

Double resonance spectroscopy of phenol(H₂O)_{1–12}: evidence for ice-like structures in aromate–water clusters?

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Abstract

Phenol(H₂O)_n clusters have been studied in the electronic ground state by dispersed fluorescence spectroscopy and in the electronically excited state by means of two-color resonant two-photon ionization (R2PI), spectral hole burning and rotationally resolved laser-induced fluorescence. Resonant spectra up to a cluster size of $n = 12$ have been obtained by two-color R2PI under ‘soft’ ionization conditions. The analysis of spectral shifts and of the intermolecular vibrations in both electronic states is used to assign structures for these bi-, tri- and (partially) tetracoordinated hydrogen bonded systems, which may be comparable to H-bond-deficient water structures at the surface of liquid water and ice. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Although water, as omnipresent solvent in nature, has been studied for decades, the structure of smaller aggregates remained vague until the development of new laser spectroscopical tools and larger computing capacities. The aim of this study is to investigate the structures of medium-sized phenol(water)_n clusters as model substances for solute–solvent interactions. Aromate–water clusters can be probed easily due to their spectroscopically accessible chromophor.

There has been a great deal of work done on phenol–water clusters which has been referred to in detail elsewhere [1,2].

Recent experiments [3,4] with jet-cooled water clusters and theoretical results [5–13] show strong

evidence that the water trimer, tetramer and pentamer have cyclic minimum energy structures and that the transition to three-dimensional structures starts with the cage-like water hexamer forming eight hydrogen bonds. The lowest energy structure for the water octamer is predicted by ab initio calculations to be cubic with either D_{2d} or S₄ symmetry [14,15]. Recently Buck et al. [16] succeeded in obtaining the IR spectra of (H₂O)_{8–10}.

In Ref. [17] we could show that the corresponding phenol(H₂O)_{2–5} clusters have similar structures as the pure water clusters with phenol replacing one of the water molecules. In the following we present vibronic spectra of phenol(H₂O)_{6–8,12} and evidence for at least two isomers for some of the larger clusters $n > 5$, with phenol hydrogen-bonded to a free oxygen lone pair of the water cluster (monocoordinated) or with the phenolic hydroxy group incorporated in the H-bond network (at least bicoordinated).

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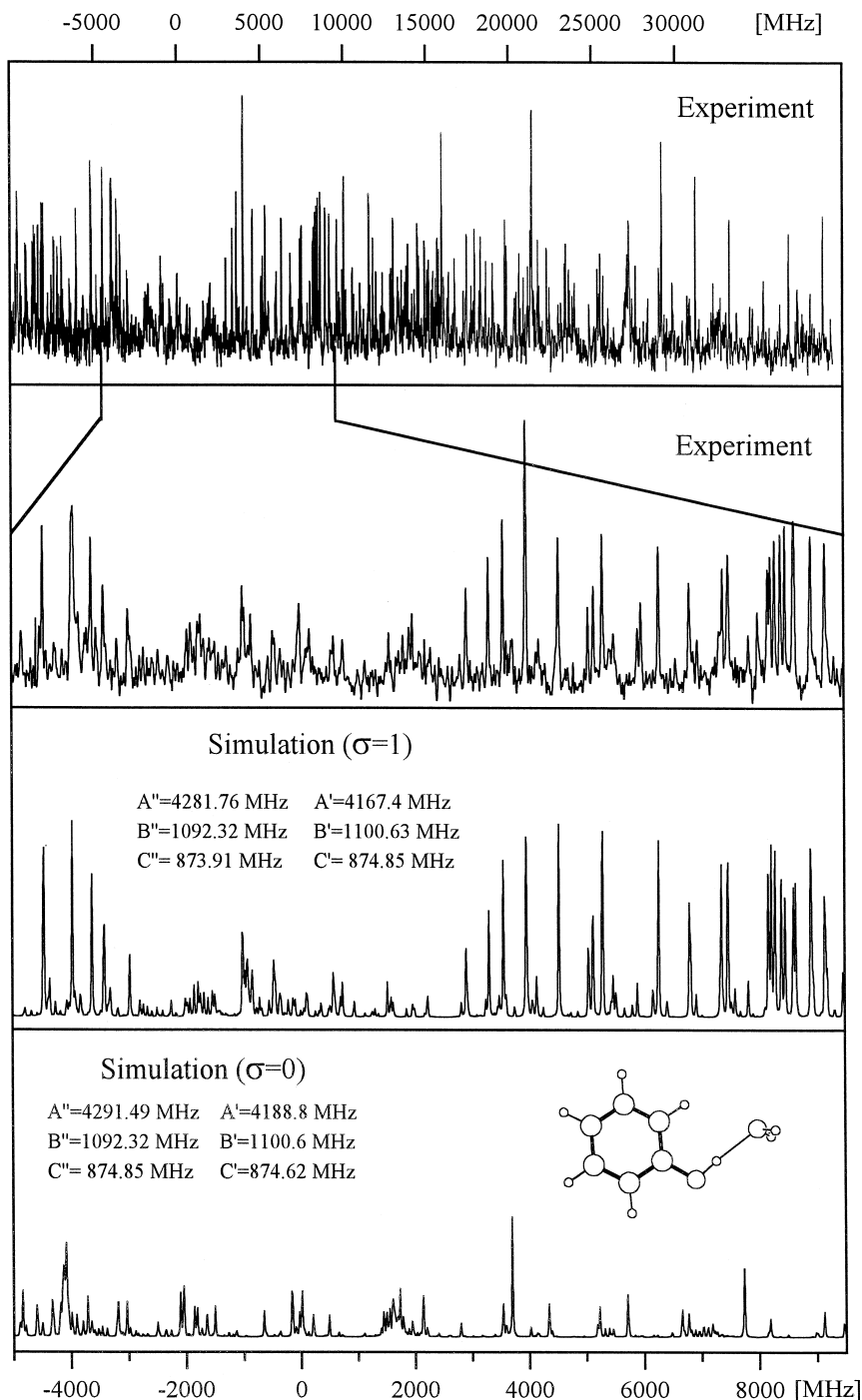


Fig. 1. Part of HRLIF of phenol(H_2O)₁. The upper trace shows a portion of 50 GHz, with the origin at 35996.47 cm^{-1} (0 at the scale of the figure). The central part of this spectrum is expanded to 14 GHz in the second trace. The last two traces show the simulation for the two torsional components together with the rotational constants used in the fit of the spectrum.

2. Experimental

Our experimental setups for high-resolution laser-induced fluorescence (HRLIF) [18], one-color resonant two-photon ionization (R2PI) [1], spectral hole burning (SHB) [1] and dispersed fluorescence (DF) [19] have been described in detail in the cited literature. The two-color R2PI measurements for the soft ionization of larger phenol–water clusters were performed in the apparatus described in Ref. [1]. For ionization with 355 nm, part of the 1064 nm of a Nd:YAG laser was frequency tripled, while the second harmonic was used to pump the excitation dye laser. The two counterpropagating beams were aligned for optimum spatial and temporal overlap with a variable delay line, monitoring the ratio of one- and two-color signal.

3. Results and discussion

3.1. HRLIF and SHB of phenol(H_2O)₁

The electronic origin 0_0^0 of phenol(H_2O)₁ at 35996.47 cm^{-1} has been measured using HRLIF spectroscopy [18]. Fig. 1 shows the central part of the spectrum at a resolution of 10^{-4} cm^{-1} with ~ 3000 fully resolved rotational lines. It is red-shifted from the phenol origin by 356 cm^{-1} , indicating a correspondingly stronger hydrogen bond in the S_1 state in qualitative agreement with the increased acidity of phenol after electronic excitation.

A closer look to the spectrum reveals two rotational band systems, separated by $\sim 0.85\text{ cm}^{-1}$ which can be fit separately using a rigid rotor Hamiltonian. The observed splitting arises from a torsional motion which interchanges the two equivalent H atoms in H_2O . Indeed the observed 3:1 intensity ratio of the two bands is expected from the spin statistical weights arising from two equivalent protons. The torsional components of the electronic origin (labeled $0^+ \leftarrow 0^+$ and $0^- \leftarrow 0^-$) exhibit different rotational constants due to the interaction of overall rotation and torsion. From the analysis of this perturbation, barriers of 180 and 130 cm^{-1} could be estimated for the hindered H_2O rotation in the S_0 and S_1 state, respectively.

The analysis of the perturbed and unperturbed rotational constants from the HRLIF [18] and from a

Fourier transform microwave investigation [20] leads to a cluster structure with a nearly linear hydrogen bond, a trans position of the water protons and the plane containing phenol bisecting the plane of the water molecule (trans-linear structure with C_s symmetry).

The 1:1 cluster has six intermolecular normal modes which arise from the loss of three rotations and three translations after complexation. These vibrational modes are the out-of-plane and in-plane bend vibrations ρ_1 and β_1 , the torsion τ , the stretching vibration σ and the out-of-plane and in-plane wag vibrations ρ_2 and β_2 [21]. The in-plane wag motion would lead to a cis-linear configuration which represents no minimum on the potential energy surface but manifests itself as flatter curvature near the $\beta_2(v=1)$ energy. A 180° torsion would bring the cis-form back to the trans-linear configuration. This indicates that the torsional motion of the water moiety about the hydrogen bond axis is strongly coupled to the β_2 vibration [21]. The minimum energy path on this two-dimensional surface can be approximately described by a rotation about the symmetry (b) axis of H_2O .

Similar to the electronic origin all intermolecular vibrations can be expected to be split due to torsional

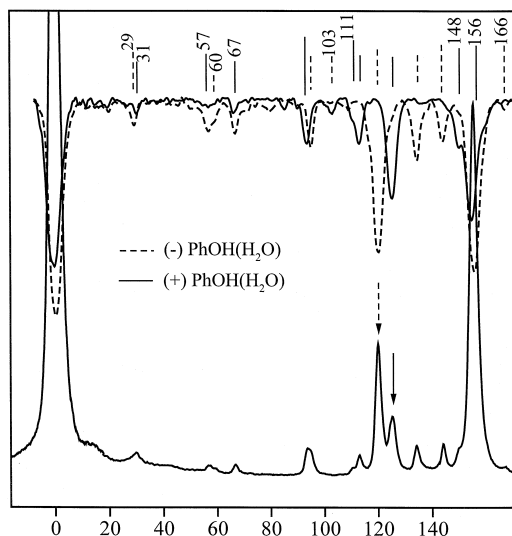


Fig. 2. The lower trace shows the R2PI spectrum of phenol(H_2O)₁, the solid line represents the SHB spectrum upon analysis of the (+) component at 126 cm^{-1} , the dashed trace the SHB spectrum upon analysis of the (-) component at 121 cm^{-1} .

tunneling. The size of the splitting gives information about the effective tunneling barriers after excitation of specific intermolecular S_1 vibrations. Since (+) and (–) transitions originate from different ground state levels we employed SHB to determine the torsional symmetries.

Since the splitting of several vibrations is by far larger than the splitting of the origin, we utilized the bands at 121 cm^{-1} (a pure (–) component) and 126 cm^{-1} ((+) component) for analysis.

Fig. 2 shows the SHB spectra (upper traces) together with the corresponding R2PI spectrum (lower trace). Apparently the large number of low-frequency transitions in phenol(H_2O)₁ can be traced back to the existence of two torsional ladders, with different spacings of the components. Table 1 presents the results for some isotopically substituted clusters together with the vibrational and torsional

assignments. Especially the β_2 vibration shows a large torsional splitting in the S_1 state which points to a substantial change of the effective torsional barrier after β_2 excitation.

3.2. Hole burning spectra of phenol(H_2O)_{2–5}

Contrary to the vibronic spectra of phenol(H_2O)_{1,3,4,5}, the R2PI and SHB spectra of phenol(H_2O)₂ show very broad bands with congested structure, i.e. progressions of probably two low-frequency vibrations of ~ 3 and $\sim 6\text{ cm}^{-1}$ in the $\sim 20\text{ cm}^{-1}$ broad electronic origin. From SHB experiments the possibility of different conformers contributing to the structured band could be ruled out. Upon analysis at 36228 cm^{-1} we obtained SHB spectra of the intermolecular vibrations of

Table 1
Intermolecular vibrational frequencies of the phenol–water cluster in the S_1 state

PhOH(H_2O)	PhOD(H_2O)	PhOH(HDO)	PhOD(HDO)	PhOH(D_2O) ^a	PhOD(D_2O)	Assignment
29.2 (–)	29.5 (–)	27.4 (–)	27.2 (–)	24.8 ^b	25.0 ^b	ρ_1^-
30.9 (+)	29.7 (+)	27.1 (+)	27.4 (+)			ρ_1^+
56.8 (–)		51.9 (–)	52.5 (–)	47.9	48.2 (+)	$2\rho_1^-$
57.2 (+)		53.0 (+)	54.1 (+)		48.3 (–)	$2\rho_1^+/\tau(1^+-0^+)$
					55.8 (+)	
59.5 (–)		58.1 (–)	58.5 (–)			$\tau(1^-0^-)$
67.1 (+)	67.1 (+)	65.4 (+)	66.4 (+)	59.3	59.9 (+)	β_1^+
66.7 (–)		66.2 (–)	66.7 (–)		60.0 (–)	β_1^-
		67.8 (+)				
94.3 (+)	94.9 (+)	81.9 (+)	83.3 (+)	77.9	78.6 (+)	$\tau(2^+-0^+)$
95.0 (–)	95.5 (–)	86.4 (–)	86.9 (–)			$\beta_1^- + \rho_1^-$
103.4 (+)						
111.2 (+)	111.6 (+)					$4\rho_1^+$
113.4 (+)	114.4 (+)	98.8 (+)	99.4 (+)	85.5	86.5 (+)	$\beta_2^+?$
120.5 (–)	120.3 (–)	104.0 (–)	104.5 (–)	87.6	88.5 (–)	β_2^-
		109.6 (+)	110.4 (+)			
125.9 (+)	126.2 (+)	112.2 (+)	113.3 (+)	103.1	103.5 (+)	$\beta_2^+?$
		130.1 (+)	132.0 (+)	120.3	120.6 (±)	$2\beta_1^+$
134.5 (–)	135.3 (–)	130.7 (–)	131.5 (–)			$2\beta_1^-$
143.9 (–)	144.1 (–)	139.5 (–)	141.6 (–)			
148.4 (+)	148.0 (+)	140.3 (+)		141.7	142.7 (+)	
155.6 (+)	155.5 (+)	150.7 (+)	151.4 (+)	144.9	145.7 (+)	σ^+
155.6 (–)	155.8 (–)	150.7 (–)	151.3 (–)		145.1 (–)	σ^-
				150.3	150.9 (+)	$\tau(4^+-0^+)$
				154.1	154.6 (+)	$\beta_1^+ + \beta_2^+$
					154.9 (–)	$\beta_1^- + \beta_2^-$
				158.0	158.7 (+)	$2\beta_2^+?$

^aThe symmetry species of this isotopomer could not be separated.

^bValues taken from the R2PI spectra.

phenol(H₂O)₂ as shown in Fig. 3a. Similar to the electronic origin, the intermolecular vibrations of phenol(H₂O)₂ are broad (~ 15 cm⁻¹). According to

ab initio calculations the minimum energy structure of the electronic ground state is cyclic. A linear structure, derived from the opening of the weaker H

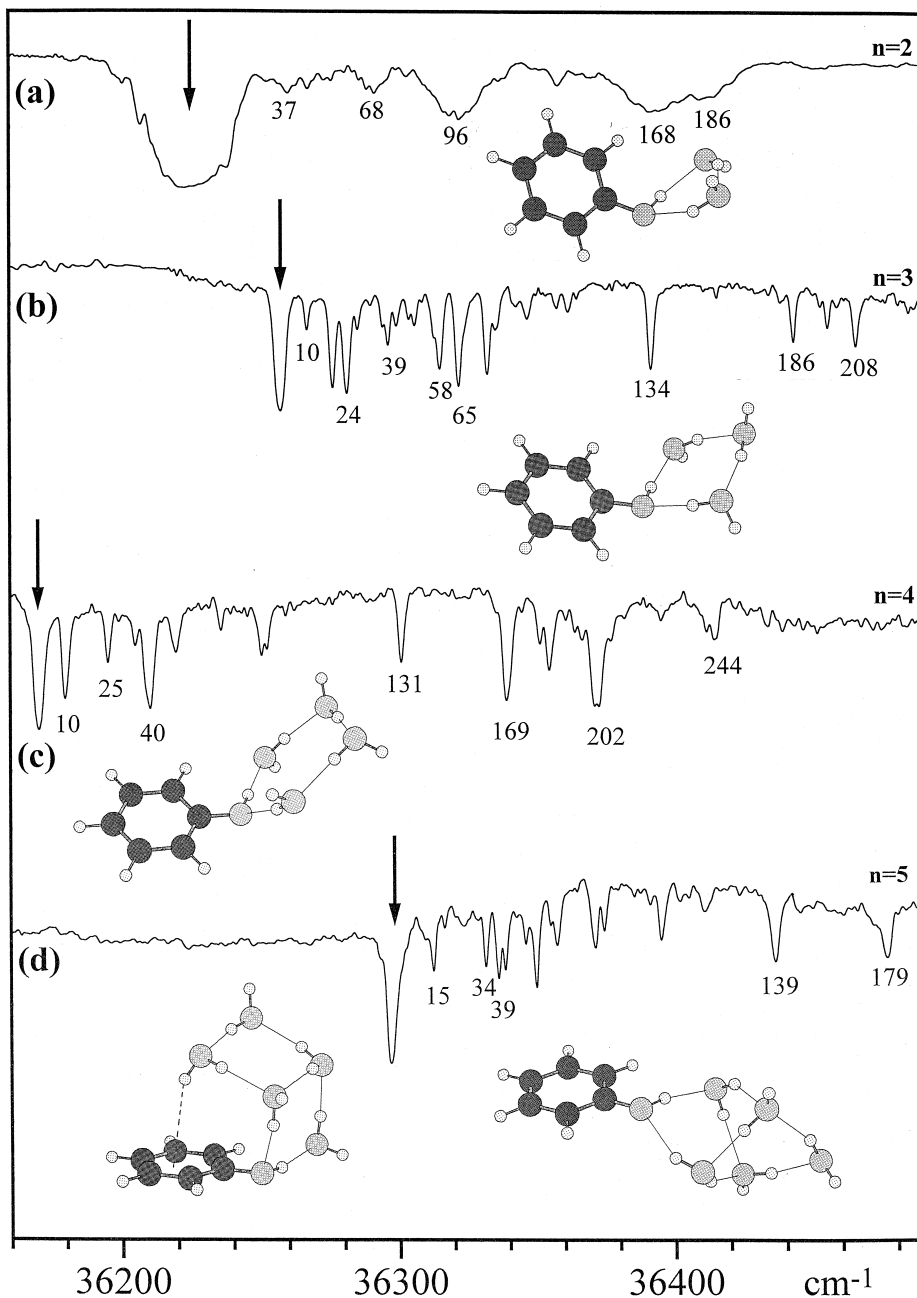


Fig. 3. Hole burning spectra of phenol(H₂O)₂₋₅. The arrows indicate the analysis positions and the insets show the calculated minimum energy structures.

bond of the donor H₂O, is supposed to be another local minimum energy structure. In the S₁ state, transfer of electron density from the phenolic oxygen atom to the aromatic ring takes place, thus decreasing the ability of the O atom to act as proton acceptor. If we assume that in the S₁ state the linear structure is more stable than the cyclic arrangement, vibronic excitation of phenol(H₂O)₂ leads to motions of a cyclic structure which couples strongly to vibrational modes of the linear structure. This coupling and the high vibrational mode density resulting from low-frequency vibrations of linear phenol(H₂O)₂ leads to a broadening of the electronic origin in the R2PI, SHB and LIF spectra.

For the cyclic phenol(H₂O)_{*n*} (*n* ≥ 2) clusters several intermolecular vibrations exist, which exhibit quite common motions. These are the butterfly motion ν_1 of the aromatic plane vs. the hydrogen-bonded cycle, the mutual twisting ν_2 and the cog-wheel motion ν_3 of the two rings, followed by 0, 2, 4, 6, ... oxygen ring deformations for *n* = 2, 3, 4, 5, ... and *n* + 1 stretching vibrations σ . The remaining vibrations are coupled H₂O torsions, which do not seem to be vibronically active.

As a general rule for the cyclic clusters, the H₂O donor–phenol acceptor stretch vibration σ_a has the lowest frequency of all stretch vibrations (weakest H bond). The phenol donor–H₂O acceptor stretch σ_d follows. The *n* – 1 stretch vibrations between the water moieties have the highest frequencies of all intermolecular stretch vibrations.

The phenol cluster with three water molecules exhibits narrow (~ 2 cm⁻¹) vibronic bands in the R2PI and SHB spectra. The SHB spectrum of phenol(H₂O)₃ displayed in Fig. 3b shows that only one isomer absorbs in this frequency range. The assignment of the low-frequency fundamentals ν_1 , ν_2 , ν_3 , the oxygen ring deformation vibrations ν_4 and ν_5 and the intermolecular stretch vibrations σ is given in Table 2.

Ab initio calculations (HF/6-31G(d,p)) again show a cyclic minimum energy structure for phenol(H₂O)₄ with a ududu (u = up, d = down) position of the phenyl ring and the free H atoms. The SHB spectrum of the low-frequency intermolecular vibrations is built upon the electronic origin at 36170.4 cm⁻¹ displayed in Fig. 3c. Vibrational assignments are given in Table 2.

Table 2

Assigned intermolecular fundamental vibrations of phenol(H₂O)_{2–5}

Phenol(H ₂ O) ₂			Phenol(H ₂ O) ₃			Phenol(H ₂ O) ₄			Phenol(H ₂ O) ₅				Ass.
calc.	S ₀ ^b	S ₁ ^b	calc.	S ₀ ^c	S ₁ ^d	calc.	S ₀ ^c	S ₁ ^d	calc. ^e	calc. ^f	S ₀ ^c	S ₁ ^d	
21.6	–	37	21.3	16	9.6	12.8	12	9.9	13.9	10.1	22	15.4	ν_1
41.2	–	43	29.6	25	18.8	25.8	24	25.1	27.7	28.8	27	34.5	ν_2
62.9	–	68	45.7	39	38.9	33.3	40	40.0	38.8	32.7	39	39.1	ν_3
–	–	–	69.3	64	57.7	41.3	–	–	47.3	49.9	42	41.6	ν_4
–	–	–	74.6	77	64.6	53.5	–	–	60.9	55.2	56	52.9	ν_5
–	–	–	–	–	–	64.7	–	–	70.6	64.7	74	60.3	ν_6
–	–	–	–	–	–	79.0	–	82.4	80.5	94.8	–	–	ν_7
–	–	–	–	–	–	–	–	–	91.8	129.8	91	98.1	ν_8
125.1	–	103	153.2	152	134.4	147.3	–	130.9	142.9	146.3	148	139.4	σ_1
170.1	–	168	190.7	186	185.5	187.6	184	169.3	166.9	155.5	167	179.3	σ_2
206.6	–	186	217.1	208	197.9	203.5	202	184.7	175.6	183.5	176	198.5	σ_3
–	–	–	237.6	–	208.1	241.6	–	201.9	186.5	203.5	–	–	σ_4
–	–	–	–	–	–	271.2	–	244.7	206.5	207.1	205	215.5	σ_5
–	–	–	–	–	–	–	–	–	265.5	223.9	–	–	σ_6

^aEmission of phenol(H₂O)₂ broad and structureless.^bAccuracy ± 2 cm⁻¹.^cAccuracy ± 1 cm⁻¹.^dAccuracy ± 0.1 cm⁻¹.^eVibrations of the 'book' structure.^fVibrations of the 'cage' structure.

One-color R2PI measurements show another intense band at 36297.2 cm^{-1} when monitoring the phenol(H_2O)₄ mass channel. Stanley and Castleman assigned this band to a conformer of the $n=4$ cluster, because ionization with 347.5 nm revealed no sign of this band on the phenol(H_2O)₅ mass channel. However, our two-color R2PI spectra with 355 nm ionization clearly show that this band belongs to the $n=5$ cluster, cf. Fig. 5. Fig. 3d shows that a number of low-frequency vibronic transitions are built upon this band, which is the electronic origin of phenol(H_2O)₅.

There are several possible structures which look cage-, prism-, book- and boat-like for phenol(H_2O)₅. The inset of Fig. 3d shows the minimum energy book structure of phenol(H_2O)₅ calculated at the HF/6-31G(d,p) level including correction for electron correlation on the MP2 level, basis set superposition error and zero-point energy. This cluster is stabilized by an additional π hydrogen bond between a free H atom of the water moiety and the aromatic ring. It exhibits several bands in the region of the frequency gap between the free OH and single donor-bound OH stretch vibration as the experimental infrared spectrum does [22,23]. However, other double donor structures like the displayed cage structure which are less stable on this level of theory fulfill this requirement as well.

3.3. Dispersed fluorescence spectra of phenol(H_2O)_{3,4,5}

The assignments of intermolecular vibrations in the last paragraph is assisted by comparison to ab initio normal mode calculations. As a direct check for the quality of these calculations, the S_0 spectra of some phenol(H_2O)_{*n*} clusters have been measured. The exact frequencies from the hole burning spectra of these clusters guarantee selective excitation and therefore single vibronic level fluorescence.

Fig. 4 shows part of the dispersed fluorescence spectra of the $n=3, 4$ and 5 clusters. The emission from the $n=2$ cluster is broad and structureless. The maximum of $n=2$ emission is shifted by several thousand cm^{-1} to the red.

The three mutual ring motions ν_1 , ν_2 and ν_3 which have been described in the last paragraph are observed in each of the spectra as the lowest-

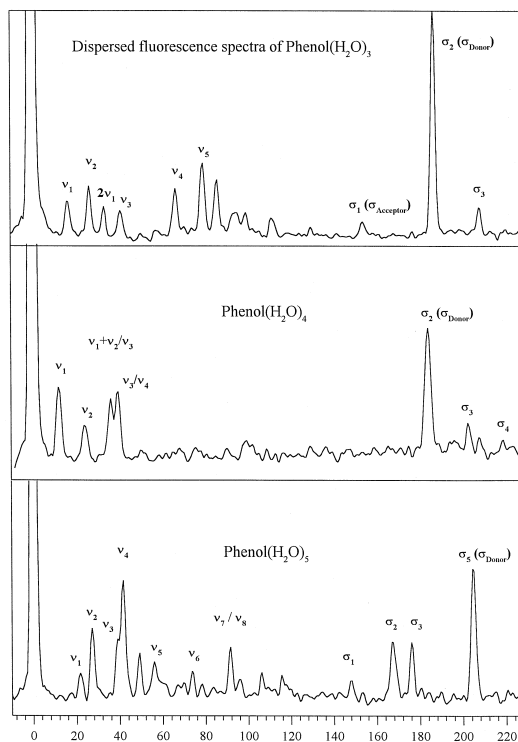


Fig. 4. DF spectra of phenol(H_2O)_{3–5} between the electronic origin and 230 cm^{-1} . Accuracy of the band positions is $\pm 1\text{ cm}^{-1}$.

frequency vibrations. The phenol donor– H_2O acceptor vibrations (σ_2 for the cyclic clusters, σ_5 for both possible phenol(H_2O)₅ structures) are especially Franck–Condon active. In phenol(H_2O)₅ the intermolecular stretch vibrations show considerable delocalization over the oxygen ‘cage’ or ‘book’ and the mutual ring motions partially couple to the oxygen ring deformation vibrations. Table 2 presents the relative frequencies together with the vibrational assignments. For phenol(H_2O)₅ the intermolecular S_0 and S_1 vibrations do not allow a distinction between the ‘cage’ and the ‘book’ geometry of phenol(H_2O)₅.

3.4. Two-color R2PI spectra of phenol(H_2O)_{5–8,12}

Two-color R2PI spectra of the larger phenol–water clusters have been measured by using an ionization wavelength of 355 nm to overcome the problem of extensive fragmentation.

Fig. 5 shows the two-color R2PI spectra on the mass traces $n=5–8$ and 12. The electronic origin of

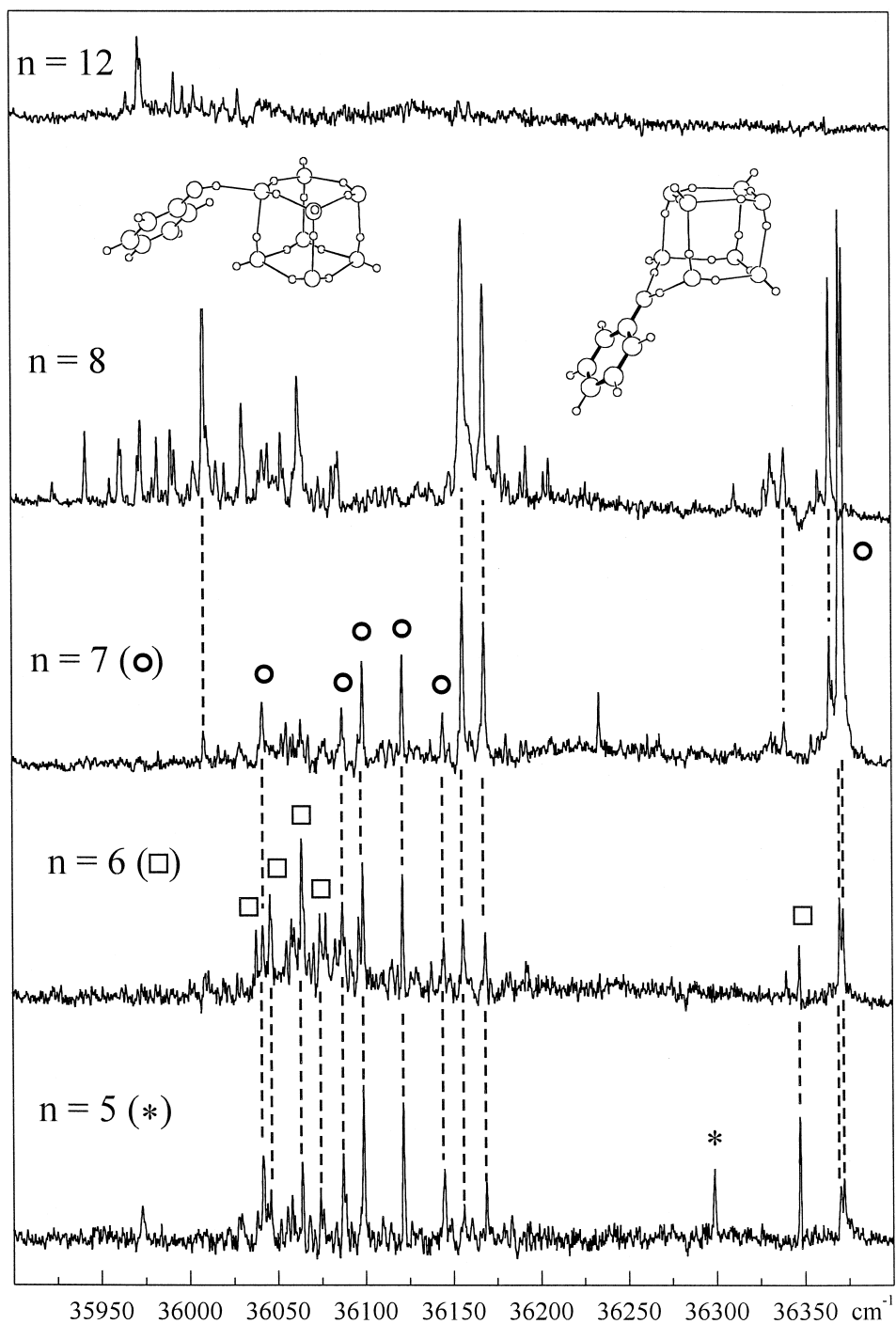


Fig. 5. Two-color R2PI spectra of phenol(H_2O) $_{5-8,12}$. The dashed lines connecting neighbored mass traces show the fragmentation paths. None of the stronger $n=8$ transitions could be traced back to fragmentation of $n \geq 9$ clusters upon ionization with 355 nm. The inset shows two tentative structures of phenol(H_2O) $_8$.

phenol(H₂O)₅ which up to now was assigned to another conformer of the $n = 4$ cluster is marked with an asterisk.

One of the most striking features in the R2PI spectra, shown in Fig. 5 is the large red shift of the cluster spectra with $n = 6–8$ and $n = 12$. The origin of phenol(H₂O)₈ is red-shifted by 73.1 cm⁻¹ compared to the electronic origin of the phenol(H₂O)₁ cluster. This points to a structure in which a water unit is bound solely to the H atom of the phenol moiety, without any ring closure involving the phenolic oxygen [24]. The same considerations apply to the $n = 12$ cluster. We believe that in case of phenol(H₂O)₈ a water octamer, which forms an especially stable cubic structure [14], is hydrogen bonded via one of the corner oxygen atoms to the proton-donating phenol, cf. the inset in Fig. 5. From their IR–UV double resonance spectra of benzene(H₂O)₈, Zwier and Jordan [25] deduced a cubic water octamer structure, π -bonded to the aromatic ring. Attachment of a further cyclic tetramer subunit to one of the sides of the cube may lead to the dodecamer. The $n = 8$ mass trace shows two groups of bands, which are not observed on higher-mass channels and exhibit a considerably different fragmentation pattern. We tentatively assign the band system between 36150 and 36400 cm⁻¹ to at least one other conformer of the $n = 8$ cluster, possibly the cyclic phenol(H₂O)₄ cluster with a tetramer subunit attached to the (H₂O)₄ moiety. The existence of isomers of the higher phenol–water clusters is examined via SHB at the moment and will be presented soon.

4. Conclusions

Two-color R2PI with an intense ionization laser at a sufficient long wavelength turns out to be a valuable tool for obtaining high-quality vibronic spectra of larger phenol–water clusters. SHB is necessary to discriminate between cluster isomers and allows to obtain a nearly complete picture of the intermolecular vibrations because this method (unlike two-color R2PI) is not hampered by fast intracluster vibrational relaxation in the S₁ state. Ionization at 355 nm is still accompanied by considerable ion fragmentation and a change to longer wavelengths may allow the mea-

surement of large clusters with an increased portion of tetracoordinated water molecules.

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