

Size-selected vibrational spectra of phenol-(H₂O)_n (n=1–4) clusters observed by IR–UV double resonance and stimulated Raman-UV double resonance spectroscopies

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OH and CH stretching vibrations of bare phenol, phenol-(H₂O)_n clusters (n=1–4), and partially deuterated clusters in the S₀ state were observed by using IR–UV double resonance and stimulated Raman-UV double resonance spectroscopies. Characteristic spectral features of the OH stretching vibrations of the phenol as well as of the H₂O sites were observed, which are directly related to their structures. The cluster structures were investigated by comparing the observed spectra with the calculated ones obtained by the *ab initio* molecular orbital calculation with (self-consistent field) SCF 6-31G and SCF 6-31G* basis sets given by Watanabe and Iwata. It was found that for the clusters with n ≥ 2, the isomer of ring form hydrogen-bonded structure is most stable and the simulated IR spectra based on the calculated structure showed good agreements with the observed ones. For a particular cluster, which was assigned as an isomer of the n=4 cluster, an anomalous IR spectrum was observed. Two forms of the isomer are proposed with respect to the structure of water moiety: (1) an ‘ice’ structure and (2) an ‘ion-pair’ structure. The relative IR absorption cross sections of each bands were also investigated for the clusters with n=1 to 4. It was found that the IR absorption cross section of the phenolic OH stretching vibration of the n=1 cluster increases by a factor of 6 compared to that of bare phenol and it further increases with the cluster size. © 1996 American Institute of Physics. [S0021-9606(96)02426-9]

I. INTRODUCTION

Recent development of laser spectroscopy of molecular beams has enabled us to investigate the structure and dynamics of molecular clusters in detail. Clusters in which one molecule is surrounded by other molecules are thought to be a good model for solute-solvent systems. Of special importance and interest are the hydrogen-bonding systems of molecules having OH group. In condensed phase, environmental effects on the OH stretching vibrations have been extensively studied for many years. Characteristic frequency shifts and intensity enhancement of the hydrogen-bonded (H bonded) OH vibrations are the most interesting feature.¹ However, the correlation between the observed bands and the intermolecular structure has not been directly revealed yet because of the difficulty of determining the local structure in the condensed phase. In this respect, H-bonded clusters will provide us with substantial information for the investigation of the local structure in solutions and also H-bond network in biological systems.

Among many clusters, phenol-water H-bonded clusters have been extensively studied by many workers to investigate their structure and dynamics by using various spectroscopic techniques.^{2–14} Up to now, most of the spectroscopic studies of the clusters have been done with the use of electronic spectroscopy. Ito and coworkers measured the laser-induced fluorescence (LIF) and dispersed fluorescence spectra of the S₁–S₀ electronic transitions.^{2–4} Colson and coworkers assigned the bands of the electronic transition with respect to the cluster size and also studied dynamics of the electronically excited clusters by pump-probe spectroscopy

combined with the REMPI (resonantly enhanced multiphoton ionization) Mass detection.^{6–9} Stanley and Castleman reported the assignments of intra and inter molecular vibrations of phenol-(H₂O)_n (n=0–4) in their electronically ground state by using ion-dip spectroscopy.^{11,12} They also extended the band assignments with respect to the cluster size by means of mass-selected (1+1') two-color multiphoton ionization. In the theoretical work, *ab initio* molecular orbital calculations have been done by several groups for the clusters with n=1 to 3 (Refs. 15–19). However, the structures of the phenol-(H₂O)_n clusters have not been directly determined by experiments based on the electronic spectroscopy so far. The difficulty in determining the geometrical structure of the clusters is mainly due to a lack of information of the vibrations especially for the OH stretching modes, which are most sensitive to the intermolecular H bonding.

Very recently, vibrational spectroscopy of gas phase molecular clusters has become possible by using double-resonant spectroscopic techniques, such as IR-UV double resonant spectroscopy^{20,21} and stimulated Raman-UV double resonant spectroscopy.^{21–24} In a previous paper, we reported IR spectra of the OH stretching vibrational region (3000–3800 cm⁻¹) of ground state phenol-(H₂O)_n (n=1–3) by using IR-UV double resonance or ionization detected infrared (IDIR) spectroscopy.²⁰ It was demonstrated that IR-UV double resonance spectroscopy is a powerful technique to observe the vibrational spectra of low density clusters prepared in a supersonic expansion. In the phenol-(H₂O)_n spectra, we observed the bands due to the OH stretching vibration of phenol site as well as those of H₂O sites, and found that

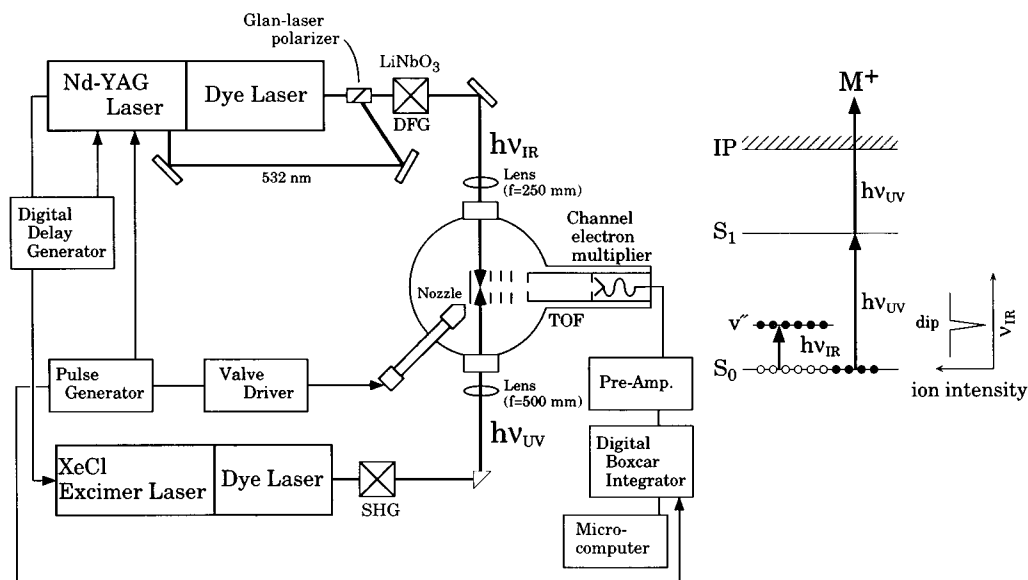


FIG. 1. Experimental setup (left) and the excitation scheme (right) for IDIR spectroscopy.

the frequencies of the phenolic OH stretching vibration and of the symmetric OH vibrations of H₂O moieties drastically decrease with increase of the cluster size, *n*. On the other hand, frequencies of antisymmetric vibrations of H₂O moieties are almost unchanged even in the cluster with *n*=3. The observed spectra were analyzed by comparing with the IR spectra of pure (H₂O)_n clusters. We suggested that the IR spectra of H₂O site in phenol-(H₂O)₂ cluster resemble with that of pure (H₂O)₂ cluster reported by Page *et al.*²⁵ Very recently, however, it is suggested that their IR spectrum of (H₂O)₂ is contaminated with the (H₂O)₃ cluster bands.²⁶ It should be noted that the IR spectra of completely size selected (H₂O)_n clusters in the whole spectral region has not been observed yet, though their vibrational spectra are predicted by many theoretical studies.²⁷

In the present paper, we report the IR-UV double resonance spectroscopic study of phenol-(H₂O)_n (*n*=1–4) and also the stimulated Raman-UV double resonance spectroscopic study for phenol-(H₂O)_n (*n*=1,2). The observed spectra showed characteristic features depending on the cluster size. Very recently, *ab initio* molecular orbital calculation with SCF/6-31G and SCF/6-31G* basis sets have been performed for phenol-(H₂O)_n (*n*=1–4) by Watanabe and Iwata.²⁸ They obtained stabilization energies of the clusters, harmonic frequencies and IR intensities of the OH stretching vibrations. The observed IR spectra were readily analyzed by comparing with the calculated IR spectra of energy minimized clusters. The structures of the clusters with respect to the intermolecular hydrogen bonds were determined and discussed. We also investigated the enhancement of the IR absorption intensity upon the cluster formation. It was found that the IR absorption intensity of phenolic OH stretching vibration increases by a factor of 6 in phenol-H₂O compared to that of bare phenol, and it increases with the cluster size. The deuterium isotope effect was also investigated by measuring the IR spectra for phenol-*d*₁ and phenol-*d*₁-D₂O.

II. EXPERIMENT

Figure 1 shows the experimental setup and the excitation scheme of IR-UV double resonance spectroscopy. The setups of IR-UV double resonance and stimulated Raman-UV double resonance spectroscopies are essentially the same described in previous papers.^{20,21,24} The phenol-(H₂O)_n clusters were generated by a supersonic expansion of a gaseous mixture of phenol/water diluted with He, through a pulsed nozzle. The samples were maintained at room temperature before the expansion and the vapor pressures of phenol and water were 0.4 torr and 25 torr, respectively and they were diluted with He at a total pressure of 4 atm. The mixture was expanded into vacuum through a nozzle having an 800 μm orifice.

As was described previously, the IR absorption spectra and the Raman spectra of the phenol-(H₂O)_n clusters were obtained as ion-dip spectra, so called ionization detected infrared (IDIR) and ionization detected stimulated Raman (IDSR) spectra. The ground state population of a particular cluster was monitored by an ion current generated by resonance enhanced MPI (REMPI) through the S₁ state with an UV source. The UV source used was a second harmonic of a XeCl excimer laser pumped dye laser (Lambda Physik LPX 100/FL2002). The pulse energy, spectral resolution and a pulse duration of the UV laser were 5 μJ, 0.2 cm⁻¹ and 12 ns, respectively. Either total ions or mass separated ions were observed by a conventional time-of-flight mass spectrometer. The ion current was amplified by a preamplifier (NF model BX-31) and the signal was processed by a boxcar integrator (Par 4402/4420) connected with a microcomputer (NEC).

Tunable IR laser pulse was generated by a difference-frequency mixing between a second harmonic of a Nd:YAG laser (Quantel YG 581-10) and a Nd:YAG laser pumped dye laser (Quantel TDL 50 with DCM dye) with a LiNbO₃ crystal. The IR pulse duration was 8 ns and the pulse was intro-

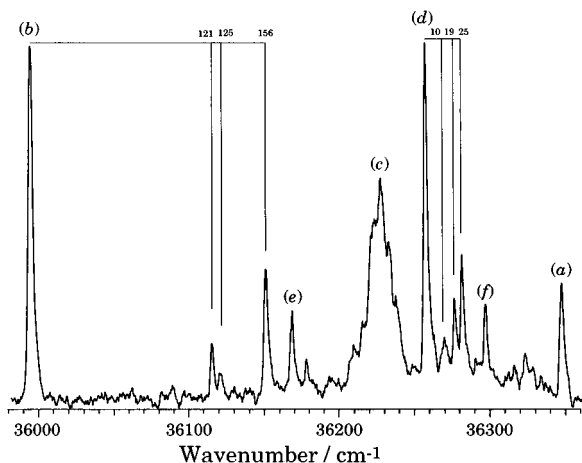


FIG. 2. 1+1 REMPI spectrum of the S_1-S_0 electronic transition of bare phenol and phenol-(H₂O)_{*n*} in the (0,0) band region. The labeled bands are used to monitor their population for the measurement of the IDIR and IDSR spectra. (a) bare phenol, (b) phenol-H₂O, (c) phenol-(H₂O)₂, (d) phenol-(H₂O)₃, (e) phenol-(H₂O)₄ and (f) phenol-(H₂O)₄^{*}.

duced 50 ns prior to the UV laser pulse. For the IR laser, a typical laser energy was 0.4 mJ and the spectral resolution was 1 cm⁻¹. The lasers and the pulsed valve were operated with a repetition of 10 Hz. The IR and UV beams were coaxially focused by lenses ($f=250$ mm lens for IR and an $f=500$ mm lens for UV) inside a vacuum chamber in the counterpropagated direction and they crossed the supersonic jet at 15 mm downstream of the pulsed nozzle. When the IR frequency is resonant to the vibrational transition of a particular cluster, the ground state population of the cluster is

reduced, resulting in the depletion of the ion current. Thus, by scanning the IR wavelength while monitoring the ion current, the ion-dip spectrum is obtained, which represents the vibrational spectrum of the selected cluster.

Same laser systems were used for the measurement of the Raman spectra. In this measurement, the stimulated Raman excitation was performed with two laser beams, a second harmonic of the Nd:YAG laser (ν_1) and an output of the Nd:YAG laser pumped dye laser (ν_2). The pulse energy for the ν_1 and ν_2 lasers were 30 mJ and 20 mJ and they were combined by a beam combiner. The laser beams were coaxially introduced to a vacuum chamber in the opposite direction to the UV laser beam and were focused at 15 mm downstream of the pulsed nozzle. The Raman spectrum was observed by scanning the ν_2 laser frequency while monitoring the ion signal.

Phenol (98%) was purchased from Wako Chemical Industries, Ltd. and was purified by vacuum sublimation. In the case of the deuterated phenol experiment (phenol-*d*₁ and phenol-*d*₁-D₂O), the samples were prepared by an isotopic exchange with an excess amount of D₂O.

III. RESULTS AND DISCUSSION

Figure 2 shows the S_1-S_0 (1+1) REMPI spectra of the phenol-(H₂O)_{*n*} clusters in the band origin region, where the total ion current was monitored. Prominent bands have already been assigned with respect to the cluster size by several groups with REMPI-Mass spectroscopic studies,^{6–11} and a good agreement is obtained for the clusters up to $n=3$. The band labeled by (a) is due to the (0,0) band of bare phenol. The bands denoted by (b) and (d) are assigned to the (0,0)

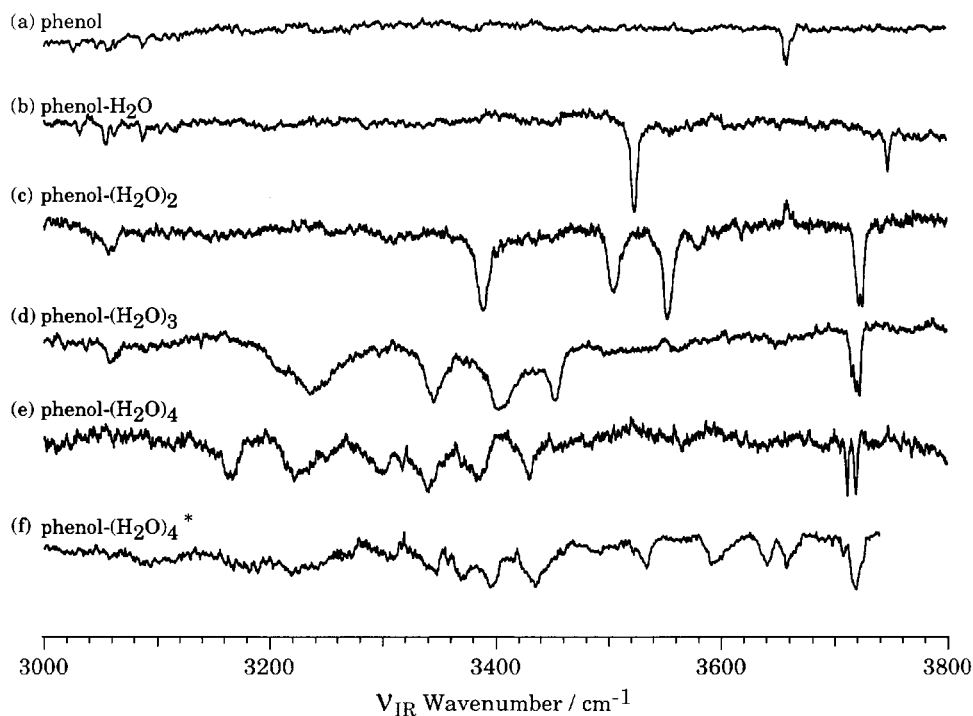


FIG. 3. Ionization detected infrared (IDIR) spectra of bare phenol and phenol-(H₂O)_{*n*} in the region between 3000 and 38000 cm⁻¹.

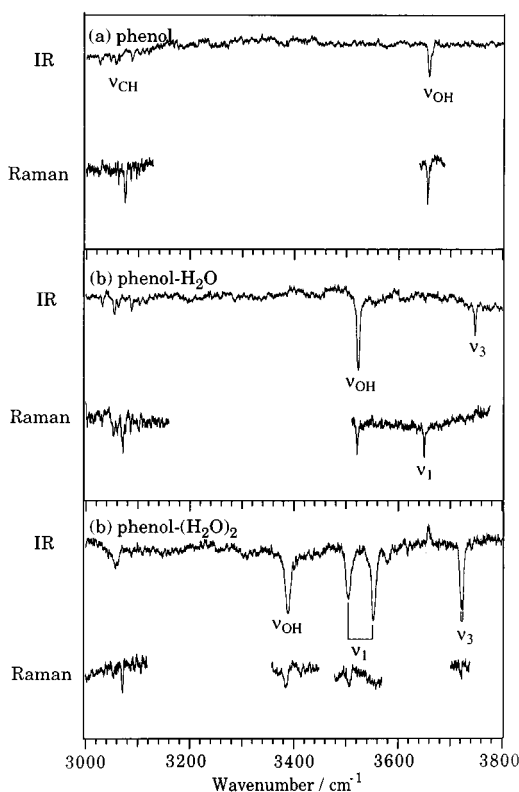


FIG. 4. Ionization detected infrared (IDIR) and ionization detected stimulated Raman (IDSRS) spectra of (a) bare phenol, phenol-H₂O and phenol-(H₂O)₂.

bands of the clusters with $n=1$ and 3, respectively. The broad band (*c*) was previously assigned to the (0,0) band of phenol-(H₂O)₂. However, very recently, it was found that this band should be the vibronic band of the same cluster and its (0,0) band itself is too weak to be observed.²⁹ The assignments for the $n \geq 4$ clusters were given by Stanley and co-workers with REMPI-Mass spectrometric study.⁹ They reported that the band (*e*) is assigned to the (0,0) band of the $n=4$ cluster and the band (*f*) to the (0,0) band of its isomer, because their ionization potentials were different. However, as will be described later, the obtained IR spectrum suggests that the band (*f*) might belong to phenol-(H₂O)₅. Other peaks have been assigned to the intermolecular vibrational bands accompanied to each clusters.^{6–15} For the observation of the IDIR and IDSRS spectra of each cluster, the UV laser frequency was set to the bands (*a*)–(*f*), respectively.

A. IR and Raman spectra of bare phenol and phenol-(H₂O)_n clusters

Figure 3 shows the IR spectra of bare phenol and phenol-(H₂O)_n, $n=1–4$ in the frequency region of 3000–3800 cm⁻¹. Figure 4 shows a comparison of the IR spectra and the Raman spectra for bare phenol and phenol-(H₂O)_n, $n=1$ and 2. Both spectra are not normalized with respect to the laser intensity. In Table I, frequencies of all the observed bands are listed. Also listed are the vibrational frequencies obtained by Watanabe and Iwata with *ab initio* calculation.²⁸

The typical dip intensity in the IDIR spectra was 70~80%. Such a large dip intensity exceeding 50% is not expected in a model with two levels system under a saturated condition. The dip intensity seems to represent that the lifetimes of the vibrationally excited states of the clusters are very short owing to the fast decay processes, such as intracluster vibrational redistribution or vibrational predissociation. The evidence of the short lifetime of the vibrationally excited levels can also be seen in their bandwidths, which will be discussed later. In the following sections, we describe the structure of the observed spectra in detail.

1. Bare phenol

As shown in Figs. 3(a) and 4(a), both the IR and Raman spectra show a single peak of the OH stretching vibration at 3657 cm⁻¹. The frequency of the observed band is in good agreement with that reported by Bist *et al.*³⁰ and by Hartland *et al.*²² In the CH stretching region, six bands are observed in the IR spectrum, while five bands are observed in the Raman spectrum. Especially, the most intense Raman band at 3075 cm⁻¹ is completely missing in the IR spectrum. The intense Raman band is assigned to the totally symmetric CH stretching vibration of phenol (ν_2), while the other bands are assigned to asymmetric CH stretching vibrations. Thus, there is a clear intensity alternation between IR and Raman activities for the CH stretch vibrations. It is noted that the total number of the observed vibrational bands is six, which is larger than the total number of CH bonds, five, in phenol. The result suggests an anharmonic coupling between the CH stretching and other vibrational modes.

2. Phenol-H₂O

Figure 3(b) shows the IR spectrum of phenol-H₂O, in which two intense bands due to the OH stretching vibrations are observed at 3524 and 3748 cm⁻¹, and weak bands due to the CH stretching vibrations are observed at ~3050 cm⁻¹. Hartland *et al.* applied IDSRS spectroscopy to phenol-H₂O and observed two OH stretching vibrational bands at 3524 and 3650 cm⁻¹. They assigned the former band to be the phenolic OH stretching vibration and the latter band to the symmetric OH stretching vibration (ν_1) of H₂O site. In accord with their assignment, the band at 3524 cm⁻¹ in Fig. 3(b) is assigned to the OH stretching vibration of phenol site. It is evident that the OH vibrational frequency is largely reduced by the H-bond formation with H₂O; its frequency is red shifted by 133 cm⁻¹ from that of bare phenol. The peak at 3748 cm⁻¹ is assigned to the antisymmetric stretching vibration (ν_3) of the H₂O site. This band is expected to be strong in the IR spectrum since the IR/Raman intensity alternation is observed in bare H₂O molecule. To confirm the IR/Raman intensity alternation of the vibrations of the H₂O site, we observed the Raman spectrum under the same condition by using IDSRS spectroscopy, which is shown in Fig. 4(b). As can be seen in the figure, the ν_1 vibration strongly appeared, while the ν_3 vibration is very weak in the Raman spectrum. Thus, the IR/Raman propensity rule is upheld in the OH stretching vibrations of the H₂O site.

TABLE I. The frequencies, assignments, band widths and relative IR intensities^a for bare phenol, phenol-(H₂O)_n and their isotopomer.

	Frequency/cm ⁻¹	Assignment	Band width/cm ⁻¹	Relative IR intensity	Frequency (calculated)/cm ⁻¹ ^b
phenol	OH stretching phenol site				
	3657	ν_{OH}	4.3	1.0	3683
	CH stretching				
	3103			IR, Raman	
	3097			Raman	
	3087	ν_{20a}		IR, Raman	
	3075	ν_2		Raman	
	3062			Raman	
	3057	ν_{7b}		IR	
	3047			IR	
	3031	ν_{13}		IR	
3026			IR		
phenol-H ₂ O	OH stretching H ₂ O site				
	3748	ν_3	1.7	1.9	3779
	3650	ν_1			3642
	phenol site				
	3524	ν_{OH}	1.7	6.3	3503
	CH stretching				
	3102			IR, Raman	
	3087	ν_{20a}		IR, Raman	
	3072	ν_2		Raman	
	3063			IR, Raman	
	3054	ν_{7b}		IR, Raman	
3032	ν_{13}		IR, Raman		
phenol-(H ₂ O) ₂	OH stretching H ₂ O site				
	3725	ν_3	1.7	2.2	3757
	3722	ν_3	2.0	1.7	3754
	3553	ν_1	3.6	7.5	3534
	3505	ν_1	6.0	5.3	3463
	phenol site				
	3388	ν_{OH}	3.7	5.1	3369
	CH stretching				
	3088	ν_{20a}		IR, Raman	
	3071	ν_2		Raman	
	3057	ν_{7b}		IR, Raman	
3044			IR, Raman		
3035	ν_{13}		Raman		
phenol-(H ₂ O) ₃	OH stretching H ₂ O site				
	3722	ν_3	1.2	3.9	3750
	3719	ν_3	1.7	3.7	3749
	3715	ν_3	1.6	1.6	3748
	3451	ν_1	4.3	13.9	3426
	3401	ν_1	14.9	16.2	3350
	3345	ν_1	7.2	5.0	3298
	phenol site				
	3236	ν_{OH}	55.5	11.0	3208
	phenol-(H ₂ O) ₄	OH stretching H ₂ O site			
3719		ν_3			3748 3752
					3746 3745
3711		ν_3			3743 3745
					3742 3744
3430		ν_1			3389 3385
3386		ν_1			3315 3318
3341		ν_1			3273 3276
3299		ν_1			3226 2332
3221		ν_1			
phenol site					
3167	ν_{OH}			3135 3143	

TABLE I. (Continued.)

	Frequency/cm ⁻¹	Assignment	Band width/cm ⁻¹	Relative IR intensity	Frequency (calculated)/cm ⁻¹ ^b	
phenol-(H ₂ O) ₄ [*]	OH stretching					
	3719					
	3708					
	3658	window region				
	3641					
	3591					
	3534					
	3435					
	3395					
	3370					
	3348					
	3309					
	3218					
	3183					
3094						
phenol-d ₁	2705		ν_{OD}			
phenol-d ₁ -D ₂ O	2787		ν_3			
	2608	ν_{OD}				
H ₂ O	3755.79 ^c	ν_3				
	3657.79 ^c	ν_1				
H ₇ O ₃ ⁺	3721.6 ^d	H ₂ O ν_3		1.00		
	3667.0 ^d	H ₃ O ⁺ OH stretching		0.23		
	3637.4 ^d	H ₂ O ν_1		0.41		
OH ⁻	3555.5932 ^e					
D ₂ O	2788.05 ^f	ν_3				
	2671.46 ^f	ν_1				
HDO	3707.47 ^f	ν_3/ν_{OH}				
	2726.73 ^f	ν_1/ν_{OD}				

^aThese values are normalized by taking the IR intensity of bare phenol to the unity.

^bReference 28, The calculated frequencies for the ring structure are shown. A scale factor of 0.9102 was applied to the calculated frequencies. In the case of phenol-(H₂O)₄, two ring structures with small energy difference were obtained.

^cReference 42.

^dReference 34.

^eReference 35.

^fReference 43.

The remarkable redshift of the phenolic OH stretching vibrational frequency, 133 cm⁻¹, represents that the OH bond strength is drastically weakened by the H-bond formation, which is in accord with the expectation that phenol should act as a proton donor. On the other hand, frequency shifts of the symmetric (ν_1) and antisymmetric (ν_3) stretching vibrations of the H₂O site are 7 cm⁻¹ and 8 cm⁻¹, respectively. Thus, not only the IR/Raman propensity is upheld but also the frequency shifts are very small in the OH stretching vibrations the H₂O site. Therefore, it is concluded that the force field of the H₂O site is not so affected by the H-bond formation and that H₂O is the proton acceptor site. This result agrees well with *ab initio* calculations by Watanabe and Iwata.²⁸ In Fig. 5(b) is shown a comparison of the observed IR spectrum with the calculated one (stick diagram) of phenol-H₂O. As can be seen in the figure, the phenolic OH stretching vibration largely shifts to red by H-bond formation, and the IR absorption intensity of ν_3 band is much stronger than ν_1 band in H₂O site in the calculated spectrum.

In contrast to the large red shift of the OH stretching vibration, the CH stretching vibrations in the phenol site are less affected by the cluster formation. As shown in Figs. 3(b)

and 4(b), the IR/Raman activities and the frequencies of the CH stretching vibrations are almost the same with those of bare phenol.

3. Phenol-(H₂O)₂

The IR spectrum of phenol-(H₂O)₂ is shown in Fig. 3(c) and corresponding Raman spectrum is shown in Fig. 4(c). Five bands are observed in the OH stretching vibrational region; three bands at 3388, 3505, and 3553 cm⁻¹ with relatively broad bandwidths and two closely separated bands at 3722 and 3725 cm⁻¹. The number of the observed OH bands is equal to the number of OH oscillators in this cluster. In a previous paper, we tentatively assigned the observed bands by comparing them with the IR spectrum of water dimer, (H₂O)₂, reported by Page *et al.*²⁵ However, in a recent work done by Huisken and coworkers,²⁶ it is suggested that the IR spectrum of (H₂O)₂ reported by Page *et al.* was contaminated with the absorption bands of the water trimer, (H₂O)₃. The results indicate that the IR spectrum of pure water dimer was not helpful for the assignments of the bands of the phenol-(H₂O)₂ spectrum.

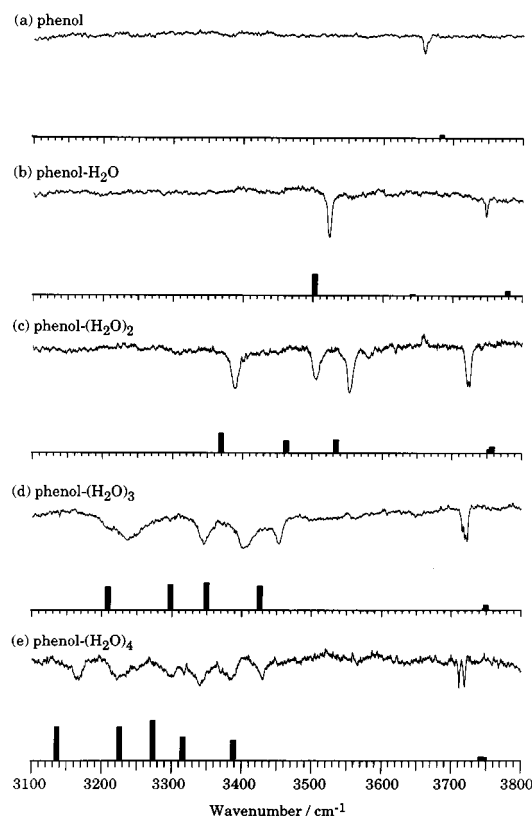


FIG. 5. Comparison between the observed IR spectra of the OH stretching vibrations (top) and the calculated ones (stick diagram) obtained by Watanabe and Iwata (Ref. 28). The intensity of the calculated IR spectra are normalized to that of ν_{OH} of bare phenol. For phenol-(H₂O)_n with $n \geq 2$, only the spectra of the ring-form structure is shown in the calculated spectra.

In this respect, the previous assignments must be revised by comparing the observed spectrum with the results of the *ab initio* calculations in the subsequent paper of Watanabe and Iwata.²⁸ According to their results, the most stable form of phenol-(H₂O)₂ is the ring form shown in Fig. 6(b) and a good agreement is obtained between the observed and the calculated IR spectra of the ring form phenol-(H₂O)₂ as is seen in Fig. 5(c). Very recently, Gerhards and Kleinermanns reported the stable form and vibrational modes of phenol-(H₂O)₂ based on *ab initio* molecular orbital calculations.¹⁴ Though they reported only the results of the ring form, their calculated frequencies of the OH stretching vibrations are also in good agreement with those of the observed spectrum reported in a previous paper.²⁰

In the ring form cluster, there are three H-bonded OH groups and two OH groups protruding from the ring. Therefore, as a first approximation, three bands at 3388, 3505, and 3553 cm⁻¹ can be assigned to the H-bonded OH stretching vibrations in the H-bonded ring and the bands at 3722 and 3725 cm⁻¹ can be assigned to the OH stretching vibrations free from H bonds. According to the *ab initio* calculations, the band at 3388 cm⁻¹, which is the lowest frequency vibration, is assigned to the H-bonded phenolic OH stretching vibration and other two bands are assigned to the symmetric OH stretching vibrations of H₂O sites. On the other hand, the

bands appeared at 3722 and 3725 cm⁻¹ are assigned to the asymmetric OH stretching vibrations of H₂O sites. It should be noted that the frequencies of the latter two bands are close to the OH stretching vibration of HDO (3707.47 cm⁻¹) in the gas phase,³¹ in which the OH and OD stretching vibrations are described as local modes. Therefore, the vibrations of the two OH oscillators which are protruding from the ring seem to change to local mode vibrations. As can be seen in Fig. 3, the bands at ~ 3720 cm⁻¹ remain almost unperturbed irrespective of the cluster size.

4. Phenol-(H₂O)₃

The IR spectrum of phenol-(H₂O)₃ is shown in Fig. 3(d). Corresponding Raman spectrum could not be measured because of weak Raman dip intensity. Seven bands are observed for the OH stretching vibrations; four intense bands at 3236, 3345, 3401, and 3451 cm⁻¹ with broad bandwidths and three sharp bands at 3715, 3719, and 3722 cm⁻¹. In a previous paper, we made a tentative assignment of the vibrational bands by comparing them with the IR spectrum of (H₂O)_n cluster reported by Vernon *et al.*³² In this paper, the assignment of the bands is provided on the basis of the calculated results in the subsequent paper of Watanabe and Iwata.²⁸ They reported that the most stable structure of phenol-(H₂O)₃ is the ring form as shown in Fig. 6(c) and the simulated IR spectrum of the ring form cluster well reproduces the observed one as is seen in Fig. 5(d). The intense four bands at lower frequency side are due to the OH stretching vibrations in the ring, and the three bands at higher frequency side to the OH stretching vibrations protruding from the ring. According to the calculated results, the lowest frequency vibration consists mainly of the H-bonded phenolic OH stretching vibration, and the other three low frequency vibrations are attributed predominantly to the symmetric OH stretching vibrations of H₂O sites. Very recently, Bürgi *et al.* predicted also the ring form isomer by *ab initio* calculations, though they did not give the vibrational frequencies of the OH stretching vibrations.¹⁹

5. Phenol-(H₂O)₄

In the S_1-S_0 electronic spectrum, as was described in a previous section, there are two band origins for phenol-(H₂O)₄;⁹ the peaks at 36 167 [band (e)] and 36 295 cm⁻¹ [band (f)] in Fig. 2. Figure 3(e) shows the IR spectrum measured by monitoring the ion signal with the UV laser frequency fixed at the band (e). The observed bands in the IR spectrum are classified into two groups; one group consists of the bands located between 3150 and 3450 cm⁻¹, and the other group consists of the bands located at ~ 3720 cm⁻¹. Similar to the IR spectrum of phenol-(H₂O)₃, the spectral feature of phenol-(H₂O)₄ is well characterized by the ring form shown in Fig. 6(d). According to the *ab initio* calculations by Watanabe and Iwata,²⁸ it is shown that the ring form is the most stable structure for phenol-(H₂O)₄. The calculated IR spectrum of the ring form phenol-(H₂O)₄ reproduces the observed one very well as is seen in Fig. 5(e). The bands belonging to the former group are assigned to the OH

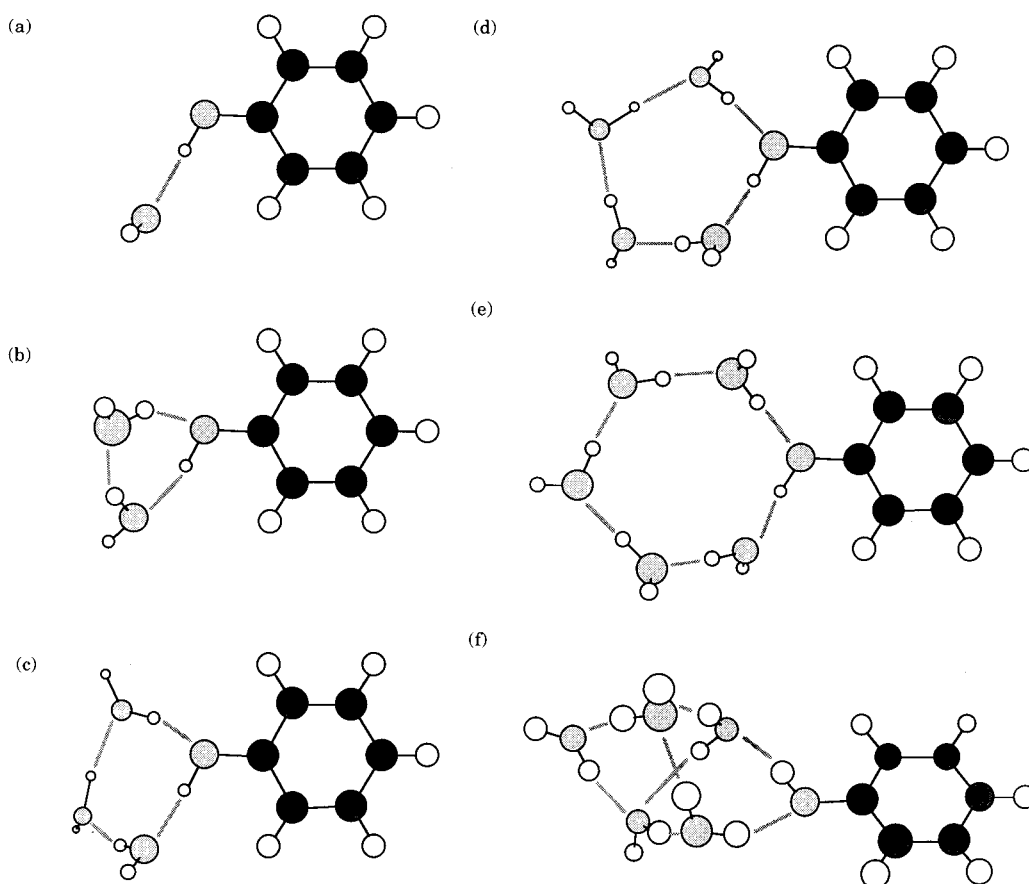


FIG. 6. (a)–(e) Structures of ring form clusters of phenol-(H₂O)_n obtained by *ab initio* calculation performed by Watanabe and Iwata. (f) One of the isomeric form of phenol-(H₂O)₅, called “ice(I)” form. For detailed calculation see Watanabe and Iwata (Ref. 28).

stretching vibrations in the ring and the bands in the latter group are assigned to the OH stretching vibrations protruding from the ring.

As seen in Figs. 3(c)–3(e) and also Figs. 5(c)–5(e), it is noticed that the IR spectra the ring form clusters exhibit a characteristic feature; all the bands due to the H-bonded OH stretching vibrations in the ring are broad and extremely red-shifted depending on the ring size, while all the bands due to the OH stretching vibrations protruding from the ring appear at $\sim 3720\text{ cm}^{-1}$ irrespective of the size. Thus, the interval between the H-bonded OH and the H-bond free OH stretching vibrations increases with the cluster size. Since no band is observed this region, we call it a “window” region.

6. The anomalous IR spectrum of phenol-(H₂O)₄*

Figure 3(f) shows the IR spectrum obtained by monitoring the band (*f*) at $36\,295\text{ cm}^{-1}$ in Fig. 2, which has been assigned as an isomer of phenol-(H₂O)₄ by Stanley *et al.*¹¹ The spectrum exhibits a remarkable feature; more than 11 bands are observed and four of them appear in the window region. Based on the classification described above, the characteristic spectrum of this particular isomer of phenol-(H₂O)₄ represents that the cluster structure should be substantially different from the ring form. Since the spectrum is so anomalous, we carefully examined a possibility of the excitation of

a mixture of different cluster species. If there are two species whose electronic transitions accidentally overlapped at $36\,295\text{ cm}^{-1}$ in Fig. 2, the IR spectrum obtained by using REMPI via the band would consist of two components associated with the different species. In such a case, the relative band intensity of the IR spectrum would depend on the jet expansion condition, because the cooling condition may change the abundance of two species in the jet. Also the spectral feature may change when the UV laser frequency is slightly tuned within the band envelope, because a slight difference of the transition energy may lead a change in relative ratio of the monitoring species. Though we measured the IR spectrum under different conditions, we did not find any spectral change due to such a mixed excitation. Therefore, the results suggest that the IR spectrum of Fig. 3(f) is due to a single species, though we can not exclude the possibility of the mixture of different species.

There are several interpretations for the anomalous IR spectrum of the “isomer of phenol-(H₂O)₄.” As was described previously, more than 11 bands are observed in the region of the OH stretching vibrations. Since one OH band is due to phenol and the remaining ten bands are due to the H₂O sites, the observed IR spectrum indicates that five H₂O molecules must be involved in this species. Therefore, we tentatively assigned the species as a particular form of

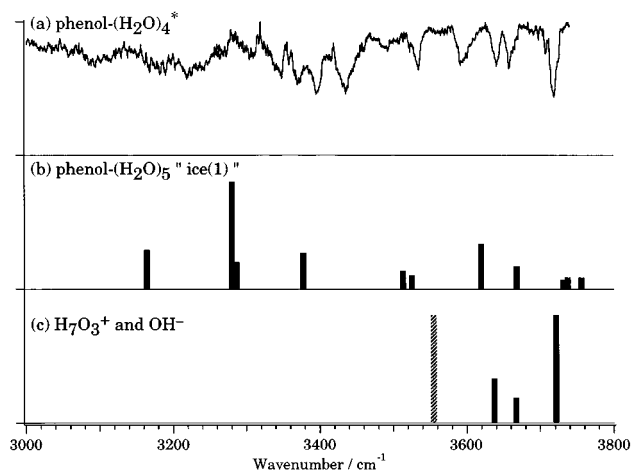


FIG. 7. (a) IDIR spectrum of anomalous species of phenol-(H₂O)₄*. (See text.) (b) Calculated IR spectrum of the non ring form phenol-(H₂O)₄ cluster shown in Fig. 4(f). (c) IR spectrum of H₃O₃⁺ (solid stick diagram see Ref. 34) and OH⁻ (hatched stick diagram Ref. 35).

phenol-(H₂O)₅, though Stanley *et al.* assigned it an isomer of phenol-(H₂O)₄ by two-color REMPI detection. An explanation of this discrepancy is that one of the H₂O molecules in this cluster may evaporate easily after the ionization even by using two-color ionization.

Second interesting point is what is the origin for the bands appearing in the window region, and consequently what kind of cluster form is appropriate for the phenol-(H₂O)₅. One possibility is provided by *ab initio* calculations given in the subsequent paper of Watanabe and Iwata.²⁸ They demonstrate that the simulated IR spectra for branched forms of the n=4–6 clusters exhibit the characteristic feature showing OH bands in the window region. Among them, it is shown that one of isomers of phenol-(H₂O)₅ shows the similar feature to the observed spectrum. In Fig. 7 is shown a comparison between the observed and the simulated spectra for a particular isomer of phenol-(H₂O)₅, which is called “ice (I),” and is illustrated in Fig. 6(f). Though the agreement between the calculated and the observed spectra is not satisfactory, it is seen this isomer exhibits characteristic bands in the window region. In addition to the isomeric form of phenol-(H₂O)₅, Watanabe and Iwata suggested the possibility of the mixed excitation of several branch form isomers to describe the observed IR spectrum in the subsequent paper.²⁸

The other possibility of the species has been proposed in a previous paper.³³ It was pointed out that the frequencies of the bands appeared in the window region are very close to those of hydrated hydronium ion, H₇O₃⁺ and of OH⁻. The similarity suggested that an ion-pair moiety may be involved in the cluster, in spite of that it is the neutral species in the ground electronic state. In Fig. 7 is also shown the band positions of H₇O₃⁺ and of bare OH⁻, which were reported by Lee and coworkers,³⁴ and by Owrutsky *et al.*,³⁵ respectively. The observed bands at 3641, 3658, and 3720 cm⁻¹ for the species of interest correspond very well to the bands of 3637.4, 3667.0, and 3721.6 cm⁻¹ of H₇O₃⁺, respectively. As

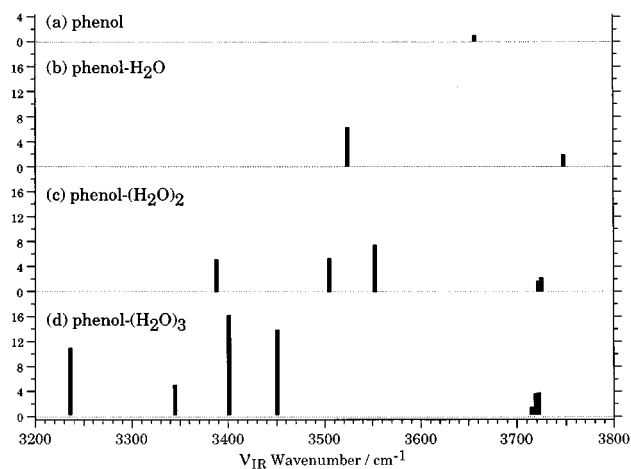


FIG. 8. Normalized IR absorption intensity of the OH stretching vibrations of bare phenol and phenol-(H₂O)_n obtained by using Eq. (3). The height of the bars represents the integrated absorption intensity.

can be seen in the figure, the relative band intensities are also similar to those of H₃O⁺(H₂O)₂. Though the stretching vibrational frequency of hydrated OH⁻ has not been reported, the frequency of bare OH⁻ (3555 cm⁻¹) is close to the band at 3535 cm⁻¹ of the present species. As it was proposed, thus, it is suggested that the ion-pair form of [phenol-(H₇O₃⁺)(H₂O)(OH⁻)] may characterize vibrational bands appeared in the window region. Although the idea is not supported by theoretical confirmation, Lee and Sosa very recently reported that the ion-pair type isomer is stable for (H₂O)₅ and (H₂O)₈ clusters base on the *ab initio* calculations at HF/MP2 level with 6–31+G(D,P) basis sets.³⁶ This result suggests that the ion-pair type isomer can be also possible in phenol-(H₂O)₅. Further investigations are necessary to reveal the structure of this species experimentally and theoretically as well.

7. Intensity and bandwidth of the OH bands

As was reported in a previous paper,²¹ the apparent dip depth is not in proportional to the absorption intensity, and the quantitative IR absorption cross section can be obtained by using the following expression

$$\sigma_{\text{IR}} I_{\text{IR}} \Delta t = \ln(C_{\text{off}}/C_{\text{on}}). \quad (1)$$

Here, σ_{IR} is the IR absorption cross section, I_{IR} is the IR laser intensity, Δt is the pulse duration of the IR laser. C_{on} and C_{off} are REMPI signal intensities with ν_{IR} is resonant or off-resonant to the IR transition, respectively. Therefore, we can obtain the absolute vibrational transition cross section, σ_{IR} , by measuring the ratio of the REMPI intensities, C_{off} and C_{on} and the IR laser intensity under the condition that the transition is not saturated. Actually, it is very difficult to estimate the IR laser intensity at the focusing position and only the relative absorption cross section was obtained. The stick diagrams in Fig. 8 are the IR spectra of bare phenol and phenol-(H₂O)_n (n=1–3) obtained by this procedure. Here, the absorption intensity is normalized so that the intensity of bare phenol is unity. As shown in the figure, the IR intensity

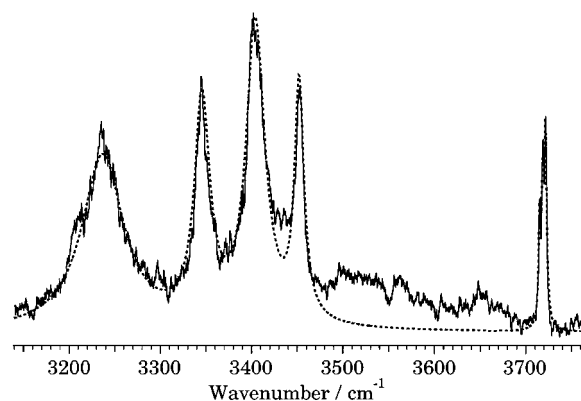


FIG. 9. IR spectrum of phenol-(H₂O)₃, where $\ln(C_{\text{off}}/C_{\text{on}})$ is plotted vs IR frequency. The best fitted Lorentzian curves are indicated by dotted lines (see text).

of phenolic OH band of phenol-H₂O increases by a factor of 6 compared with that of bare phenol. The IR intensity of the H-bonded OH stretching vibrations of the H₂O sites show also large increases in the ring form clusters. That is, the IR intensity of the OH stretching vibrations greatly increase when the OH group acts as a proton donor. This intensity enhancement is well known in liquid phase, and Tsubomura proposed that the intensity enhancement is attributed to the contribution of the charge transfer forms.³⁷ It is also possible to explain the enhancement of the IR cross section by expressing the transition moment using Herzberg Teller expansion, where the intensity enhancement in the cluster can be explained by the mixing of electronic excited states upon OH stretching vibration. Among the electronic excited states, contributions of the charge transfer or the proton transfer states are characteristic in the clusters. Since the energy of these states are stabilized with the increase of the number of solvent molecules, H₂O, the IR intensity will increase with the size. Actually, the absorption intensity of the lowest frequency OH stretching vibration, 3237 cm⁻¹, of phenol-(H₂O)₃ cluster is enhanced by a factor of 11 compared with that of bare phenol. It should be noted that the stabilization of the first excited state, S₁, is only a few hundreds of wavenumber, whose contribution to the intensity enhancement is very small.

In addition to the intensity enhancement, the bandwidth was also found to increase for the OH bands upon the H-bond formation. Figure 9 shows the IR spectrum of phenol-(H₂O)₃, where the ordinate is scaled by using Eq. (1). Each vibrational bands were fitted by Lorentzian curves and obtained bandwidths are also listed in Table I for phenol-(H₂O)_n with n=1–3. It is clear in the figure that the bandwidths of the H-bonded OH stretching vibrations are much wider than those of the OH stretching vibrations free from H bond. Though it is not clear that the observed bandwidths purely involve vibrational relaxation rates, the results strongly indicate that the relaxation of the OH vibrations in the ring is much faster than that of the OH vibrations free from H bond. For pure (H₂O)₂, Huang and Miller determined the predissociation lifetimes of the levels of the OH stretch

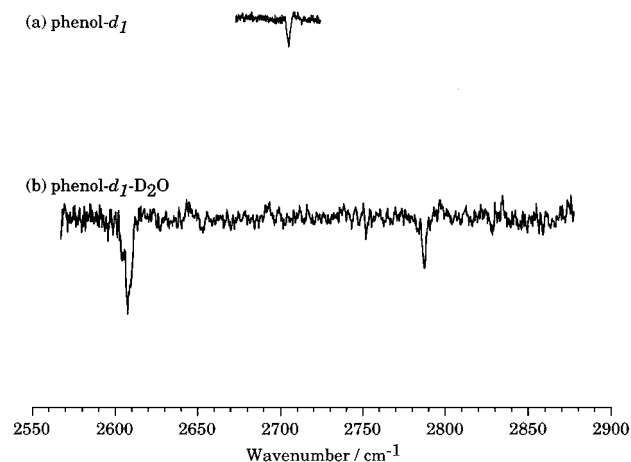


FIG. 10. IDIR spectra of bare phenol-*d*₁ and phenol-*d*₁-D₂O.

vibrations from the linewidth measurement by high-resolution spectroscopy.³⁸ They reported that the lifetime of the H-bonded OH stretching vibrational level of donor H₂O is shorter than that of the free OH stretching vibrational level of acceptor H₂O. They interpreted the results as follows; the coupling of the H-bonded OH stretching vibrations with other modes, especially low frequency intermolecular vibrations, is much stronger than that of the free OH stretching vibrations. In the present work, the same interpretation may be adopted for the observed difference in the bandwidth of the phenol-(H₂O)_n clusters.

8. IR spectrum of bare phenol-*d*₁ and phenol-*d*₁-D₂O

The electronic spectra of bare phenol-*d*₁ and phenol-*d*₁-D₂O were investigated by Lipert *et al.*³⁹ and Dopfer *et al.*⁴⁰ in the region of band origins. The (0,0) band of phenol-*d*₁ is redshifted by 2.5 cm⁻¹ from that of bare phenol-*h*₁, while the (0,0) band of phenol-*d*₁-D₂O is blue shifted by 10 cm⁻¹ from that of phenol-H₂O. Figure 10 shows the IDIR spectrum of (a) bare phenol-*d*₁ and (b) phenol-*d*₁-D₂O obtained by monitoring their (0,0) bands. The OD stretching vibration of bare phenol-*d*₁ is observed at 2705 cm⁻¹, and that of the phenol-*d*₁-D₂O cluster was observed at 2608 cm⁻¹ which is red shifted by 97 cm⁻¹ from that of bare phenol-*d*₁. On the other hand, the frequency shift of the antisymmetric vibration of D₂O, 2787 cm⁻¹, is only 2 cm⁻¹ from that of D₂O(2789 cm⁻¹) in the gas phase.⁴¹ Therefore, the effect of the H bond on the D₂O site is essentially the same with that of phenol-H₂O.

Then, we compared the ratio of the vibrational frequency, $\nu_{\text{OH}}/\nu_{\text{OD}}$ for bare phenol, $\nu_{\text{OH}}(\text{phenol})/\nu_{\text{OD}}(\text{phenol-}d_1)$, and hydrogen-bonded cluster, $\nu_{\text{OH}}(\text{phenol-H}_2\text{O})/\nu_{\text{OD}}(\text{phenol-}d_1\text{-D}_2\text{O})$. The ratio is obtained to be 1.352 for phenol-water (1:1) cluster, which is very close to the value of 1.350 for bare phenol. The result indicates that in phenol-H₂O, the phenolic OH vibration is well localized in phenol site and that the force field of the OH stretching vibration is weakened by the H-bond formation with H₂O which merely behaves as a spectator. These results

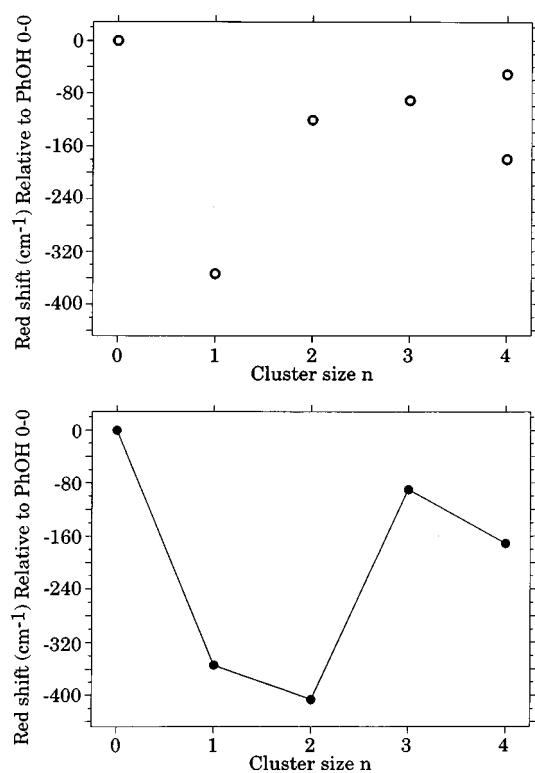


FIG. 11. Redshifts of the (0,0) band of the electronic transition of phenol-(H₂O)_n relative that of bare phenol; (upper) Stanley *et al.* (Ref. 11). (lower) Present result. The shift of phenol-(H₂O)₂ was adopted from Ebata *et al.* (Ref. 29).

are in good agreement with the facts that the vibrational frequency and IR/Raman activity of the H₂O site is very close to those of bare H₂O molecule.

B. Electronic spectrum and the cluster structure

Finally, we would like to mention the relationship between S_1-S_0 electronic spectrum and the structure of phenol-(H₂O)_n. In general, the structure of clusters are speculated from the shift of electronic spectrum relative to that of bare molecule. The structures of phenol-(H₂O)_n were predicted by Stanley *et al.* on the basis of the spectral redshift as well as the mass spectroscopic analysis combined with two-color REMPI.¹¹ Figure 11 shows the red-shifts of the electronic origins of the clusters with respect to that of bare phenol. Here, open circles are the redshifts reported by them. They thought the clusters would be essentially the ring structure and it becomes larger with the size, since the band origins monotonically shift to blue for $n \geq 2$. However, it turned out that the electronic band origin does not show smooth shift even within the ring structure clusters. First, Ebata *et al.* recently measured the dispersed fluorescence spectrum after exciting the band (c) at 36 230 cm⁻¹, which was assigned to the (0,0) band of phenol-(H₂O)₂.²⁹ They observed only broad relaxed fluorescence with its maximum at 35 700 cm⁻¹. They concluded that the band (c) is not the (0,0) band and predicted that the (0,0) band of phenol-(H₂O)₂ should locate at $\sim 36\,000$ cm⁻¹. Second, as was described

previously, the electronic band origin of the ring formed phenol-(H₂O)₄ is the band labeled (f) but not (e) in Fig. 2. Thus, obtained redshifts are plotted as solid circles and redshifts of ring form clusters are connected. As can be seen in Fig. 11, the redshifts do not show monotonic change with n , even for the ring form clusters. The change in the electronic transitions induced by the H-bond formation is determined by various properties, such as dipole moment, polarizability, electronic and geometrical structures, and acidity in both ground and excited states. The results represent that the prediction of the spectral shifts of the electronic transition of H-bonded clusters is quite difficult unless most of the solvation effects are understood in both electronic states.

In conclusion, the IR and Raman spectra of the OH and CH stretching vibrations of the specific phenol-(H₂O)_n clusters have been observed for the first time by using the double resonant techniques which involve the tunable IR laser excitation and also the stimulated Raman pumping combined with the UV laser with REMPI detection. The observed vibrational spectra showed characteristic feature depending on the cluster size and it was found the structures are characteristic of the ring-form clusters for $n=2-4$ by the comparison with the *ab initio* calculation by Watanabe and Iwata. The OH stretching vibrations can be classified into two; the vibrations of H-bonded OH groups in the cluster ring and those of H-bond free OH protruding from the ring. An anomalous IR spectrum was observed for the particular cluster which may be assigned to be an isomer of phenol-(H₂O)₅. For the anomalous species, two cluster forms are presented; an isomer having the water cluster form of “ice (I)” type which involves a prismatic network of H bonds, and the other involving an ion-pair cluster of water, though more theoretical works and related experiments are thought to be necessary.

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