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Absorption intensity changes and frequency shifts of fundamental and first overtone bands for OH stretching vibration of methanol upon methanol–pyridine complex formation in CCl₄: analysis by NIR/IR spectroscopy and DFT calculations

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Infrared (IR) and near infrared (NIR) spectra were measured for methanol and the methanol–pyridine complex in carbon tetrachloride. Upon the formation of the methanol–pyridine complex, the frequencies of both the fundamental and first overtone bands of the OH stretching vibration shifted to lower frequencies, and the absorption intensity of the fundamental increased significantly, while that of the first overtone decreased markedly. By using quantum chemical calculations, we estimated the absorption intensities and frequencies of the fundamental and first overtone bands for the OH stretching vibration based on the one-dimensional Schrödinger equation. The calculated results well reproduced the experimental results. The molecular vibration potentials and dipole moment functions of the OH stretching vibration modes were compared between methanol and the methanol–pyridine complex in terms of absorption intensity changes and frequency shifts. The large change in the dipole moment function was found to be the main cause for the variations in absorption intensity for the fundamental and first overtone bands.

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1. Introduction

Basic near-infrared (NIR) spectroscopy studies, including those on overtones, combination modes, anharmonicity and vibrational potentials have recently shown marked progress, partly because of advances in spectral analysis in the NIR region and partly due to the development of quantum chemical calculations.^{1–4} Bands due to overtones are forbidden in harmonic oscillator approximations, and such bands arise from the anharmonicity of molecular vibrations so that the frequencies and intensities of the bands are sensitive to molecular structure as well as intra- or intermolecular interactions such as those related to NH–N, OH–O, and N(O)H... π hydrogen bonds.^{1,2,4}

The intensities of overtones decrease in an exponential manner with an increase in the vibrational quantum number. There is a well-known characteristic called the normal intensity

distribution law.⁵ The absorption intensity is calculated from the vibrational wave functions and the dipole moment functions.⁶ Yabushita *et al.* calculated the fundamental and overtone band intensities for the OH stretching of alcohols and acids, as well as for the CH stretching of hydrocarbons with different types of hybridization.^{7–10} They reported that the conditions for the dipole moment functions are related to the small variations in the overtone intensities for XH (X = C, O) stretching vibrations that depend on the nature of the adjacent substituents.

It is well known that the formation of OH and NH hydrogen bonds increases the absorption intensity of the fundamental band, but that it is very difficult to observe the first overtone for the stretching mode of a hydrogen bonded OH (NH) group.^{11–13} Kjaergaard *et al.* studied intramolecular hydrogen-bonding of 1,2-ethanediol, 1,3-propanediol, and 1,4-butanediol and found that the intensities of the fundamental bands for the OH stretching modes increased upon the formation of OH–O intramolecular hydrogen bonds, while the intensities of the first overtones decreased.^{14,15} The first overtones were so weak that they could not be observed. Moreover, they predicted that the increase in the strength of the hydrogen bond made the observation of the first overtones more difficult. They also reported similar studies for the OH–N intramolecular hydrogen

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bonds of 2-aminoethanol and 3-aminopropanol.¹⁶ Furthermore, Kjaergaard *et al.* measured the absorption intensities and frequencies of the fundamental and first overtone bands for the OH stretching mode of methanol–trimethylamine complexes in gaseous states, and compared these experimental results with the results of quantum chemical calculations.¹⁷ The band at 3358 cm^{−1} was assigned to the fundamental band for the OH stretching mode of intermolecular OH–N hydrogen bonds, and the band at 6450 cm^{−1} was tentatively assigned to the first overtone. However, they did not describe the absorption intensity of the first overtone. Perchard *et al.* measured the NIR/IR spectra of methanol monomers and dimers trapped in solid N₂ and reported the absorption intensities and frequencies of the fundamental and first overtone bands for the OH stretching mode.¹⁸ According to their study, the intensity of the first overtone compared with that of the fundamental of OH stretching mode is much weaker for the proton acceptor OH group of the methanol dimer than that of the methanol monomer. However, they did not report the absorption intensity ratio of the fundamental and the first overtone bands between the monomer and the dimer; hence, there is no clear understanding of changes in the absorption intensity upon hydrogen bonding.

We used NIR/IR spectroscopy and density functional theory (DFT) calculations to investigate absorption intensity changes and frequency shifts of the fundamental and first overtone bands for the NH stretching vibration of pyrrole upon the formation of the pyrrole–pyridine complex in carbon tetrachloride solutions, and upon solvent changes.^{19–21} Variations in absorption intensity variations with a frequency shift were quite different between hydrogen bond formation and solvent change. In the comparison of absorption intensity changes and frequency shifts of fundamentals and the first overtones of the NH stretching mode of pyrrole between pyrrole and the pyrrole–pyridine complex. We reported that for the absorption intensity per one pyrrole molecule the fundamental of the NH stretching vibration band increases upon the formation of the pyrrole–pyridine complex but that of the first overtone of the complex is missing or too weak to be observed. There is no report on the clear observation of any band due to the first overtone for the methanol OH stretching mode that is involved in intermolecular hydrogen-bonding, or on changes in the absorption intensity of the first overtone before and after hydrogen bond formation.

In the present study, we have investigated absorption intensity changes and frequency shifts of the fundamental and first overtone bands for the OH stretching vibration of methanol upon the formation of a methanol–pyridine complex in carbon tetrachloride solutions using NIR/IR spectroscopy and DFT calculations. Pyridine is a representative proton acceptor, and it does not have a peak that overlaps with an OH stretching band. In our previous NIR/IR study on the pyrrole–pyridine complex, we were unable to experimentally observe the band due to the first overtone for the stretching mode of the hydrogen-bonded NH group.¹⁹ However, in the present study, we succeeded in observing a band due to the first overtone for the stretching mode of the hydrogen-bonded OH group of

methanol experimentally, by adjusting the amounts of the hydrogen donor and the hydrogen acceptor.

We estimated the optimized structures of methanol and the methanol–pyridine complex by using DFT calculations and then calculated the absorption intensities and frequencies of the fundamental and first overtone bands for the OH stretching vibration based on the one-dimensional Schrödinger equation. The calculated frequencies and absorption intensities were in good agreement with the experimental results. The calculations of the vibrational wave function and the dipole moment function along with the potential energy curves of OH stretching modes of the methanol monomer and its complex with pyridine led us to conclude that the transition dipole moment containing the dipole moment function plays a key role in the remarkable intensity decrease in the overtone of the stretching mode of the hydrogen-bonded OH group. We also compared the absorption intensity changes and frequency shifts of the fundamental and first overtone bands for the OH stretching vibration of methanol upon the formation of the methanol–pyridine complex with those for the NH stretching mode of pyrrole upon the formation of the pyrrole–pyridine complex.

2. Experimental and quantum chemical calculation methods

Carbon tetrachloride (Wako, 98% purity) solutions of methanol (Wako, 99.5% purity) and pyridine (Wako, 98% purity), as well as a mixture of methanol and pyridine in carbon tetrachloride, were prepared with methanol concentrations ranging between 0.005 and 0.500 mol dm^{−3}. NIR/IR spectra of the solutions in the 12 000–2500 cm^{−1} region were measured using a Fourier-transform infrared spectrophotometer (JASCO FT-IR6000SS). The spectral resolution used was 1.0 cm^{−1}, and the number of spectral accumulations was 16. The spectra were measured at room temperature using a rectangular quartz cell with a pass length of 10 mm.

The Gaussian 09 program²² 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 for the calculation of vibrational potential curves and dipole moment functions.^{23,24} The one-dimensional Schrödinger equation for the OH stretching mode, as shown in eqn (1) was solved:

$$H\psi_v(q) = \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dq^2} + V(q) \right] \psi_v(q) = E_v \psi_v(q) \quad (1)$$

where q , μ and $V(q)$ are the normal coordinate, reduced mass, and potential energy function, respectively. The oscillator strength for each O–H stretching transition was calculated by using the relation

$$f_{v0} = \frac{4m_e\pi}{3e^2\hbar} |\bar{\mu}_{v0}|^2 \tilde{\nu}_{v0} = 4.702 \times 10^{-7} |\bar{\mu}_{v0}|^2 \tilde{\nu}_{v0} \quad (2)$$

where $\tilde{\nu}_{v0}$ is the transition energy in cm^{-1} and $|\bar{\mu}_{v0}|^2$ is the sum of the squared transition dipole moments of the x, y, and z components with $(\text{debye})^2$ as the unit.^{10,25} $|\bar{\mu}_{v0}|^2$ is given by

$$\begin{aligned} |\bar{\mu}_{v0}|^2 &= |\bar{\mu}_{v0}^x|^2 + |\bar{\mu}_{v0}^y|^2 + |\bar{\mu}_{v0}^z|^2 \\ &= \left| \int \psi_v(q) \bar{\mu}^x \psi_0(q) dq \right|^2 \\ &\quad + \left| \int \psi_v(q) \bar{\mu}^y \psi_0(q) dq \right|^2 + \left| \int \psi_v(q) \bar{\mu}^z \psi_0(q) dq \right|^2. \end{aligned} \quad (3)$$

Here, $|\bar{\mu}_{v0}^z|^2 = 0$ because the O–H stretching is in the A' mode.

We obtained numerical results for the energy levels and wave functions using Johnson's method.²⁶ The potential energy curves used for the calculations cover the range 0.5–2.0 Å, in steps of 0.02 Å around the equilibrium position. The number of calculation points is sufficient for the numerical calculations; no other assumptions such as the Morse function were used. This ensures converged energy levels with a precision higher than 0.001 cm^{-1} . The calculation conditions for Gaussian 09 were tight convergence in the SCF and the standard grid in DFT.

3. Results and discussion

Fig. 1 shows IR spectra in the $3900\text{--}3100 \text{ cm}^{-1}$ region for CCl_4 and for CCl_4 solutions with various concentrations of methanol (0.005, 0.010, 0.025, 0.050, 0.075, and $0.100 \text{ mol dm}^{-3}$). Kristiansson *et al.* assigned bands at 3645, 3519, and 3362 cm^{-1} to the monomer, dimer, and various chain aggregated of methanol, respectively.²⁷ In the case of the fundamentals we cannot find any additional bands by calculating second derivatives. Fig. 2a–c shows IR spectra in the region of $3900\text{--}3100 \text{ cm}^{-1}$ for CCl_4 solutions of pyridine (a), methanol (b), and mixed pyridine and methanol (c). Fig. 2d shows the difference spectra calculated by subtracting the spectra of methanol and pyridine from the spectra of the methanol–pyridine mixture. In the difference spectra, the concentrations of methanol and pyridine in the mixed solution are equal to those of methanol and pyridine in the respective

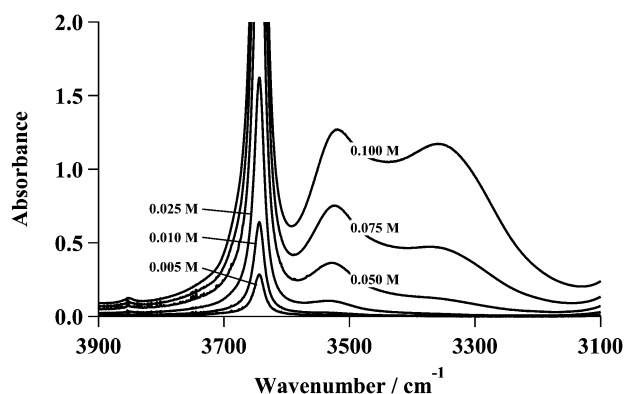


Fig. 1 Concentration dependence of IR spectra of methanol in carbon tetrachloride. The absorptivity at 3465 cm^{-1} of a monomer is $6.5 \text{ m}^2 \text{ mol}^{-1}$.

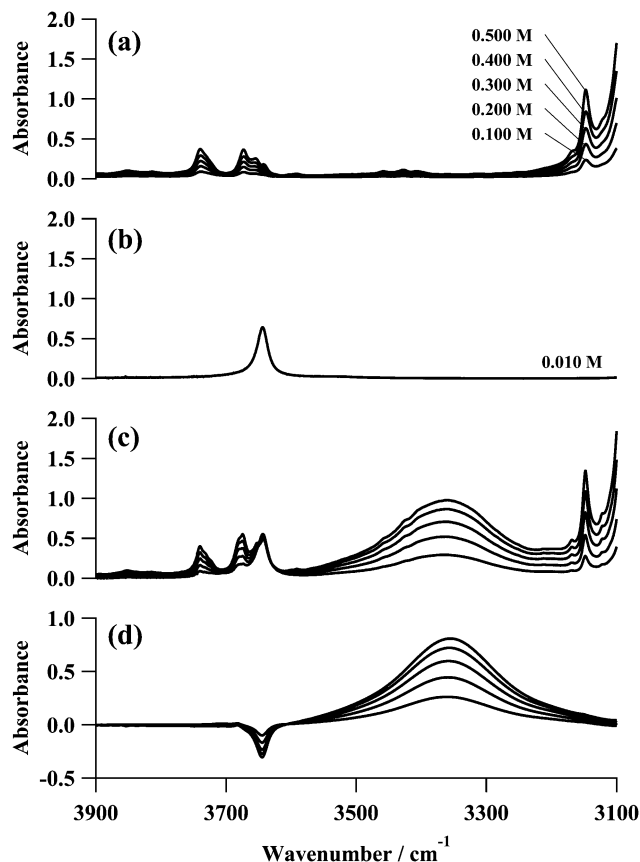


Fig. 2 IR spectra of (a) pyridine, (b) methanol, and (c) mixed pyridine and methanol, and (d) the difference spectrum [(mixed methanol and pyridine)–(methanol)–(pyridine)] in carbon tetrachloride.

CCl_4 solutions. The concentrations of methanol and pyridine in the mixed solutions were 0.010 and 0.100, 0.200, 0.300, 0.400, $0.500 \text{ mol dm}^{-3}$, respectively.

By varying the concentrations of the CCl_4 solutions, we confirmed that no dimers of methanol were present in any detectable amount under the above experimental conditions (Fig. 1). The CCl_4 solution of methanol showed a very strong and sharp band at 3645 cm^{-1} , assignable to the OH stretching mode of the methanol monomer (Fig. 2b). A notable point in Fig. 2d is a strong feature observed near 3356 cm^{-1} . This peak could be assigned to the OH stretching mode of the OH–N hydrogen bond of the methanol–pyridine complex. The difference spectrum demonstrates that the OH stretching band of the methanol monomer, at 3645 cm^{-1} , is weakened, while the band at 3356 cm^{-1} emerges only in the spectra of the mixture, indicating the formation of a hydrogen-bond complex.

Fig. 3 shows the corresponding NIR spectra in the $7700\text{--}6100 \text{ cm}^{-1}$ region. One can expect the first overtones of the OH stretching modes in this region. The overtone and combination bands of the CH stretching modes are also expected to appear in this region. The first overtone for the OH stretching mode of the methanol monomer is clearly observed at 7121 cm^{-1} . The first overtone band of the methanol–pyridine complex is not initially clear, but is detectable near 6400 cm^{-1} upon close

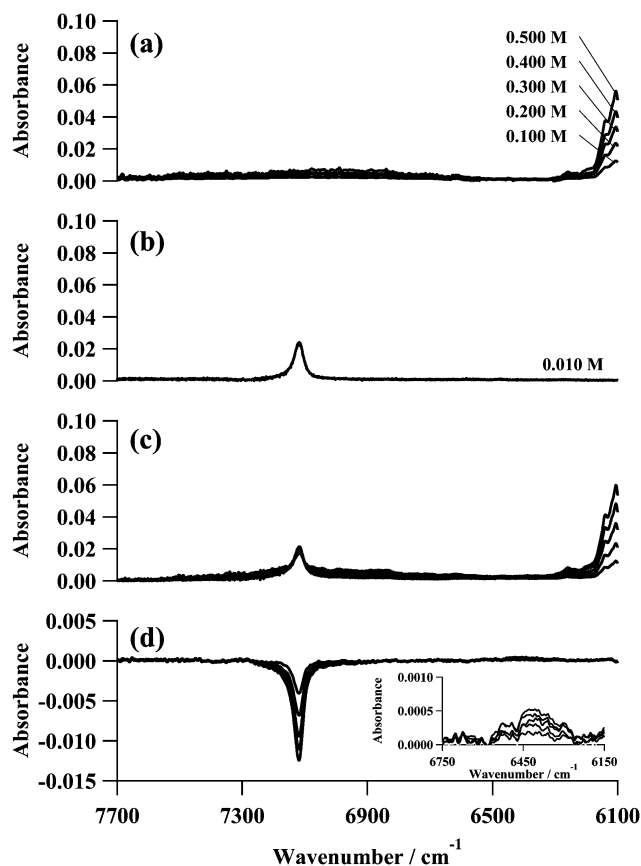


Fig. 3 NIR spectra of (a) pyridine, (b) methanol, and (c) mixed pyridine and methanol, and (d) the difference spectrum [(mixed methanol and pyridine) - (methanol) - (pyridine)] in carbon tetrachloride. Inset: enlargement of the 6750–6150 cm^{-1} region in (d).

inspection (see the inset). The first overtone for the OH stretching mode of the methanol–pyridine complex is observed at 6404 cm^{-1} . The detection of additional peaks by the second derivative for overtones was difficult because of the insufficient S/N of the spectra. The region in the vicinity of 6400 cm^{-1} both methanol and pyridine do not have a significant peak, and moreover, the observed band is very broad. Thus, we have assigned the band to the first overtone of the stretching vibration of an OH group which is involved in a hydrogen-bonding. The integrated intensity was estimated by the integral

calculus of the Gauss function. The observed peak is very broad, and in addition it is very weak. Its frequency may have an error of *ca.* 30 cm^{-1} , and it is very likely that its area intensity includes an error of 30%. The observed frequency and relative absorption intensities of the fundamental band and the first overtone for the OH stretching mode of methanol and methanol–pyridine complexes are given in Table 1, with the calculated anharmonicity coefficients.

The area intensity of the fundamental band assigned to the complex is about 19 times larger than that of the monomer. If the absorption intensity of the overtone had increased similar to that of the fundamental band, the overtone of the complex should have been clearly observable. However, the area intensity of the first overtone for the OH stretching mode of the methanol–pyridine complex was very weak, about 0.01 times that of the fundamental band of the monomer.

Fig. 4 depicts the optimized structures of methanol and the methanol–pyridine complex. Their structures have C_s symmetry. The calculated OH–N distance (1.94 Å) is much shorter than the van der Waals radius (2.70 Å), and the calculated bond length of the hydrogen-bonded OH group (0.97 Å) is greater than the bond length of the free OH group of methanol (0.96 Å). The stabilization energy, ΔE , is calculated to be 25.7 kJ mol^{-1} ,

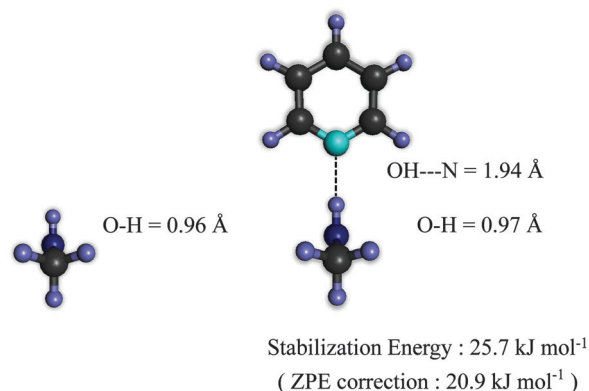


Fig. 4 Optimized structures of methanol and methanol–pyridine complex calculated at the DFT//B3LYP/6-311++G(3df,3pd) level. The stabilization energy of the methanol–pyridine complex is 25.7 kJ mol^{-1} , or 20.9 kJ mol^{-1} after correction for zero-point energy. The OH–N distance is 1.94 Å (sum of van der Waals radii is about 2.70 Å).

Table 1 Observed and calculated wavenumbers (cm^{-1}) and relative absorption intensities of the fundamental and the first overtones bands for the OH stretching mode of methanol and methanol–pyridine complexes

V	Obs.								Calc.						
	Gas ¹⁷				Ar-matrix ¹⁸				B3LYP						
	CH ₃ OH		CH ₃ OH		CH ₃ OH		CH ₃ OH ··· NC ₄ H ₄		CH ₃ OH		CH ₃ OH ··· NC ₄ H ₄			CH ₃ OH ··· NC ₄ H ₄	
	ν	Int.	ν	Int.	ν	Int.	ν	Int.	ν	ν	Int.	ν	ν	Int.	Int.
1	3681	—	3664	1.00	3645	1.00	3356	19.05	3846	3677	1.00	3553	3314	48.71	
2	7196	—	7159	0.05	7121	0.06	6404	0.01		7189	0.15		6380	0.06	
χ	−83		−85		−85		−154			−82			−124		

Anharmonicity coefficient $\chi = 2\nu \times 0.5 - \nu$.

and the zero-point energy correction gives 20.9 kJ mol^{-1} . The harmonic oscillator calculation yields frequencies of the OH stretching mode of methanol and the methanol-pyridine complex at 3846 cm^{-1} and 3553 cm^{-1} , respectively (Table 1). According to the one-dimensional wave equation, the frequencies of the fundamental and first overtone bands of the OH stretching mode of the methanol monomer are 3677 and 7189 cm^{-1} , respectively, which are close to the observed frequencies (3681 and 7196 cm^{-1}) of the methanol monomer in the gas phase.¹⁷ The observed frequencies of the fundamental and first overtone bands for the OH stretching mode of methanol in CCl_4 solution, 3645 and 7121 cm^{-1} , are 36 and 75 cm^{-1} lower than those of the monomer in the gas phase, respectively. The frequencies of the fundamental and first overtone bands for the OH stretching mode of the methanol-pyridine complex are calculated to be 3314 and 6380 cm^{-1} , respectively. The observed frequencies of the fundamental and first overtone bands are 3356 and 6404 cm^{-1} , respectively (Table 1). Generally, positions of the fundamental bands are calculated more precisely than those of the overtones. However, the calculated position of the first overtone of the methanol-pyridine complex is closer to the experimental position than the calculated position of the fundamental. The fact may occur because the quantum chemical calculations did not involve an effect of solvent and/or it may occur accidentally due to the errors of observed frequencies of overtones.

Note that the experimental and calculated values of the anharmonicity coefficient of the monomer are in good agreement with each other. The anharmonicity coefficient of the methanol-pyridine complex is significantly larger than that of

the methanol monomer. This means that the OH vibrational potential deviates from the potential of the harmonic oscillator upon the formation of the hydrogen bond. The anharmonicity coefficient of -154 cm^{-1} of the methanol-pyridine complex is somewhat far from the anharmonicity coefficient of -115 cm^{-1} of liquid methanol reported by Bourdreon.²⁸ One of the reasons of the discrepancy may be the fact that the band due to the first overtone is broad, and thus, it was difficult to obtain accurate frequency. However, the anharmonicity of the gaseous methanol-trimethylamine complex reported by Howard¹⁷ was -133 cm^{-1} , suggesting that the anharmonicity is larger for the one-to-one complex than for the polymeric state. Moreover, the difference between the observed anharmonicity and calculated anharmonicity may be caused by the fact that the calculation did not consider the interaction with the solvent. According to the present calculation based on the one-dimensional wave equation, the intensity of the first overtone for the OH stretching band of the methanol monomer is 0.15 times weaker than that of the fundamental band (Table 1). The observed area intensity of the first overtone for the OH stretching band is only 0.06 times that of the fundamental band. Thus, the calculated overtone intensity is overestimated by a factor of about 2.5 . The first-overtone intensity for the OH stretching band of the methanol-pyridine complex was calculated to be 0.06 times of that of the fundamental of the methanol monomer. Although the calculated overtone intensity of the complex is, therefore, overestimated, the calculation results clearly reproduce the trend of the experimental results. Fig. 5 illustrates the total dipole moment function, vibrational potential curve, and wave functions of the OH stretching mode of (a) the

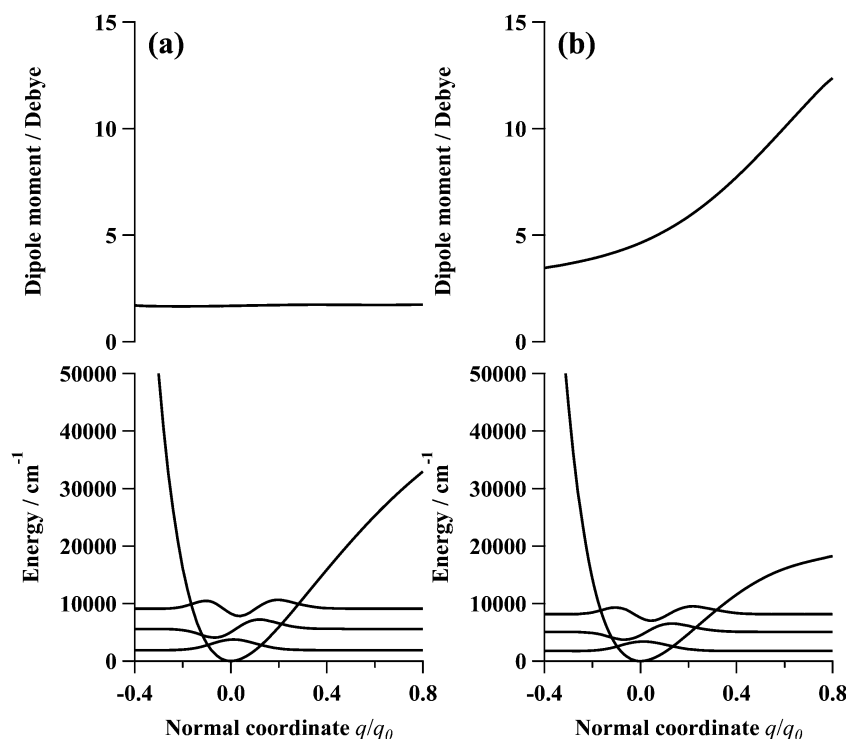


Fig. 5 Vibrational wave functions and total dipole moment functions along the potential energy curves of the OH stretching mode of (a) the methanol monomer and (b) the methanol-pyridine complex calculated at the DFT//B3LYP/6-311++G(3df,3pd) level.

methanol monomer and (b) the methanol-pyridine complex calculated at the DFT//B3LYP/6-311++G(3df,3pd) level. The OH stretching mode of methanol needs two axes for representing the variation in the dipole moment function because the symmetry of the molecular structure of methanol is lower as compared to that of pyrrole, whose NH stretching mode needs only one axis. However, the total dipole moment function is shown as a dipole moment function, because methanol and the methanol-pyridine complex in a solvent do not orient.

Of note in Fig. 5 is that the shape of the vibrational potential and dipole moment functions change greatly before and after the formation of the hydrogen bond. The dissociation energy decreases upon the formation of the hydrogen bond, and the vibrational potential curve deviates significantly from the curve for the harmonic oscillator. This result is in good agreement with the fact that the anharmonicity coefficient increases upon the formation of the hydrogen bond.

If only wave functions are considered, it is expected that the formation of the hydrogen bond induces an increase in the absorption intensity of the first overtone for the OH stretching mode. One can easily predict that the overlap integral of the wave functions of ν_1 and ν_3 increases upon the formation of the hydrogen bond, and thus, the absorption intensity of the first overtone seems to increase. However, the formation of the hydrogen bond causes a decrease in the absorption intensity of the first overtone. To explain the experimental results, one must consider a dipole moment function of the OH stretching mode. The transition dipole moment includes a dipole moment function as well as wave functions.

The variation in the dipole moment with the vibration of the OH stretching mode for the methanol-pyridine complex differs more significantly from that of the methanol monomer. A change in the dipole moment function of the OH stretching mode of methanol upon the formation of the hydrogen bond is similar to that of the NH stretching mode of pyrrole upon the formation of the methanol-pyridine complex.¹⁹ The large variations in the dipole moment function are the main cause for the variations in the strengths of the fundamental and first overtone bands. Under harmonic oscillator approximation, the larger the slope of the dipole moment function, the greater is the increase in the intensity of the fundamental band. The same result can be obtained under anharmonicity.^{19,20}

The reason for the overestimation of absorption intensities in the present calculation is probably because the effect of CCl_4 solution was not adequately taken into account. Despite the overestimation of the absolute values of the intensities, the calculation results clearly reproduce the experimental results related to the effects of hydrogen-bonding on the frequency shifts and intensity variations.

Both the experimental and calculation results show that the relative intensity of the first overtone *versus* the fundamental band for the OH stretching mode of the methanol monomer is larger than that of pyrrole. Moreover, DFT calculation estimates that the absorption intensity increase of the first overtone upon the formation of the methanol-pyridine complex is 20 times larger than that in the case of the pyrrole monomer.

Because of these differences, the first overtone for the NH stretching mode of the pyrrole-pyridine complex cannot be observed, while that of the OH stretching mode of the methanol-pyridine complex can be observed.

4. Conclusions

IR and NIR spectra were measured for methanol and the methanol-pyridine complex in carbon tetrachloride to investigate the effects of the formation of this complex on variations in the absorption intensities and frequencies of both the fundamental and first overtone bands for the OH stretching vibration. Quantum chemical calculations were also carried out to estimate the absorption intensities and frequencies of the fundamental and first overtone bands for the OH stretching vibration based on the one-dimensional Schrödinger equation.

We could observe a very weak peak due to the first overtone for the OH stretching mode of the OH-N hydrogen bond of the methanol-pyridine complex. The formation of the hydrogen bond increases the absorption intensity of the fundamental by 19 times and decreases that of the first overtone by 1/6. The absorption intensity of the fundamental band for the OH stretching mode increases, while that of the first overtone decreases markedly upon the formation of the methanol-pyridine complex. The quantum chemical calculations closely reproduced these intensity changes. The DFT calculation demonstrates that the vibrational potential and dipole moment function change greatly upon the formation of the hydrogen bond. In the vibrational potential, the dissociation energy decreases and the slope of the dipole moment function increases upon hydrogen-bonding. The decrease in the dissociation energy also appears in the change in anharmonicity.

The variation in the dipole moment function of the OH stretching mode of methanol upon the formation of the OH-N hydrogen bonds, as determined by the quantum chemical calculation, is similar to that of the NH stretching mode of pyrrole. In both cases, the large change in the dipole moment function is the main cause for the absorption intensity changes of the fundamental and first overtone bands.

The present study reported the frequency and absorption intensity of the first overtone of the stretching mode of an OH group that is involved in a hydrogen-bonding. This result may provide a basic knowledge for the future application of NIR spectrochemical analysis.

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