

# Hydrogen Bonding Effects on the Wavenumbers and Absorption Intensities of the OH Fundamental and the First, Second, and Third Overtones of Phenol and 2,6-Dihalogenated Phenols Studied by Visible/Near-Infrared/Infrared Spectroscopy

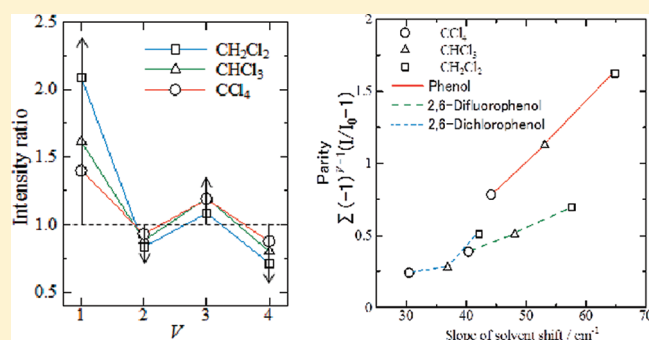
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 Supporting Information

**ABSTRACT:** Visible, near-infrared (NIR) and IR spectra in the 15600–2500  $\text{cm}^{-1}$  region were measured for phenol and 2,6-difluorophenol, 2,6-dichlorophenol, and 2,6-dibromophenol in *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  to study 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. A band shift of the OH stretching vibrations from a gas state to a solution state (solvent shift) was plotted versus vibrational quantum number ( $\nu = 0, 1, 2$  and 3), and it was found that there is a linear relation between the solvent shift and the vibrational quantum number. The slope of solvent shift decreases in the order of phenol, 2,6-difluorophenol and 2,6-dichlorophenol. For all of the solute molecules, the slope becomes larger with the increase in the dielectric constant of the solvents. The relative intensities of the OH stretching vibrations of phenol in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  against the intensity of the corresponding OH vibration in *n*-hexane increase in the fundamental and the second overtone but decrease in the first and third overtones; the relative intensities show so-called “parity”. The parity is more prominent for phenol that has an intermolecular hydrogen bonding than for 2,6-dihalogenated phenols that have an intramolecular hydrogen bond. These observations suggest that the intermolecular hydrogen bond between the OH group and the Cl atom plays a key role for the parity and that the intermolecular interaction between the solutes and the solvents (solvent effects) does not have a significant role in the parity.



## INTRODUCTION

Studies of overtones and combinations of OH and NH stretching modes by near-infrared (NIR) spectroscopy stretched back more than 60 years.<sup>1</sup> Their band assignments, anharmonicities, and hydrogen bonding and solvent effects on wavenumbers of the overtones and combinations have been investigated.<sup>2–16</sup> Foldes et al.<sup>2</sup> investigated anharmonicities of OH and NH stretching vibrations of alcohols and amides in  $\text{CCl}_4$  by measuring their fundamentals and first and second overtones. Singh et al.<sup>3,4</sup> studied solvent and temperature dependencies of anharmonicities for alcohols, such as methanol and *t*-butyl alcohol. Furthermore, Detoni et al.<sup>5</sup> explored anharmonicities for intermolecular hydrogen bondings of phenol and alcohols in various solvents, comparing the wavenumbers of OH fundamentals with those of their first overtones. It was found that the anharmonicity of phenol OH that has a character of strong donor increases in the order of solvent basicity, although those of alcohols do not always change in the same order.<sup>5</sup> Czarnik-Matusiewicz et al.<sup>6</sup> investigated the vibrational

potentials of OH stretching modes of phenol and phenol derivatives by changing a substituent.

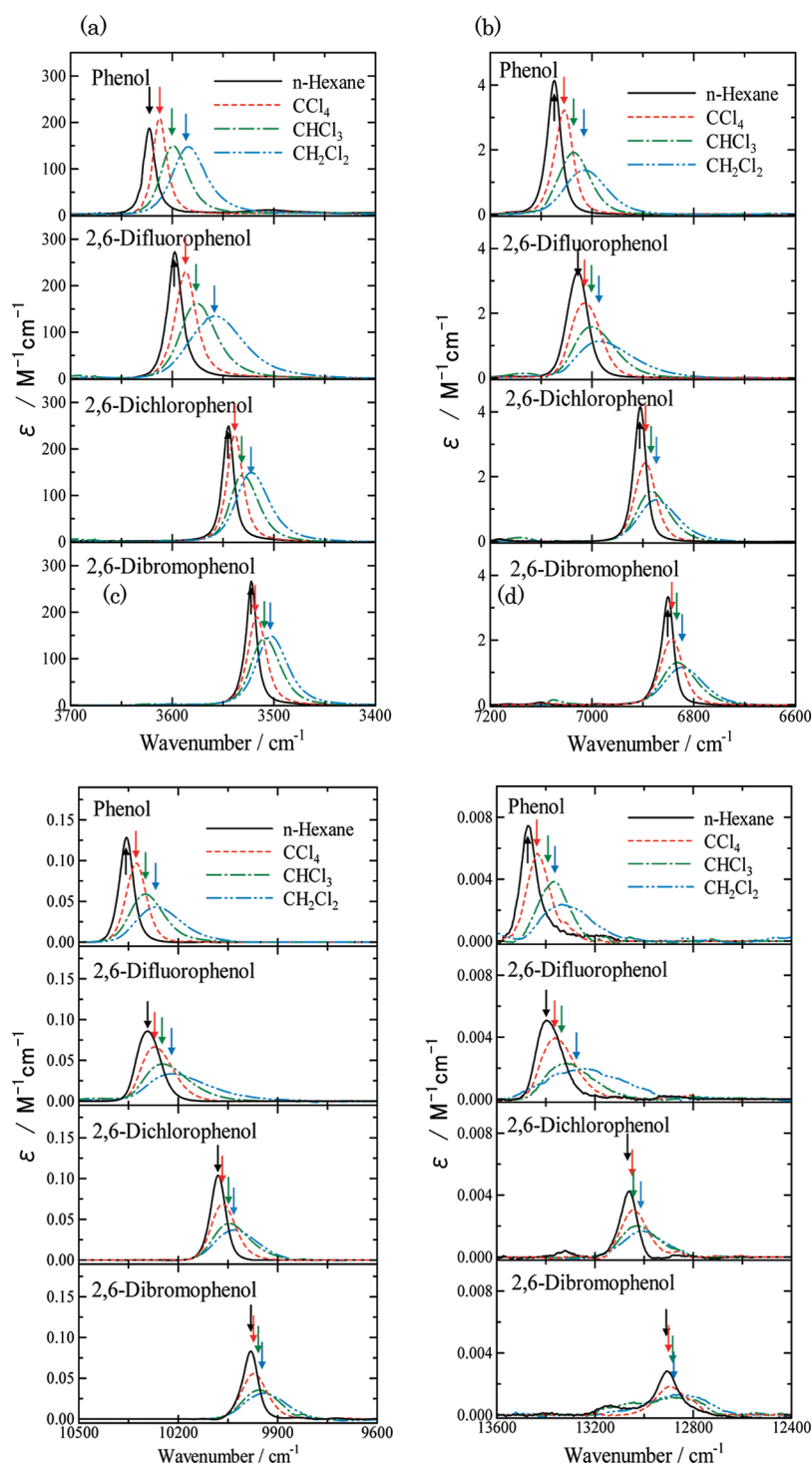
Although there are many such studies using fundamentals and first overtones for investigating anharmonicities and solvent and hydrogen bonding effects, studies using higher order overtones are rather rare. Also these past studies mainly discussed the wavenumbers and seldom treated the absorption intensities.

However, remarkable developments of FT-spectrometers have enabled one to measure spectra in the 16000–100  $\text{cm}^{-1}$  region where bands due to the fundamental and the first, second, and third overtones of OH, NH, and CH stretching modes appear under the same experimental conditions except for a path length of a cell used. Moreover, recent development of theoretical calculations like density functional theory (DFT) has allowed one to calculate the wavenumbers and absorption

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**Figure 1.** Vis/NIR/IR spectra of phenol, 2,6-difluorophenol, 2,6-dichlorophenol and 2,6-dibromophenol in *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ . (a) Fundamental region. (b) First overtone region. (c) Second overtone region. (d) Third overtone region.

intensities of not only fundamentals but also those of higher order overtones.<sup>7–9</sup>

We investigated the effects of hydrogen bonding on wave-number shifts and intensity changes in the NH fundamental and its first overtone of pyrrole–pyridine complex by using NIR/IR spectroscopy and DFT calculation.<sup>15</sup> The first overtone of the NH stretching vibration band of free pyrrole was observed at  $6856\text{ cm}^{-1}$ , but that of the pyrrole–pyridine complex was

missing or extremely weak. The DFT calculations of molecular vibrational potentials and dipole moment functions of the NH stretching modes of free pyrrole and pyrrole–pyridine complex successfully explained the remarkable intensity decrease in the overtone of the hydrogen-bonded NH group.<sup>15</sup>

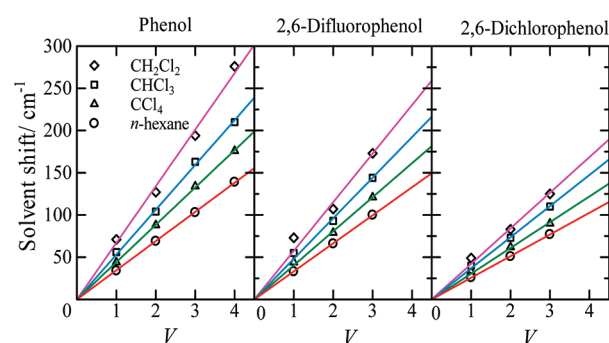
We also investigated solvent dependencies on wavenumbers and absorption intensities of the fundamental and the first overtone of the NH stretching vibration of pyrrole in  $\text{CCl}_4$ ,

**Table 1.** Observed Wavenumbers and Relative Intensities of the OH Fundamentals and the First, Second, and Third Overtones of OH Stretching Modes of Phenol and 2,6-Dihalogenated Phenols in a Gas State and in CCl<sub>4</sub>, CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>

X <sub>2</sub> -PhOH	solvent	fundamental		first overtone		second overtone		third overtone	
		1ν	int	2ν	int	3ν	int	4ν	int
H	gas	3656		7143		10461		13611	
	<i>n</i> -hexane	3622	100	7074	4.43	10358	0.19	13472	0.021
	CCl <sub>4</sub>	3612	140	7055	4.12	10327	0.22	13435	0.018
	CHCl <sub>3</sub>	3600	161	7036	3.92	10298	0.22	13391	0.015
	CH <sub>2</sub> Cl <sub>2</sub>	3586	209	7016	3.71	10267	0.20	13362	0.015
F	gas	3631		7094		10392			
	<i>n</i> -hexane	3598	157	7028	4.58	10292	0.20	13395	0.017
	CCl <sub>4</sub>	3587	188	7015	4.15	10271	0.21	13360	0.016
	CHCl <sub>3</sub>	3576	211	7001	3.99	10248	0.21	13331	0.017
	CH <sub>2</sub> Cl <sub>2</sub>	3558	242	6987	3.98	10219	0.20	13270	0.016
Cl	gas	3571		6957		10157			
	<i>n</i> -hexane	3545	113	6906	3.55	10080	0.16	13063	0.010
	CCl <sub>4</sub>	3538	142	6895	3.48	10067	0.17	13044	0.011
	CHCl <sub>3</sub>	3531	144	6884	3.27	10047	0.16	13041	0.010
	CH <sub>2</sub> Cl <sub>2</sub>	3522	175	6874	3.25	10032	0.15	13008	0.011
Br	gas								
	<i>n</i> -hexane	3522	113	6851	2.99	9980	0.14	12907	0.006
	CCl <sub>4</sub>	3518	126	6843	3.04	9972	0.15	12897	0.007
	CHCl <sub>3</sub>	3509	143	6833	2.89	9957	0.13	12880	0.004
	CH <sub>2</sub> Cl <sub>2</sub>	3503	159	6823	2.84	9947	0.12	12876	0.004

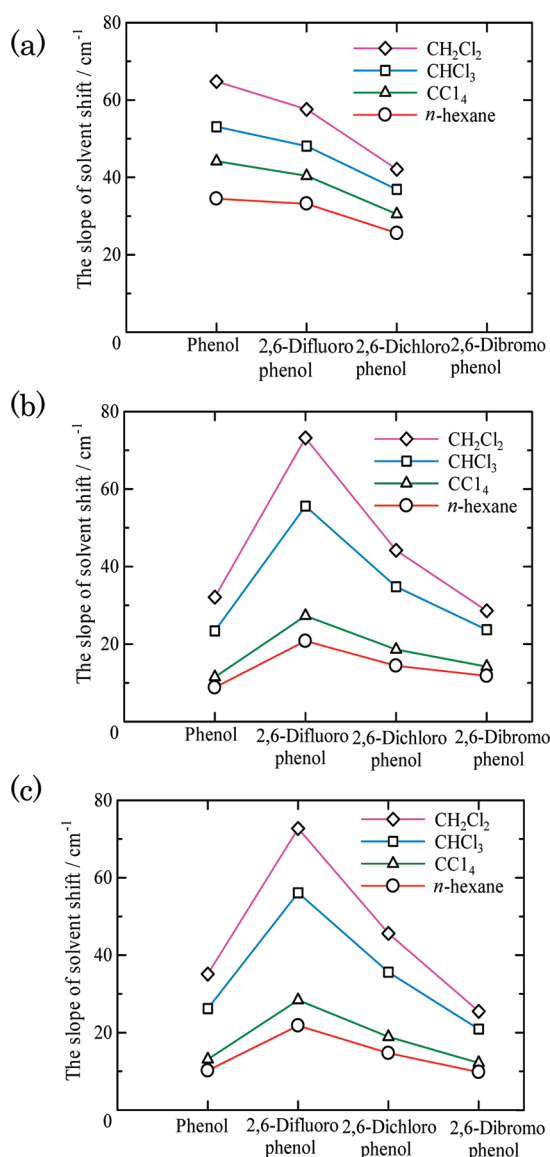
CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, and found that the wavenumbers of the NH fundamental and its first overtone decrease in the order of CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, which is the increasing order of the dielectric constant of the solvents.<sup>16</sup> Their absorption intensities increase in the same order, and the intensity increase is more significant for the fundamental than the overtone. These results for the solvent dependence of the wavenumbers and absorption intensities of NH stretching bands of pyrrole are quite different from those for the formation of hydrogen bond in the pyrrole–pyridine complex.<sup>15,16</sup> SCRF/IPC calculations, which consider solvent effects (effects of dielectric constant), suggested that the decreases in the wavenumbers of both the fundamental and the overtone of the NH stretching mode and their intensity increases come from the gradual increase in the slope of the dipole moment function.<sup>16</sup>

However, NIR/IR spectroscopy studies with DFT calculations on hydrogen bonding and solvent effects of OH and NH groups are limited mostly to the analyses of the fundamentals and the first overtones. The purpose of the present work is to investigate wavenumber shifts and absorption intensity changes of the OH fundamental and the first, second, and third overtones of phenol and 2,6-dihalogenated phenols caused by changes in solvents by Vis/NIR/IR spectroscopy and DFT calculations. We selected phenol and 2,6-difluorophenol, 2,6-dichlorophenol, and 2,6-dibromophenol as target molecules for the present work because in enough dilute solutions, all of the solutes do not form self-aggregated dimers or oligomers and have an intermolecular interaction with a solvent (solvent effect), and moreover, phenol has an intermolecular hydrogen bond between its OH group and the Cl atom of solvents<sup>17–19</sup> while 2,6-dihalogenated phenols have a weak to strong intramolecular hydrogen bond and a weak to

**Figure 2.** Observed solvent shifts of phenol, 2,6-difluorophenol and 2,6-dichlorophenol versus vibrational quantum number ( $V = 1, 2, 3, 4$ ).

much weak intermolecular hydrogen bondings with solvent molecules. Among the 2,6-dihalogenated phenols, 2,6-difluorophenol has a much weaker intramolecular hydrogen bonding and a significant intermolecular hydrogen bonding with solvent. Thus, by comparing the four kinds of phenols, we can explore the effects of inter- and intramolecular hydrogen bondings and solvent effects on the wavenumber shifts and changes in absorption intensities of the OH stretching bands. As the solvents we employed *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. It is considered that *n*-hexane does not have a significant interaction with the solute molecules and the latter three show solvent effects in the order of CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, which is the order of the dielectric constant. They form hydrogen bonds between their Cl atoms and the OH group of phenol and 2,6-dihalogenated phenols.

The clear novelty of the present work is to explore from the fundamental to the third overtone. We observed “parity” for



**Figure 3.** The slopes of solvent shifts of phenol, 2,6-difluorophenol, 2,6-dichlorophenol and 2,6-dibromophenol in *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ . (a) Observed and (b) calculated with the base set; 6-311++G(3df,3pd). (c) Calculated with base set; cc-pVTZ.

relative intensities of OH stretching vibrations of phenol and 2,6-dihalogenated phenols in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  against the intensity of the corresponding OH vibration in *n*-hexane; they increase in the fundamental and the second overtone and decrease in the first and third overtones. We explored the parity and other interesting results for the wavenumbers and absorption intensities changes of OH vibrations based on the inter and intramolecular interactions.

## EXPERIMENTAL SECTION

Phenol (Wako, 99%), 2,6-difluorophenol (Tokyo Kasei Kogyo, 95%), 2,6-dichlorophenol (Aldrich, 99%) and 2,6-dibromophenol (Aldrich, 99%) were purchased and used without further purification. *n*-Hexane (Wako, 97.0%),  $\text{CCl}_4$  (Wako 99.8%),  $\text{CHCl}_3$  (Wako 99.0%) and  $\text{CH}_2\text{Cl}_2$  (Wako 99.5%) were treated with molecular sieves (3 Å and 4 Å) before use. The concentration of

phenol in *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  was  $0.05 \text{ mol L}^{-1}$ , and those of 2,6-dihalogenated phenols were  $0.1 \text{ mol L}^{-1}$ . Under these conditions, phenol and 2,6-dihalogenated phenols do not form self-aggregated dimers or oligomers in the solution.

Vis/NIR/IR spectra of the solutions in the region of  $15600\text{--}2500 \text{ cm}^{-1}$  were measured with an FT-NIR/IR spectrophotometer (Perkin-Elmer Spectrum One NTS FT-NIR spectrometer). The spectral resolution used was  $2 \text{ cm}^{-1}$  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  $256 \text{ cm}^{-1}$ , respectively. Gas spectra were measured with a spectral resolution of  $2 \text{ cm}^{-1}$  for phenol, 2,6-difluorophenol, 2,6-dichlorophenol, and 2,6-dibromophenol by using the same spectrometer and a white cell made by Yokogawa Co.

The DFT calculations were carried out by using the Gaussian 09 program<sup>20</sup> with 6-311++G(3df,3pd) basis sets. 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.<sup>21,22</sup> Quantum chemical calculations based on a SCRF/IPCM model were carried out by using the chemical structures in the gas phase.

In the present work, we solved the Schrödinger equation of one-dimensional OH 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  $q$ ,  $\mu$ , and  $V(q)$  are the normal coordinate, the reduced mass and the potential energy function, respectively.

We calculated the integrated absorption coefficient ( $\text{km mol}^{-1}$ , base  $e$ )  $A(v)$  for each OH stretching transition by the following:

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

where  $\varepsilon(\tilde{\nu})$  is the molar extinction coefficient (base 10),  $\tilde{\nu}_{v0}$  is the transition energy in  $\text{cm}^{-1}$ , and  $|\bar{\mu}_{v0}|^2$  is the sum of the squared transition dipole moments of the  $x$ ,  $y$ , and  $z$  components in (debye)<sup>2</sup> units.<sup>23</sup>  $|\bar{\mu}_{v0}|^2$  is given by the following:

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

Here,  $|\bar{\mu}_{v0}^z|^2 = 0$ , because these are the plane symmetry.

We obtained the numerical results for the energy levels and the wave functions using the method given by Johnson.<sup>24</sup>

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 OH stretching mode; they are represented by the



**Table 2.** Calculated Wavenumbers and Relative Intensities of the Fundamentals and the First, Second and Third Overtones of OH Stretching Modes of Phenol and 2,6-Dihalogenated Phenols in a Gas State and in CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

X <sub>2</sub> -PhOH	solvent	fundamental		first overtone		second overtone		third overtone	
		1ν	int	2ν	int	3ν	int	4ν	int
H	gas	3664		7167		10511		13702	
	<i>n</i> -hexane	3654	100	7147	8.98	10483	0.47	13667	0.029
	CCl <sub>4</sub>	3650	109	7141	9.61	10475	0.48	13658	0.029
	CHCl <sub>3</sub>	3635	153	7114	12.90	10438	0.44	13614	0.023
	CH <sub>2</sub> Cl <sub>2</sub>	3624	188	7093	15.15	10411	0.39	13582	0.016
F	gas	3639		7117		10440		13613	
	<i>n</i> -hexane	3618	188	7075	6.42	10377	0.27	13529	0.039
	CCl <sub>4</sub>	3611	200	7062	6.36	10357	0.25	13503	0.047
	CHCl <sub>3</sub>	3584	255	7006	6.32	10272	0.16	13390	0.089
	CH <sub>2</sub> Cl <sub>2</sub>	3568	289	6972	6.49	10219	0.13	13319	0.109
Cl	gas	3572		6970		10199		13262	
	<i>n</i> -hexane	3559	172	6943	5.97	10156	0.34	13202	0.010
	CCl <sub>4</sub>	3555	180	6935	6.27	10144	0.44	13185	0.011
	CHCl <sub>3</sub>	3540	220	6904	6.92	10096	0.74	13118	0.089
	CH <sub>2</sub> Cl <sub>2</sub>	3531	244	6886	6.69	10068	0.70	13080	0.121
Br	gas	3539		6897		10076		13088	
	<i>n</i> -hexane	3532	177	6880	3.93	10046	0.24	13032	0.042
	CCl <sub>4</sub>	3530	182	6876	3.90	10039	0.23	13022	0.047
	CHCl <sub>3</sub>	3523	204	6850	4.28	10011	0.21	12981	0.101
	CH <sub>2</sub> Cl <sub>2</sub>	3520	222	6851	6.68	9997	0.58	12960	0.198

<sup>a</sup> The basis set used was 6-311++G(3df,3pd).

displacement vectors of atoms in Å unit as follows:

$$q_0 = \{O(0.06, -0.02, 0), H(-0.92, 0.39, 0)\}$$

The number of calculation points is sufficient for the numerical calculations without such assumption like the Morse function. This ensures converged energy levels with precision higher than 0.001 cm<sup>-1</sup>. This calculation method could reproduce very well solvent dependency of NH stretching mode of pyrrole.<sup>16</sup>

## RESULTS AND DISCUSSION

**Vis/NIR/IR Spectra of OH Stretching Vibrations of Phenol and 2,6-Dihalogenated Phenols in *n*-Hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>.** Figure 1(a)–(d) shows absorption spectra of phenol and 2,6-dihalogenated phenols in *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub> in the regions of 3650–3450, 7200–6800, 10500–9900, and 13700–12900 cm<sup>-1</sup>, respectively. Bands observed in the 3650–3450, 7200–6800, 10500–9900, and 13700–12900 cm<sup>-1</sup> regions in Figure 1 are assigned to the fundamentals and the first, second, and third overtones of the OH stretching modes of phenol and 2,6-dihalogenated phenols, respectively.

Table 1 summarizes the wavenumbers and absorption intensities of OH stretching vibrations of phenol, 2,6-difluorophenol, 2,6-dichlorophenol, and 2,6-dibromophenol in *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. The wavenumbers were determined by the first derivative of the Vis/NIR/IR spectra. The absorption intensities were estimated as area intensities of the bands. There are two bands in the third overtone region in the case of 2,6-dichlorophenol and 2,6-dibromophenol. We did not involve minor bands in estimating these intensities. The relative intensities of the bands were calculated by using the corresponding

intensities of phenol in *n*-hexane as the intensity standards. One should note that *n*-hexane is free from any hydrogen bondings.

Of note in Figure 1 and Table 1 is that the wavenumbers of the OH fundamentals and their overtones decrease in the order of *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, which is the increasing order of the dielectric constant of the solvents. The shifts of the OH fundamentals of phenol from the *n*-hexane solution to other solutions are 10, 22, and 35 cm<sup>-1</sup> in the order of the CCl<sub>4</sub>, CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> solutions, respectively. Those of the first, second and third overtones are 19, 36, and 58 cm<sup>-1</sup>, 31, 60, and 91 cm<sup>-1</sup>, and 37, 81, and 110 cm<sup>-1</sup>, respectively, in the same order as the fundamentals. In this way, the shifts by solvent differences increase upon going from the fundamental and the first, second and third overtones as expected. In the fundamental region, the relative area intensities of 2,6-dihalogenated phenols are larger than that of phenol (Table 1). The intensities increase as the dielectric constant becomes larger.

It can be seen from Figure 1 and Table 1 that irrespective of solvents, the fundamentals and overtones of 2,6-dihalogenated phenols which have an intramolecular hydrogen bond appear at lower wavenumbers compared with the corresponding bands of phenol. The bands show lower wavenumber shifts in the order of 2,6-difluorophenol, 2,6-dichlorophenol and 2,6-dibromophenol, which is the order of the strength of the intramolecular hydrogen bonding. However, it is noted that the wavenumbers of the bands of phenol and 2,6-difluorophenol are relatively close to each other and those of 2,6-dichlorophenol and 2,6-dibromophenol are also relatively close to each other. It should be noted that phenol has solely an intermolecular interaction and 2,6-difluorophenol, 2,6-dichlorophenol, and 2,6-dibromophenol have both inter- and intramolecular interactions. The intermolecular interaction is very weak in 2,6-dichlorophenol

**Table 3.** Calculated Wavenumbers and Relative Intensities of the Fundamentals and the First, Second and Third Overtones of OH Stretching Modes of Phenol and 2,6-Dihalogenated Phenols in a Gas State and in CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

X <sub>2</sub> -PhOH	solvent	fundamental		first overtone		second overtone		third overtone	
		1ν	int	2ν	int	3ν	int	4ν	int
H	gas	3651	-	7142	-	10476	-	13657	-
	<i>n</i> -hexane	3639	100	7120	9.96	10445	0.55	13618	0.036
	CCl <sub>4</sub>	3635	109	7113	10.52	10436	0.56	13607	0.038
	CHCl <sub>3</sub>	3619	154	7083	13.38	10395	0.50	13559	0.035
	CH <sub>2</sub> Cl <sub>2</sub>	3608	187	7062	15.33	10367	0.43	13527	0.026
F	gas	3628	-	7097	-	10411	-	13575	-
	<i>n</i> -hexane	3606	187	7053	7.09	10346	0.31	13489	0.036
	CCl <sub>4</sub>	3600	199	7040	6.96	10326	0.27	13462	0.039
	CHCl <sub>3</sub>	3573	249	6985	6.79	10242	0.13	13351	0.040
	CH <sub>2</sub> Cl <sub>2</sub>	3558	280	6952	6.92	10192	0.09	13284	0.030
Cl	gas	3560	-	6948	-	10168	-	13221	-
	<i>n</i> -hexane	3547	189	6920	7.07	10124	0.40	13161	0.011
	CCl <sub>4</sub>	3543	200	6912	7.52	10112	0.47	13144	0.009
	CHCl <sub>3</sub>	3526	246	6880	8.63	10062	0.82	13076	0.067
	CH <sub>2</sub> Cl <sub>2</sub>	3514	274	6845	8.63	9991	0.84	12955	0.120
Br	gas	3529	-	6879	-	10051	-	13047	-
	<i>n</i> -hexane	3522	189	6863	4.49	10023	0.32	13004	0.041
	CCl <sub>4</sub>	3520	194	6859	4.46	10016	0.30	12994	0.048
	CHCl <sub>3</sub>	3514	220	6845	5.78	9991	0.58	12955	0.210
	CH <sub>2</sub> Cl <sub>2</sub>	3511	244	6837	8.74	9978	0.21	12935	0.103

<sup>a</sup> The basis set used was cc-pVTZ.

and 2,6-dibromophenol and the intramolecular interaction becomes stronger in the order of 2,6-difluorophenol, 2,6-dichlorophenol and 2,6-dibromophenol. These differences may provide the differences in the wavenumbers between the former two phenols (phenol and 2,6-difluorophenol) and the latter two phenols (2,6-dichlorophenol and 2,6-dibromophenol).

The fundamental and the first, second, and third overtones of the gas states appear at higher wavenumbers than those of the solution states as expected because of the lack of the solute–solvent interaction in the gas states which induces lower wavenumber shifts. These shifts were observed for all of the solutes, but the degrees of shifts are smaller for the solutes with a stronger intramolecular hydrogen bonding. If one compares the four solvents, then the wavenumbers decrease with the increase in the dielectric constant of the four solvents.

**Solvent Shifts and Their Slopes against the Vibrational Quantum Numbers.** According to Buckingham et al.,<sup>25</sup> “solvent shift”  $\Delta\tilde{\nu}$  is defined as follows:

$$\Delta\tilde{\nu} = \tilde{\nu}_g - \tilde{\nu}_{\text{sol}} \quad (4)$$

where  $\tilde{\nu}_g$  and  $\tilde{\nu}_{\text{sol}}$  are the wavenumbers of a molecule in gas and solution states, respectively. He suggested that the solvent shift is proportional to the vibrational quantum number as follows.<sup>17</sup>

Figure 2 plots the solvent shifts of phenol, 2,6-difluorophenol and 2,6-dichlorophenol in *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> against the vibrational quantum number. It can be seen from Figure 2 that there are always clear linear relations between the solvent shifts and the vibrational quantum number. The observations are in good agreement with the equation proposed by Buckingham.<sup>25</sup>

Buckingham<sup>25</sup> pointed out that the slope of linear relation between a solvent shift and vibrational quantum number

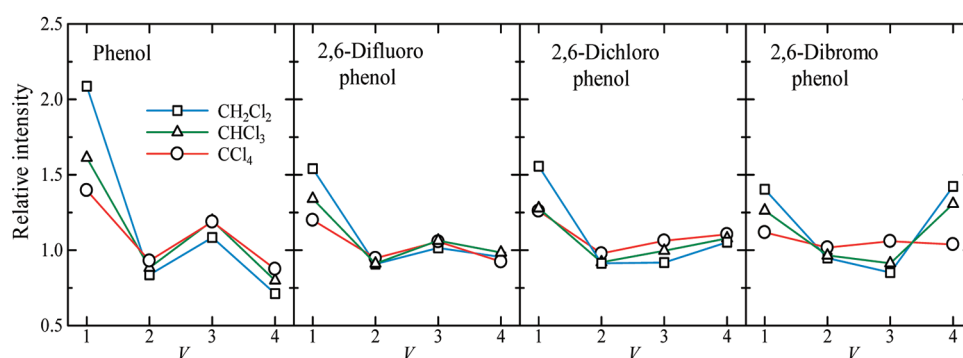
indicates the strength of a molecular interaction, i.e., a hydrogen bonding and a solvent effect. Oref et al.<sup>26</sup> investigated a solvent effect of methanol in nonpolar solvents, adapting this theory of solvent shift.

In the present work, based on the theory proposed by Buckingham et al.<sup>25</sup> we investigated effects of inter- and intramolecular hydrogen bondings and solvent effects on the wavenumbers and absorption intensities of the fundamental and the first, second, and third overtones of phenol and 2,6-dihalogenated phenols in *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. Figure 3(a) plots the slopes of observed solvent shifts for phenol, 2,6-difluorophenol, and 2,6-dichlorophenol in *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. The slopes were calculated by the method of least-squares. The slopes increase with the increase in the order of *n*-hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, which is the order of the dielectric constant. It is noted here that even in the gas states 2,6-dihalogenated phenols form intramolecular hydrogen bondings.

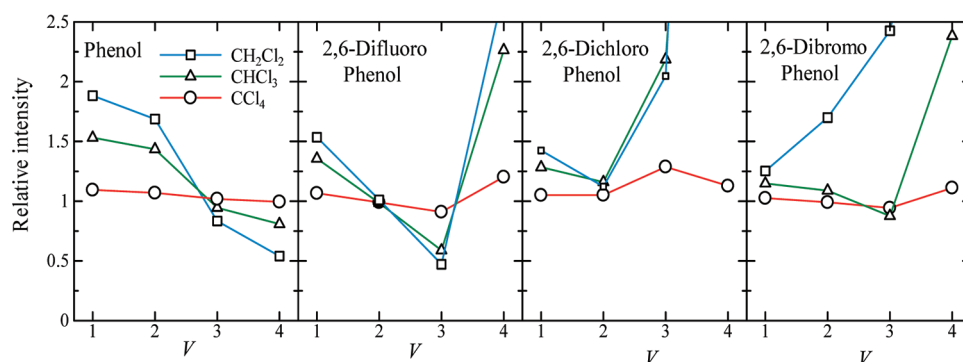
The results in Figure 3(a) suggest that as the dielectric constant increases, the intermolecular interaction between the phenol OH group and a solvent molecule becomes strong.<sup>17–19</sup> It is found that the slopes of the solvent shifts for *n*-hexane are significantly smaller than those for CCl<sub>4</sub>, which has little interaction to a solute. The slopes for 2,6-difluorophenol and 2,6-dichlorophenol are smaller than those for phenol. Therefore, it is very likely that the effect of intermolecular interaction is smaller for 2,6-difluorophenol and 2,6-dichlorophenol than phenol, and that it decreases particularly for 2,6-dichlorophenol.

The reason why the intermolecular interaction becomes weak in 2,6-difluorophenol and 2,6-dichlorophenol may be the effect of intramolecular hydrogen bonding between the OH group and the halogen atom. The intramolecular hydrogen

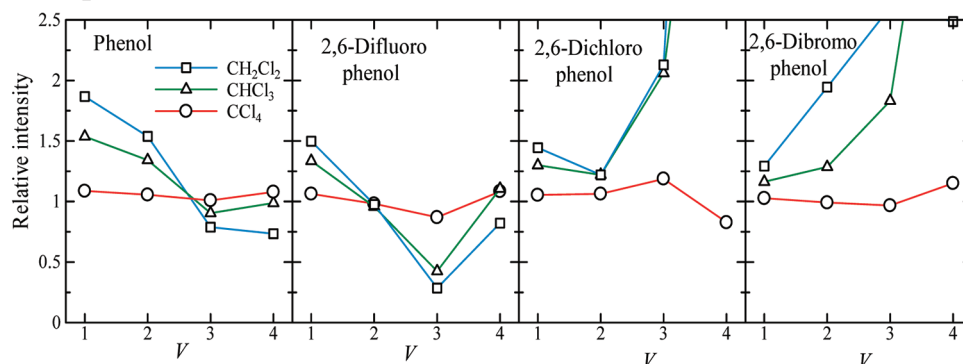
## (a) observed



## (b) 6-311++G(3df,3pd)



## (c) cc-pVTZ



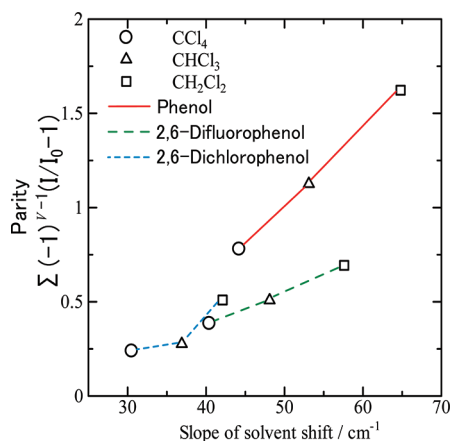
**Figure 4.** The relative intensities of phenol, 2,6-difluorophenol, 2,6-dichlorophenol, and 2,6-dibromophenol in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  versus vibrational quantum number. (a) Observed and (b) calculated by base set; 6-311++G(3df,3pd). (c) Calculated by base set; cc-pVTZ.

bonding competes with the intermolecular interactions. In other words, as the intramolecular hydrogen bonding becomes strong, the intermolecular interactions are suppressed, the slopes becoming phenomenologically smaller. However, if the intramolecular hydrogen bonding becomes weak, the intermolecular interactions become stronger, the slope becoming larger.

**Comparison between the Observed Wavenumbers and the Calculated Ones.** Tables 2 and 3 show the wavenumbers and absorption intensities of the OH fundamentals and overtones for phenol and 2,6-dihalogenated phenols in the gas states and the *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  solutions calculated by 6-311++G(3df,3pd) and cc-pVTZ, respectively. It can be seen from Figure 1 and Tables 1, 2, and 3 that the calculated

wavenumbers are considerably higher than the corresponding observed wavenumbers particularly for the higher order overtones, although the deviations are relatively smaller for the gas states. The SCRF/IPCM model yields larger deviations. These results suggest that the consideration of anharmonicities of the OH vibrations was not enough in the calculations. The deviations are particularly larger for phenol which forms an intermolecular interaction more easily than 2,6-dihalogenated phenols.

Figure 3(b),(c) depicts the slopes of solvent shifts calculated by 6-311++G(3df,3pd) and cc-pVTZ, respectively. As in the case of the experimental results, the slopes become larger with the increase in the dielectric constant of the solvents. As for the solute dependencies, contrary to the experimental results, the calculated slopes become larger upon going from phenol to



**Figure 5.** The relation between parity and the slope of solvent shift for phenol, 2,6-difluorophenol and 2,6-dichlorophenol in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ .

2,6-dichlorophenol and 2,6-difluorophenol in the calculations. This happens probably because phenol is subjected to an intermolecular hydrogen bonding more easily than 2,6-dihalogenated phenols, however, the intermolecular hydrogen bonding is not considered in the calculations.

**Relative Intensities of the OH Fundamental and the First, Second, and Third Overtones.** Figure 4 (a) depicts the observed relative intensities of OH stretching bands of phenol, 2,6-difluorophenol, 2,6-dichlorophenol and 2,6-dibromophenol in  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  versus the vibrational quantum number. The relative intensities of the OH bands of each solution were normalized by the intensity of the corresponding band of *n*-hexane solutions.

It is of particular note that the relative intensities of the OH stretching vibrations of phenol in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  increase in the fundamental and the second overtone but decrease in the first and third overtones. They exhibit so-called “parity”. The parity is more significant for phenol than the 2,6-dihalogenated phenols which have the intramolecular hydrogen bonding. Among the 2,6-dihalogenated phenols, 2,6-difluorophenol with less stronger intramolecular hydrogen bonding shows a clearer parity.

Figure 5 shows the relation between the strength of parity and the slope of solvent shift. The parity is defined as follows:

$$\sum_V (-1)^{V-1} \left( \frac{I}{I_0} - 1 \right) \quad (5)$$

where  $V$  indicates vibrational quantum number;  $V = 1, 2, 3$ , and 4,  $I_0$  and  $I$  indicate the intensities of OH stretching bands of solutes in *n*-hexane and other solvents, respectively. In Figure 5, the parity becomes more prominent as the slope becomes larger. Thus, it seems that the parity is related with the slope of the solvent shift. The slopes of OH stretching bands are the largest in phenol and then, those of 2,6-difluorophenol are next. Phenol and 2,6-difluorophenol are molecules that are affected easily by an intermolecular hydrogen bonding in this order. Thus, the observed parity indicates the intermolecular hydrogen bonding between the OH group and the Cl atom of the solvents. However, 2,6-dichlorophenol is not easily subjected to the intermolecular hydrogen bonding, yielding the smaller slopes. The reason why 2,6-dichlorophenol does not show a significant parity may be due to its strong intramolecular hydrogen bonding.

**Comparisons between the Observed and Calculated Relative Intensities.** Figure 4(b),(c) exhibits the relative intensities of phenol and 2,6-dihalogenated phenols in *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  versus the vibrational quantum number calculated by 6-311++G(3df,3pd) and cc-pVTZ, respectively. Both 6-311++G(3df,3pd) and cc-pVTZ can reproduce well the results of fundamentals. However, there are significant deviations between the experimental results and the theoretical calculations for the overtones. The reason why the calculations cannot reproduce the experimental results may be that both 6-311++G(3df,3pd) and cc-pVTZ consider only solvent effects and do not consider intermolecular hydrogen bondings. This mismatch between the experimental and calculation results indirectly suggests that the intermolecular hydrogen bonding plays an important role in the parity.

The present calculation work has revealed the simple qualitative calculations cannot reproduce the experimental results regarding the absorption intensities. Further investigations are needed.

## CONCLUSIONS

We have investigated solvent and hydrogen bonding effects on the wavenumbers and absorption intensities of the fundamentals and the first, second, and third overtones of the OH stretching modes of phenol and 2,6-dihalogenated phenols in *n*-hexane,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  by using Vis/NIR/IR spectroscopy and quantum chemical calculations. The investigations down to the third overtone have enabled us to observe a number of novel and interesting results such as “parity” in the absorption intensities. We have found that the solvent shifts of phenol and 2,6-dihalogenated phenols change linearly with the vibrational quantum number, confirming the equation proposed by Buckingham.<sup>25</sup>

The slopes of observed solvent shifts decrease in the order of phenol, 2,6-difluorophenol and 2,6-dichlorophenol, suggesting that the strength of intermolecular interaction decreases in this order. The SCRF/IPCM model could not reproduce the changes in the slopes from phenol to 2,6-dihalogenated phenols probably because this model did not consider an intermolecular interaction like a hydrogen bonding.

The relative intensities show the parity, and it is more remarkable for phenol, which does not have an intramolecular interaction. The calculated relative intensities could not reproduce the parity probably because the SCRF/IPCM model considered only the solvent effect for the dielectric constant. It seems, therefore, that the intermolecular hydrogen bond between the OH group and the Cl atom of the solvent is the cause for the parity.

## ASSOCIATED CONTENT

**S Supporting Information.** In order to determine the concentration of the solutions we used, we measured the concentration dependence of fundamental OH stretching mode of phenol and 2,6-Dihalogenated Phenols. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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