [4]. However, the proportions of the conformers of 1,4-dioxane in the liquid phase is a controversial issue. An X-ray diffraction (XRD) study by Takamuku et al. [5] showed that the proportions of the chair and twisted-boat conformers in the pure liquid are 0.65 and

0.35, respectively. However, this result has been questioned by some theoretical studies. Monte Carlo (MC) calculation [6] using the conformational proportions reported by Takamuku et al. yielded a permittivity value of 3.34, which is significantly higher than the experimental value of 2.2 [7]. Molecular dynamics simulation [8] and quantum mechanics/molecular mechanics (QM/MM) calculation [9] have shown the proportions of the twisted-boat conformers to be about 0.01 and $<10^{-4}$, respectively. The first aim of the present study is to clarify the controversial issue of the proportions of the conformers using Raman spectroscopy with the aid of density functional theory (DFT) calculations.

The conformational behavior of 1,4-dioxane in aqueous solution is poorly understood. There have been no experimental investigations of the conformational behavior in solution. A QM/MM calculation [9] showed that in aqueous solution 1,4-dioxane mainly forms the chair conformer, which is similar to the liquid. The second aim of the present study is to clarify the conformational equilibria of 1,4-dioxane in aqueous solution using Raman spectroscopy. In the present study, we investigated the concentration dependence of the equilibria in aqueous solution and determined the thermodynamic differences between the conformers to obtain the detailed conformational behavior in aqueous solution. The conformational enthalpy and entropy are important physical quantities to understand the relationship between the conformational equilibria and hydration of the solute. Our previous work [10] using 1,2-dimethoxyethane (DME) as a model for poly(oxyethylene) showed that formation of the *gauche* form around the OC–CO bond is a major reason for the high solubility of DME in water. However, an

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open question still remains: Why is hydration of the *gauche* conformer energetically favorable? In this regard, the conformational equilibria of 1,4-dioxane in aqueous solution is important, because the chair conformer of 1,4-dioxane, which is expected to be the main conformer, takes the *gauche* form around the OC–CO bond.

2. Materials and methods

2.1. Materials

1,4-Dioxane (99%) and methanol (99.8%) were purchased from Nacalai Co. (Tokyo, Japan) and were used without further purification. Pure water was prepared by the Milli-Q system. The concentrations of the samples were 0.05–1 of the mole fraction of the solute (x_{dio}).

2.2. Raman measurements

Raman spectra were recorded on a JASCO NR-1800 Raman spectrometer (JASCO, Tokyo, Japan) equipped with an Andor Technology CCD detector. The 90° scatterings were excited by a Spectra Physics Stabilite 2017 argon ion laser (Spectra Physics, Santa Clara, CA) at 514.5 nm with power of 500–800 mW. The spectral resolution was 4.5 cm^{-1} in all of the spectra. The temperature of samples was controlled at $\pm 0.3^\circ \text{C}$ by circulating thermostated water around the cells. Each Raman spectrum of the solute was obtained after subtracting the solvent spectrum from the solution spectrum. The Raman intensities were corrected by a frequency dependent factor:

$$\frac{(\nu_0 - \nu)^4}{\nu [1 - \exp(-hc\nu/k_B T)]}$$

where ν_0 , ν , h , c , k_B , and T are the wavenumber of incident light, Raman shift, Planck constant, speed of light, Boltzmann constant, and thermodynamic temperature, respectively. All of the spectral lines were fitted with Gaussian–Lorentzian mixing functions using a curve analysis program (Grams/386, Galactic Industries Co, Salem, NH).

2.3. Density functional theory and solvent-accessible surface area calculations

All of the DFT calculations were carried out using the GAUSSIAN 09 program [11]. The DFT method used the Becke (B) exchange function and Becke's three-parameter (B3) exchange function [12,13] combined with the Lee–Yang–Parr correlation function (B3LYP) [14]. For all of the conformers of 1,4-dioxane, the geometric optimization, harmonic vibrational wavenumber, and Raman scattering activity calculations were performed at the B3LYP/aug-cc-pVTZ [15] level of theory. Here, the Raman activity is defined as $(45\alpha'^2 + 7\gamma'^2)$, where α' and γ' are the derivatives of the mean polarizability and anisotropy of polarizability tensor, respectively.

For the estimation of the electrostatic and non-electrostatic contributions to the thermodynamic differences between the conformers of 1,4-dioxane, we used the polarizable continuum model (PCM) [16] and the solvation model based on density (SMD) [17] method. These calculations were performed at the B3LYP/6-311G** level. The alpha-shapes program [18] was used to calculate the solvent-accessible surface area (SASA) of the conformers of 1,4-dioxane. The calculations of the optimized geometry of the molecules were carried out using Bondi atomic radii [19] and a probe radius of 1.4 \AA .

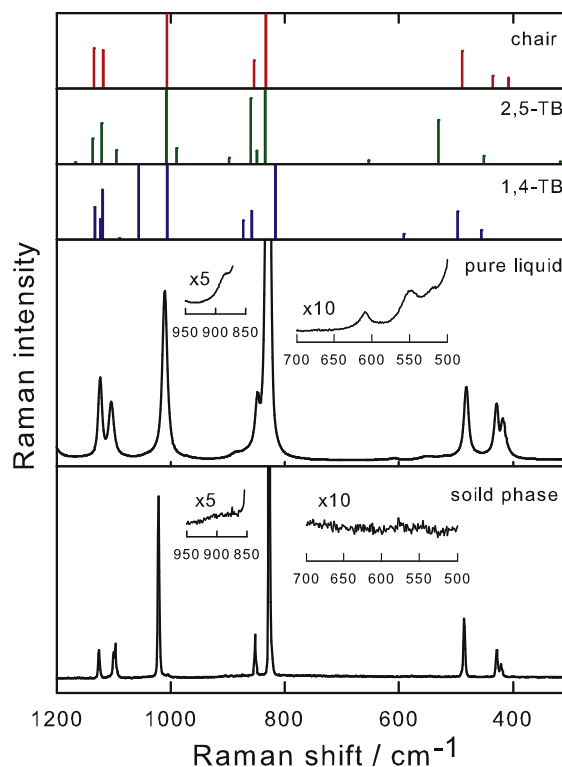


Figure 1. Raman spectra of the liquid and solid phases of 1,4-dioxane, and the Raman spectra of the chair, 2,5-TB, and 1,4-TB conformers calculated at the B3LYP/aug-cc-pVTZ level.

3. Results and discussion

3.1. Raman spectra of 1,4-dioxane and conformational analyses

From quantum chemistry calculations [20], 1,4-dioxane can be considered to have three conformers, i.e., chair, 1,4-TB, and 2,5-TB, because all of the other possible conformers correspond to transition states. The relative energies of 1,4-TB and 2,5-TB with respect to the chair conformer are 27.7 and 28.5 kJ mol^{-1} [20], so the Boltzmann ratios of the chair, 1,4-TB, and 2,5-TB conformers are calculated to be 1.0, 1.0×10^{-5} , and 1.4×10^{-5} , respectively.

Figure 1 shows the experimental Raman spectra of pure liquid (room temperature) and solid state (150K) 1,4-dioxane, and the DFT-calculated spectra of the conformers. Because the chair conformer only exists in the solid state according to XRD study [21], the observed peaks of solid state 1,4-dioxane are attributed to the chair conformer. Indeed, these peaks are consistent with the peaks of the chair conformer obtained by DFT calculation. In liquid 1,4-dioxane, additional Raman bands are observed at 525, 550, 610, and 875 cm^{-1} , which are fundamental vibrational bands because no potential bands causing overtones and combinational bands are observed in the low-frequency region. This means that as well as the chair conformer, other conformers also exist in the liquid phase. Indeed, the peak frequencies of these bands are consistent with those of the 1,4-TB and 2,5-TB conformers obtained by DFT calculation.

For detailed conformational analysis of liquid 1,4-dioxane, we performed curve analysis of the Raman spectra between 300 and 700 cm^{-1} with Gaussian–Lorentzian mixing functions, as shown in Figure 2. The peaks were successfully separated to determine the Raman intensities of the observed bands. The Raman bands at 488, 525, and 550 cm^{-1} are assigned to the OCC deformation modes [20] of the chair, 1,4-TB, and 2,5-TB conformers, respectively. These bands are convenient for conformational analysis because they are

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