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Effects of intermolecular interactions on absorption intensities of the fundamental and the first, second, and third overtones of OH stretching vibrations of methanol and *t*-butanol d_9 in *n*-hexane studied by visible/near-infrared/infrared spectroscopy

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ABSTRACT

Visible (Vis), near-infrared (NIR) and IR spectra in the 15,600–2500 cm^{-1} region were measured for methanol, methanol- d_3 , and *t*-butanol- d_9 in *n*-hexane to investigate effects of intermolecular interaction on absorption intensities of the fundamental and the first, second, and third overtones of their OH stretching vibrations. The relative area intensities of OH stretching bands of free and hydrogen-bonded species were plotted versus the vibrational quantum number using logarithm plots ($V = 1-4$) for 0.5 M methanol, 0.5 M methanol d_3 , and 0.5 M *t*-butanol- d_9 in *n*-hexane. In the logarithm plots the relative intensities of free species yield a linear dependence irrespective of the solutes while those of hydrogen-bonded species deviate significantly from the linearity. The observed results suggest that the modifications in dipole moment functions of the OH bond induced by the formation of the hydrogen bondings change transient dipole moment, leading to the deviations of the dependences of relative absorption intensities on the vibrational quantum number from the linearity.

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1. Introduction

Application of near-infrared (NIR) spectroscopy to physical chemistry stretched back more than 60 years [1–3]. Even in 1950s it was recognized that NIR spectroscopy is useful for investigating hydrogen bonding and intermolecular interactions. Studies on anharmonicity were also fairly active in 1950s and 1960s [1–3]. However, since that time, development of NIR spectroscopy particularly that in basic studies was rather slow partly because advances in spectrometers that could be used in the NIR region were insufficient and partly because spectroscopical analysis in the NIR region was not always easy. It was only since 1990s that NIR spectroscopy has received keen interest as a unique spectroscopic technique for exploring various physicochemical properties such as intermolecular interactions, solvent effects, and solvent–solute interactions [1,4–22]. In 1990s thanks to rapid progress in FT-NIR spectrometers and spectral analysis methods such as chemometrics and two-dimensional (2D) correlation analysis, NIR spectroscopy showed remarkable development not only in application studies but also in basic studies [1,2,6]. Another important point in

recent progress in NIR spectroscopy is the development of quantum chemical calculations [16–20,22–26]. Nowadays, one can calculate wavenumbers and absorption intensities of overtones of XH (X = C, O, and N) vibrations. Recently, empirically-known characteristic of absorption intensities of XH overtones were explained by theoretically. Although intensities of XH fundamentals significantly increase acidity of the molecules due to the different dipole moment function (DMF), intensities of XH overtone shows much smaller molecular variance than those for fundamentals. Takahashi et al. theoretically demonstrated that overtone intensities of OH-stretching mode among molecules are not different even if DMFs changes due to acidity of the molecules [23, 24].

Because of these marked development of NIR spectroscopy, several research groups have recently been involved in investigations on solvent and intermolecular interaction dependences of absorption intensities and wavenumbers of the fundamental and overtones of OH and NH stretching vibrations, their anharmonicities and vibrational potentials by using NIR/IR spectroscopy and quantum chemical calculations [14–22].

Putami et al. investigated effects of hydrogen bonding and solvent dependences on wavenumbers and absorption intensities of the fundamental and the first overtone of the NH stretching vibration of pyrrole in solutions by using NIR/IR spectroscopy and DFT calculations [19,20].

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They revealed the difference between the hydrogen bonding and the solvent-solute interaction in effects on the wavenumbers and absorption intensities of the NH fundamental and its first overtone. As to the first overtone of the NH stretching mode of pyrrole, absorption band for free pyrrole in the solvent was observed at 6856 cm^{-1} , but that of the pyrrole–pyridine complex was disappeared or unobservable weak [19]. The results of their DFT calculations for free pyrrole and pyrrole–pyridine complex indicated significant intensity decrease in the first overtone of the hydrogen-bonded NH group compared to that of the free pyrrole [19]. As to the solvent effects, they studied the effect of dielectric constant of the solvents on their absorption intensities and the wavenumbers of the NH fundamental and its first overtone by both experimental and theoretical approach. According to experimental results using solvent of for CCl_4 , CHCl_3 , and CH_2Cl_2 , intensities increase and wavenumbers decrease in the same order of the dielectric constant of the solvents [20]. Theoretical consideration of solvent effect regarding to dielectric constant with SCRF/PCM calculations agree with the experimental one [20].

Gonjo et al. measured VIS/NIR/IR spectra of phenol and 2, 6-difluorophenol, 2, 6-dichlorophenol, and 2, 6-dibromophenol in *n*-hexane, CCl_4 , CHCl_3 and CH_2Cl_2 to investigate hydrogen bonding effects and solvent dependences of wavenumbers and absorption intensities of the fundamental and the first, second, and third overtones of OH stretching vibrations [21]. They discussed about the relative intensities of the OH stretching vibrations of phenol and 2, 6-difluorophenol in CCl_4 , CHCl_3 , and CH_2Cl_2 against those in *n*-hexane. The relative intensities are larger than 1.0 in the fundamental and the second overtone but smaller than 1.0 in the first and third overtones [21]. Significance of even-odd exchange is more remarkable for phenol which does not have an intramolecular interaction on OH. Thus, they concluded that the intermolecular hydrogen bond between the OH group and the Cl atom plays a key role for the changes in the intensities [21].

In the present study we have investigated effects of intermolecular interactions on absorption intensities of the OH fundamental and the first, second, and third overtones of methanol, methanol- d_3 , and *t*-butanol- d_9 , in *n*-hexane by using Vis/NIR/IR spectroscopy. We selected these molecules because they easily form hydrogen-bonded species while in enough dilute solutions they do not form hydrogen-bonded species and have an intermolecular interaction with a solvent (solvent effect).

We have plotted relative intensities of OH stretching bands for the free and hydrogen bonded species versus the vibrational quantum number, and found that the free species shows linear dependence in the logarithm plot while the hydrogen bonded species yield deviations from the linear dependence. These results for the plots of the relative intensities of OH stretching bands have been analyzed by the equation of transient dipole moment which may have effects from the formation of hydrogen bondings.

2. Experimental

Methanol (Wako, 99.8%), methanol- d_3 (Cambridge Isotope Laboratories, 99.5%), and *t*-butanol- d_9 (Cambridge Isotope Laboratories, 98%) were purchased and used without further purification. *n*-Hexane (Wako, 97.0%) was treated with molecular sieves (3 Å and 4 Å) before use.

Vis/NIR/IR spectra of the solutions in the region of $15,600\text{--}2500\text{ cm}^{-1}$ were measured with an FT-NIR/IR spectrophotometer (Perkin-Elmer Spectrum One NTS FT-NIR spectrometer). The spectral resolution used was 2 cm^{-1} and the number of spectral accumulations was 64 for the fundamental and the first overtone region. For the second and third overtone region, they were 4 and 256 cm^{-1} , respectively. Quartz cells with the pathlengths of 0.5, 10, and 100 mm were employed for the spectral measurements of the $3800\text{--}3000$, $7500\text{--}6000$, and $14,500\text{--}8500\text{ cm}^{-1}$ regions, respectively.

3. Results

3.1. VIS/NIR/IR Spectra of Free and Self-associated Species of Methanol, Methanol- d_3 , and *t*-Butanol- d_9

Fig. 1 (a), (b), (c), and (d) shows an IR spectrum in the $3800\text{--}3000\text{ cm}^{-1}$ region, NIR spectra of $7500\text{--}6000$ and $10,750\text{--}8500\text{ cm}^{-1}$ regions, and VIS/NIR spectrum in the $14,500\text{--}11,500\text{ cm}^{-1}$ region of 0.5 M methanol- d_3 in *n*-hexane, respectively. The corresponding spectra of 0.5 M *t*-butanol- d_9 in *n*-hexane are depicted in Fig. 2 (a), (b), (c), and (d), respectively. Bands due to the OH stretching modes of free methanol- d_3 and *t*-butanol- d_9 are observed at 3654 and 3625 cm^{-1} , respectively (Fig. 1 (a) and Fig. 2 (a)). Bands due to their first, second, and third overtones are identified at 7137 , $10,447$, and $13,587\text{ cm}^{-1}$ for the methanol- d_3 solution, at 7074 , $10,350$, and $13,454\text{ cm}^{-1}$ for the *t*-butanol- d_9 solution.

Broad features in the $3600\text{--}3000\text{ cm}^{-1}$ region in Fig. 1 (a) and Fig. 2 (a) arise from hydrogen-bonded species of methanol- d_3 and *t*-butanol- d_9 , in *n*-hexane. The broad features consist of bands due to dimer, trimer, and oligomers. It is noted that the broad bands become much weaker in the first, second, and third overtone regions (Fig. 1 (b), (c), and (d) and Fig. 2 (b), (c), and (d)).

We estimated absorption intensities of the fundamental and the first, second and third overtones of OH stretching modes of the free and self-associated species. For the estimation of the band area of free species the area was separated by curve fitting. The band area of self-associated species was estimated by subtracting the band area of free species from the whole area. Although the band area of self-associated species is composed of the overlap of bands assigned to dimer, trimer, and oligomers, we estimated the area intensity as a whole.

Fig. 3 plots the ratio of the area intensity of hydrogen-bonded species to that of free species for the 0.5 M methanol, methanol- d_3 and *t*-butanol- d_9 versus the vibrational quantum number. Because these ratios arise from the same solution, they should be the same among the fundamental and the overtone vibrations if the effect of the hydrogen bonding on the absorption intensities is the same among the vibrations. However, as can be seen in Fig. 3, the ratios for the fundamentals are very large, while those for the overtones are very small and change little. These results demonstrate that the effect of hydrogen bondings on the absorption intensities works largely for the fundamentals than for the overtones, as in the cases of our previous studies on phenol and 2, 6-dihaloeno phenols [21].

Fig. 4 plots normalized intensities of the OH stretching bands of free and self-associated species versus the vibrational quantum number for methanol, methanol- d_3 , and *t*-butanol- d_9 in *n*-hexane. The normalization was carried out for the first overtone ($V = 2$). It can be seen from Fig. 4 that, the relative intensities of free species yield a linear dependence irrespective of the solutes while those of hydrogen-bonded species deviate largely from the linearity. Note that the normalized intensities in the third overtone ($V = 4$) coincide well between the hydrogen-bonded and free species. The intensities of the hydrogen-bonded species are stronger in the fundamentals and weaker in the second overtones than that of the free species.

4. Discussion

4.1. Logarithm Plots of Relative Intensities of OH Stretching Bands

Fig. 5 shows logarithm plot of observed $\frac{A(V)I^{\sim V_0}}{A(2)I^{\sim 2_0}}$ and $\frac{\mu_{V_0}^2}{\mu_{2_0}^2}$ of the free species of (a) methanol and (b) *t*-butanol- d_9 derived from the equation discussed below (Eq. (7)) together with the recent ab-initio results for gas phase molecules by Takahashi et al. [16]. The results in Fig. 5 can be reproduced by simple Morse type assumption. Absorption coefficient

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