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Frequencies and absorption intensities of fundamentals and overtones of NH stretching vibrations of pyrrole and pyrrole–pyridine complex studied by near-infrared/infrared spectroscopy and density-functional-theory calculations

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ABSTRACT

Near-infrared (NIR)/IR spectra were measured for pyrrole, pyridine and pyrrole–pyridine complex in CCl₄ solutions. The first-overtone of the NH stretching vibration of free pyrrole was observed at 6856 cm^{−1}, but that of pyrrole–pyridine complex was missing or barely detectable. Theoretical calculations of the molecular vibrational potentials and the dipole moment functions of the NH stretching modes of free pyrrole and pyrrole–pyridine complex revealed that the transition dipole moment is significantly decreased upon formation of the complex, resulting in the remarkably weak intensity of the overtone mode of the hydrogen-bonded NH group.

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1. Introduction

During the last two decades near-infrared (NIR) spectroscopy has made a remarkable progress in its applications [1,2]. Following the applications the basic studies of NIR spectroscopy has also shown significant advance in recent years. For example, various methods of spectral analyses such as chemometrics and two-dimensional correlation analysis have been introduced to NIR spectroscopy [1–5]. The applications of NIR spectroscopy to physical chemistry are also notable. The values of NIR spectroscopy in applied sciences have stimulated basic physicochemical studies on the overtones and combination modes, and their anharmonicities.

In the meantime, recent advances in quantum chemical calculations have enabled calculations of the frequencies and absorption intensities of overtones and combinations of simple molecules. For example, Kjaergaard et al. [6,7] measured NIR spectra of methanol–trimethylamine complex and H₂O dimer in the gas phase. They also carried out the quantum chemical calculations for frequencies and intensities of the OH fundamental and first-overtone bands of methanol in the complex. The results showed that upon the formation of hydrogen bonding the intensity of the fundamental of the OH stretching mode of methanol was enhanced while that of the first-overtone was weakened. The investigation on the relation between the intensity of the first-overtone of the OH

stretching mode and the OH hydrogen bond of trifluoroethanol was also reported [8].

The intensity of the fundamental mode of OH stretching is known to increase upon formation of hydrogen bonding [9], but it has been pointed out that no such intensity increase occurs for overtones [10,11]. Simple explanations have been given for this difference between the fundamental and overtone modes [12–14], but there is no corresponding study on the NH fundamental and overtone modes.

In the present study, we have measured the NIR/IR spectra of pyrrole and pyrrole–pyridine complex in CCl₄ solution and carried out quantum chemical calculations based on the one-dimensional wave equation to investigate the vibrational characteristics of these molecules and their 1:1 complex. We have focused on the effects of hydrogen bonding on the intensities of the NH fundamental and first-overtone modes. Since the NH stretching modes of pyrrole and the complex belong to the A₁ symmetry species of C_{2v} point group, we only need to consider a change in the transition dipole moment along the NH stretching coordinate. Thus, the calculation turns out to be simple. While previous studies used model functions such as the Morse potential in calculations of a one-dimensional wave equation, we have numerically solved the one-dimensional wave equations for the NH stretching vibrations in the present study to obtain both the vibrational energy levels and the wave functions. Moreover, we have performed the calculations not only for the local mode but also for the vibrational modes based on the normal coordinates. Our analysis has revealed that the transition dipole moment for the overtone of the NH stretching

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mode is remarkably decreased by the formation of hydrogen bonding.

2. Experimental and calculation methods

Pyrrole (Tokyo Kasei Kogyo, 98% purity), pyridine (Wako, 98% purity), and CCl₄ (Wako, 98% purity) were used without further purification. The CCl₄ solutions of pyrrole and pyridine, and a mixed CCl₄ solution of pyrrole and pyridine were prepared. The concentrations of pyrrole and pyridine in the solutions were 0.04 mol L⁻¹.

NIR/IR spectra of the solutions in the region of 15 000–2500 cm⁻¹ were measured with an FT-NIR/IR spectrophotometer (Perkin-Elmer Spectrum One NTS FT-NIR/IR spectrometer). The spectral resolution used was 0.5 cm⁻¹, and the number of spectral accumulations was 16. The spectra were measured at room temperature by use of a rectangular cell with a pass length of 1 mm.

The density-functional-theory (DFT) calculations were carried out by using the GAUSSIAN 03 program with three basis sets (6-311++G(3df,3pd), 6-31+G**, 6-31G*) [15]. Becke's three-parameter hybrid density function in combination with the Lee–Yang–Parr correlation functional (B3LYP) was used for the optimization of geometrical structures and the calculations of normal coordinates, vibrational potential curves, and dipole moment functions [16,17].

In the present study, we solved the wave equation of one-dimensional NH stretching vibration

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

where q , μ and $V(q)$ are the normal coordinate, the reduced mass and the potential energy surface, respectively.

We calculated the integrated absorption coefficient (km mol⁻¹, base e) for each NH stretching transition by

$$A(v) = \ln 10 \int \varepsilon(\tilde{\nu}) d\tilde{\nu} = \frac{8N_A\pi^3}{3 \times 10^5 hc} |\bar{\mu}_{v0}|^2 \tilde{\nu}_{v0}, \quad (2)$$

where $\varepsilon(\tilde{\nu})$ is the molar extinction coefficient (base 10), $\tilde{\nu}_{v0}$ 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 in (debye)² units [18]. $|\bar{\mu}_{v0}|^2$ is given by

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

Here, $|\bar{\mu}_{v0}^x|^2 = 0$ and $|\bar{\mu}_{v0}^y|^2 = 0$, because this is the A₁ mode.

We obtained the numerical results for the energy levels and the wave functions using the method given by Johnson [19]. The potential energy curves used for the calculations cover the range from -0.7 to $1.0 q_0$ in $0.02 q_0$ steps around the equilibrium position, where q_0 is the unit for the normal coordinate corresponding to the NH stretching mode.

This number of calculation points is sufficient for the numerical calculations without such assumption as the Morse function. This ensures converged energy levels with precision higher than 0.001 cm⁻¹.

3. Results and discussion

3.1. Near-infrared spectra of pyrrole, pyridine and pyrrole–pyridine complex in CCl₄ solution

Fig. 1 shows IR spectra in the 4000–3000 cm⁻¹ region of CCl₄ solutions of pyrrole with different concentrations (0.8, 0.4, 0.2, 0.04, 0.02 mol L⁻¹) and CCl₄ itself. From the comparison of the spectra one can assign the bands at 3497 and 3422 cm⁻¹ to the NH stretching modes of the monomer and dimer of pyrrole in CCl₄ [20].

Fig. 2a–c shows NIR/IR spectra in the region of 8000–3000 cm⁻¹ CCl₄ solutions of pyrrole (a), pyridine (b), pyrrole and pyridine mixture (c), and Fig. 2d depicts the difference spectrum calculated by subtracting the spectra (a) and (b) from the spectrum (c). The concentrations of pyrrole and pyridine were 0.04 mol L⁻¹ in both cases. We confirmed by varying the concentrations of the CCl₄ solutions that no dimer of pyrrole was present in any detectable amount under the above experimental conditions (Fig. 1).

The pyrrole solution shows a very strong and sharp band at 3497 cm⁻¹ assignable to the NH stretching mode, whereas the pyridine solution gives no band above 3500 cm⁻¹ as expected. A notable point in Fig. 2c is a weak broad feature observed near 3265 cm⁻¹. This may be assigned to the NH stretching mode of the NH⋯N hydrogen bond of the pyrrole–pyridine complex. To account for the spectral changes induced by the formation of the complex, we calculated a difference spectrum as shown in Fig. 2d. The difference spectrum demonstrates that the NH stretching band at 3497 cm⁻¹ of pyrrole monomer is weakened while the band at 3265 cm⁻¹ emerges indicating formation of the complex.

Fig. 3 exhibits the enlargement of the 7500–5500 cm⁻¹ region of the spectra shown in Fig. 2. One can expect the first-overtone of the NH stretching modes in this region. The overtone and combination bands of the CH stretching modes are also expected to appear in the same region. The first-overtone of the NH stretching mode of pyrrole monomer is clearly observed at 6856 cm⁻¹. As shown in Fig. 3d, only a negative peak at 6856 cm⁻¹ is observed, but no first-overtone band of the complex was detected even when a cell of 10 mm was used.

A comparison of the area intensities of the fundamentals assigned to the monomer and the complex, listed in Table 1, shows that the area intensity of the complex is about eight times as large as that of the monomer. If the absorption intensity of the overtone was increased similarly to that of the fundamental, the overtone of

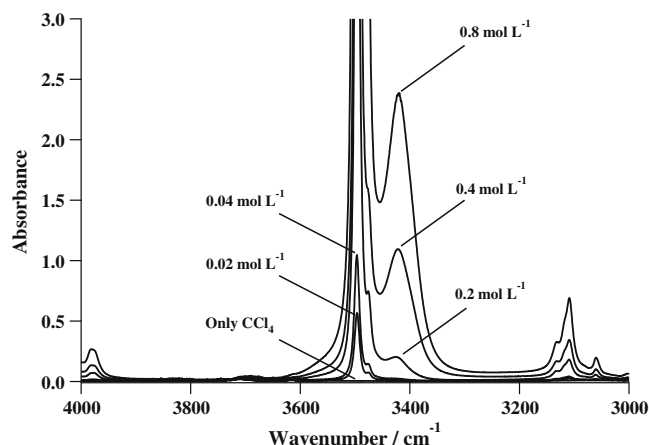


Fig. 1. IR spectra of the CCl₄ solutions of pyrrole with different concentrations (0.8–0.02 mol L⁻¹) and CCl₄ neat.

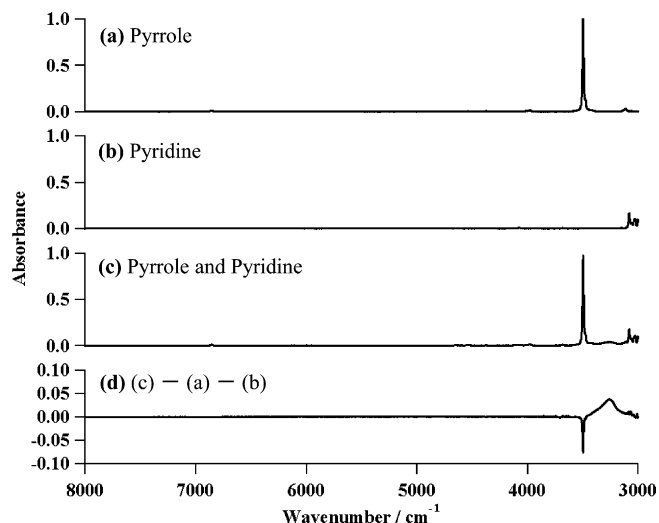


Fig. 2. FT-NIR/IR spectra of the CCl_4 solutions of (a) pyrrole and (b) pyridine, and (c) a mixed CCl_4 solution of pyrrole and pyridine; (d) [(c)–(a)–(b)]. Concentrations of pyrrole and pyridine were 0.04 mol L^{-1} for all the solutions (a)–(c).

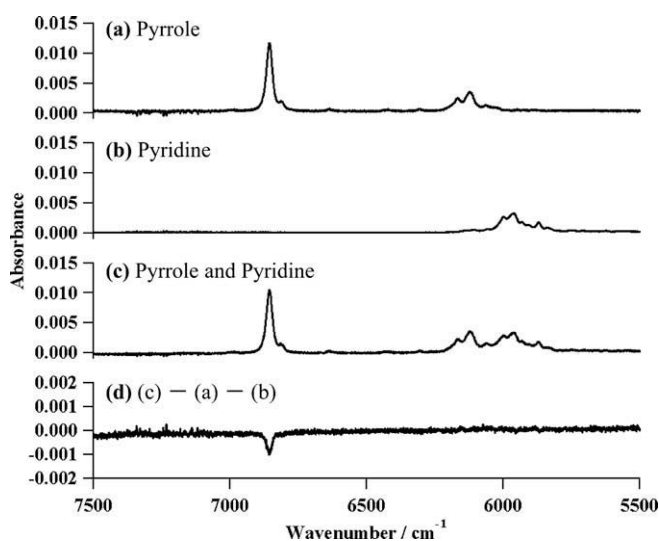


Fig. 3. FT-NIR spectra in the NH stretching overtone region of (a) pyrrole and (b) pyridine, and (c) a mixed CCl_4 solution of pyrrole and pyridine; (d) [(c)–(a)–(b)]. Concentrations of pyrrole and pyridine were 0.04 mol L^{-1} for all the solutions (a)–(c).

the complex should have been observed. However, the above-mentioned observation of the negative peak corresponding to the overtone of the complex indicates that this band is significantly weakened by complex formation.

Table 1

Observed and calculated wavenumbers (cm^{-1}) and relative absorption intensities of the fundamentals and the first-overtone of NH stretching bands of pyrrole and pyrrole–pyridine complexes.

	Pyrrole				Pyrrole–pyridine complex			
	ν	int.	2ν	int.	ν	int.	2ν	int.
Vapor ^a	3531	–	6925	–	–	–	–	–
In CCl_4	3497	1.000	6856	0.023	3265	8.184	–	–
B3LYP/6-311++G(3df,3pd)	3539	1.000	6944	0.057	3206	23.780	6200	0.003
B3LYP/6-31+G*	3547	1.000	6960	0.068	3212	23.634	6212	0.007
B3LYP/6-31+G	3528	1.000	6918	0.113	3235	31.284	6263	0.014

^a Ref. [20].

3.2. Optimized structure of pyrrole and pyrrole–pyridine complex

Fig. 4 depicts the optimized structure of pyrrole–pyridine complex. This structure has C_{2v} symmetry, and the two molecular planes are perpendicular to each other. The distance of $\text{NH} \cdots \text{N}$, calculated to be 2.02 \AA , is much shorter than the van der Waals radii (2.75 \AA), and the calculated bond length of the hydrogen-bonded NH group, 1.02 \AA , is very close to the bond length of the free NH group of pyrrole, 1.00 \AA . The stabilization energy, ΔE , is calculated to be 25.5 kJ mol^{-1} , and the zero-point energy correction gives 21.9 kJ mol^{-1} .

3.3. Vibration wave function, dipole moment function, and potential energy curves of NH stretching modes of pyrrole and pyrrole–pyridine complex

Fig. 5 depicts the vibration wave functions, dipole moment functions, and potential energy curves of the NH stretching modes of (a) pyrrole monomer and (b) pyrrole–pyridine complex. The dipole moment functions along the z-axis are shown in Fig. 5, where the z-axis is taken in the direction of the NH bond, as shown in Fig. 4. A change in the dipole moment of the NH stretching mode occurs only in the z-axis because of molecular symmetry.

It is notable in Fig. 5a and b that the potential energy curve and the dipole moment function change largely upon formation of the hydrogen bond. The potential energy curve is distorted, resulting in the lowering of the vibrational energy level. The dipole moment function is also distorted and the direction of the dipole moment vector is reversed.

3.4. Observed and calculated vibrational frequencies and absorption intensities of NH stretching bands of pyrrole and pyrrole–pyridine complex

The harmonic oscillator calculation yields frequencies of the NH stretching mode of pyrrole and pyrrole–pyridine complex at 3678 and 3405 cm^{-1} , respectively. According to the one-dimensional wave equation, the frequencies of the fundamental and first-overtone of the NH stretching mode of pyrrole monomer are 3539 and 6944 cm^{-1} , respectively. These frequencies are close to the observed frequencies (3531 and 6925 cm^{-1}) of pyrrole monomer in the gas phase [21].

The observed frequencies of the fundamental and first-overtone of the NH stretching mode of pyrrole monomer in CCl_4 solution, 3497 and 6856 cm^{-1} , are lower by 30 and 70 cm^{-1} , respectively, than those of monomer in the gas phase. The frequencies of the fundamental and first-overtone of the NH stretching mode of pyrrole–pyridine complex are calculated to be 3206 and 6200 cm^{-1} . The observed frequency of the fundamental band is 3266 cm^{-1} , but it is difficult to identify the first-overtone band (see below).

According to the present calculation based on a one-dimensional wave equation, the intensity of the first-overtone of the

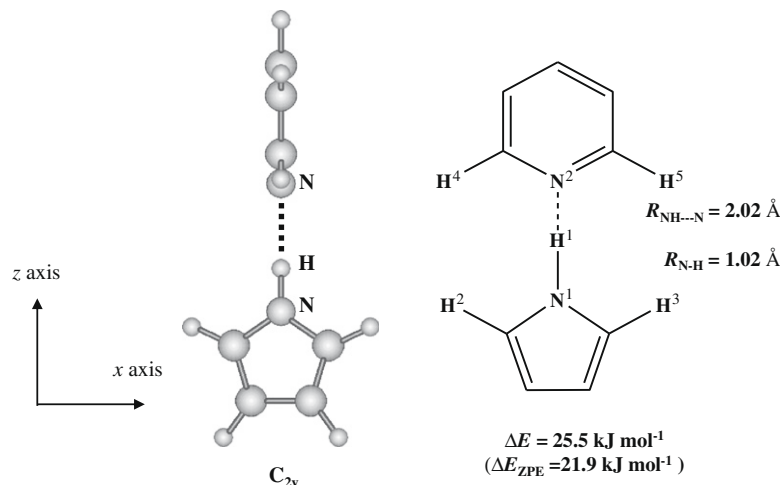


Fig. 4. Optimized structure for pyrrole-pyridine complex calculated at the DFT//B3LYP/6-311++G(3df,3pd) level. The stabilization energy, ΔE , is 25.5 kJ mol⁻¹, or 21.9 kJ mol⁻¹ after correction of the zero-point energy. The NH...N distance is 2.02 Å, and the N–H distances of pyrrole-pyridine complex and pyrrole monomer are 1.02 and 1.00 Å, respectively.

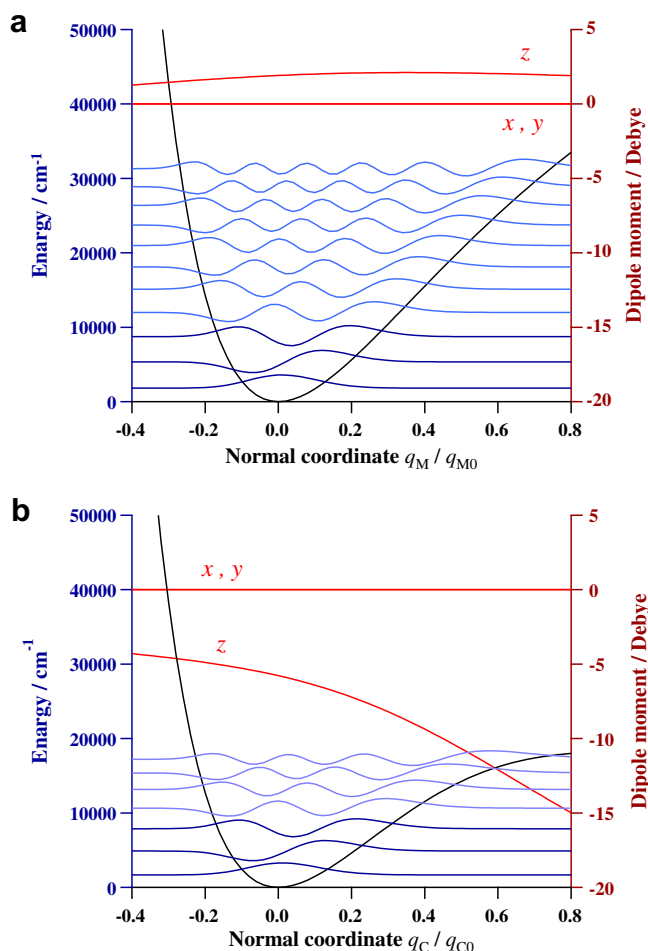


Fig. 5. Vibrational wave functions and dipole moment functions along potential energy curves of the NH stretching mode of (a) pyrrole monomer and (b) pyrrole-pyridine complex calculated at the DFT//B3LYP/6-311++G(3df,3pd) level. Symbols q_{M0} and q_{C0} denote units of the normal coordinates for the NH stretching mode in the monomer and the complex, respectively. They are represented by the displacement vectors of atoms (see Fig. 4) in Å units as follows: $q_{M0} = \{N^1(0, 0, -0.07), H^1(0, 0, 1.00), H^2(0.01, 0, 0), H^3(-0.01, 0, 0)\}$; $q_{C0} = \{N^1(0, 0, -0.08), H^1(0, 0, 1.00), H^2(0.01, 0, 0), H^3(-0.01, 0, 0), H^4(0, -0.01, -0.01), H^5(0, 0.01, -0.01)\}$.

NH stretching band of pyrrole monomer is 0.057 times as weak as that of the fundamental. The observed area intensity of the first-overtone of the NH stretching band is only 0.023 times as weak as that of the fundamental. Thus, the calculated overtone intensities are overestimated by about twofold. The first-overtone intensity of the NH stretching band of pyrrole-pyridine complex is calculated to be 0.003 times as weak as that of the fundamental of pyrrole monomer (Table 1), suggesting that upon formation of the hydrogen bonding the first-overtone is weakened by three orders of magnitude. Moreover, since the formation of hydrogen bonding broadens an absorption band, the first-overtone of the complex would hardly be observable even by use of a 10 mm cell.

Table 1 summarizes these results. The reason for the overestimation in the present calculation is probably that the effect of CCl₄ solution was not properly taken into account. The differences in the basis sets did not change the relation of the strength of the absorption intensity between the monomer and the complex. The ratio of the intensity of the first-overtone of the monomer to that of the fundamental approaches the experimental result with an increase in the basis sets.

In spite of the overestimation of the intensities, the results of the calculation clearly reproduce the experimental results related to the effects of hydrogen bonding on the frequency shifts and intensity variations.

Taking this overestimation into account, the real intensity of the first-overtone of the NH stretching mode of the pyrrole-pyridine complex seems to be about a half of the estimated value of the intensity (0.003, see Table 1). Thus, the actual intensity is estimated to be very small. This is the reason why we cannot observe the first-overtone of the NH stretching band of the pyrrole-pyridine complex.

The present study, for the first time, has reproduced the experimental results that the NH first-overtone intensity decreases largely upon the formation of hydrogen bonding. The observation of first-overtone modes has been explained by the anharmonicity of the vibrational potential energy surface. Thus, the calculated large distortion in the potential curve caused by the formation of hydrogen bonding, shown in Fig. 5b, suggests a larger intensity increase in the first-overtone modes than that of the fundamental modes. In fact, the overlap integral of the wave function for the first-overtone of the pyrrole-pyridine complex is larger than that of pyrrole monomer. However, the transition dipole moment decreases strongly upon formation of hydrogen bonding. Thus, we conclude that the dipole moment function plays a key role in the remarkable

decrease in the overtone intensities of the hydrogen-bonded NH group. This trend observed for the NH stretching band is similar to that for the OH stretching band reported in Refs. [6,7,13,14].

4. Conclusions

We have observed the fundamental and first-overtone bands of the NH stretching modes of pyrrole and pyrrole–pyridine complex in CCl_4 by FT-NIR/IR spectroscopy. The first-overtone of the NH stretching mode of pyrrole monomer has been observed, whereas no corresponding band has been identified for the pyrrole–pyridine complex.

We have also carried out quantum chemical calculations of their frequencies and absorption intensities by use of a one-dimensional wave equation. The optimized structure of the pyrrole–pyridine complex has C_{2v} symmetry, and the two molecular planes are perpendicular to each other. The present calculation suggests that the first-overtone of the NH stretching mode is weakened upon formation of the NH hydrogen bonding. The calculated results reproduce the experimental results including the intensity variations induced by the formation of hydrogen bonding.

The present calculation based on a one-dimensional wave equation reveals that upon the formation of hydrogen bonding the overlap integral of the wave function is enhanced but the transition dipole moment is much diminished, causing a marked decrease in the intensity of the first-overtone mode. In fact, the first-overtone band of NH stretching mode of the $\text{NH}\cdots\text{N}$ group is hardly detectable.

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