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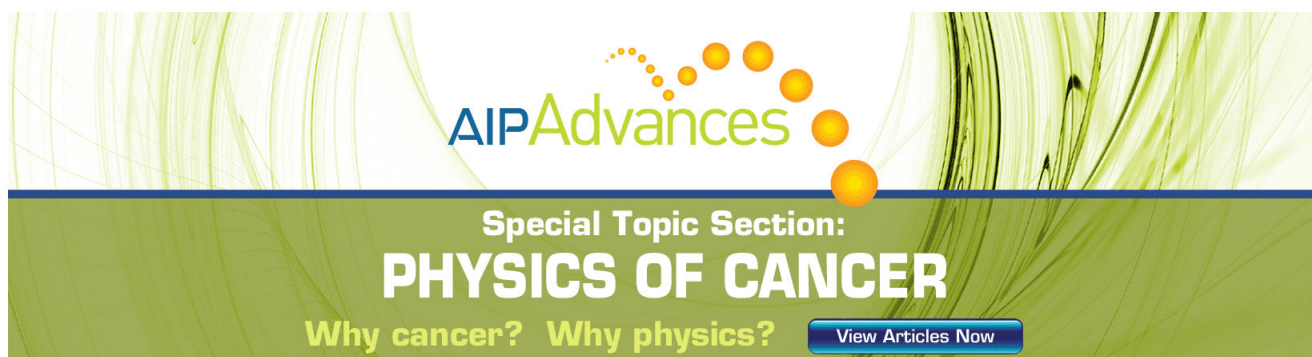
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# Microscopic shifts of size-assigned *p*-cresol/H<sub>2</sub>O-cluster spectra

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*p*-cresol and its complexes with H<sub>2</sub>O and CH<sub>3</sub>OH were cooled in a pulsed supersonic free jet and studied by resonant multiphoton ionization with time-of-flight mass analysis. Detailed mass and concentration analysis allowed an unambiguous assignment of cluster size. The electronic origins of *p*-cresol (H<sub>2</sub>O)<sub>1,2,3</sub> show irregular red- and blueshifts with change of cluster size, which is referred to the bivalent role of *p*-cresol as proton donor and acceptor. *Ab initio* and semiempirical quantum chemical calculations support this interpretation and show the spectral shifts to be essentially due to the inductive effect of the solvent molecules *Y* exerted on *X* in *X*-H...*Y*. While the vibronic bands of *p*-cresol (H<sub>2</sub>O)<sub>2</sub> are quite broad, those of *p*-cresol (H<sub>2</sub>O)<sub>3</sub> are sharp again. The *ab initio* calculations show that this may be attributed to the quite rigid "open cyclic" structure of *p*-cresol (H<sub>2</sub>O)<sub>3</sub>. Our experimental and theoretical investigations show a completely analogous behavior of phenol (H<sub>2</sub>O)<sub>1,2,3</sub> clusters

## I. INTRODUCTION

The electronic spectra of molecules exhibit a spectral shift when surrounded by solvent molecules. In supersonic expansions, it is possible to prepare isolated, ultracold molecules with simplified spectra and rotationally cooled, sharp lines especially suitable for resolved studies of microscopic shifts.

Many cluster studies of aromatic solute molecules with inert gas solvents<sup>1</sup> and metal atoms<sup>2</sup> exhibit monotonic spectral shifts with increasing condensation number *n*. Mass-selected spectral analysis and detailed study of the solvent concentration dependence of the cluster signal is necessary to unambiguously assign spectral features to clusters of specific size.

In this paper we report mass-selected two-photon multiphoton ionization (MPI) spectra of *p*-cresol-(H<sub>2</sub>)<sub>*n*</sub> and phenol (H<sub>2</sub>O)<sub>*n*</sub>. We can unambiguously assign cluster spectra with one, two, and three water molecules attached. A monotonic shift of the electronic spectra with increasing cluster size is not observed here. The spectrum of *p*-cresol (H<sub>2</sub>O)<sub>1</sub> is red shifted relative to the free *p*-cresol spectrum, while the *p*-cresol (H<sub>2</sub>O)<sub>2,3</sub> electronic origins are blue shifted relative to *p*-cresol (H<sub>2</sub>O)<sub>1</sub> but still lie on the red side of the base compound. Simple highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) considerations based on *ab initio* calculations show that this can be explained by the inductive effect exerted on the O atom of *p*-cresol which acts as proton donor and acceptor in the hydrogen bonding. We come to a different size assignment for the phenol (H<sub>2</sub>O)<sub>2,3</sub> cluster spectra than Ref. 3.

## II. EXPERIMENTAL

The experimental setup is similar to that described previously<sup>4</sup> and consists of a high vacuum apparatus, an electromagnetically pulsed, heatable injection valve (600 μs gas pulse width, 0.15 mm nozzle hole) for scimmed jet expansion of *p*-cresol/H<sub>2</sub>O/He, a differentially pumped time-of-flight (TOF) mass spectrometer, and an excimer laser

(Lambda Physik: EMG 100) pumped linear dye laser (FL 2002; 0.2 cm<sup>-1</sup> FWHM) for work in the wavelength range 270–283 nm (coumarin 153 dyes and FL 30 and FL 31 frequency doubling crystals). Background pressures were 3 × 10<sup>-4</sup>, 10<sup>-5</sup> and 2 × 10<sup>-6</sup> mbar (beam on) in the main chamber, the differentially pumped ionization chamber, and the time-of-flight chamber, respectively. The vacuum was maintained by two 2600 l/s diffusion pumps (Edwards), backed by a roots/rotatory pump system (Alcatel) and a liquid nitrogen trap, and a 150 l/s turbopump (Leybold Heraeus: Turbovac 3600) for the three chambers. The MPI spectra were usually taken at 0.12 mbar *p*-cresol, 1–5 bar Helium, 0.05–5 mbar H<sub>2</sub>O, and a laser-nozzle probe distance *X*/*D* = 500. In some of the experiments the water concentration was varied by using a peltierelement-driven cooler.

Time-of-flight spectra were obtained by averaging the preamplified ion signals from a microchannel plate detector (Galileo: Chevron type) with a digital oscilloscope (Le Croy: model 9400). The mass resolution is 90 at *m/e* = 108. Some spectra were taken with a home-built reflectron type TOF-mass spectrometer with resolution *m/e* = 800 at *m* = 108. Resonance enhanced multiphoton ionization (REMPI) spectra were recorded by integrating the ion signal within a certain TOF-interval (mass) with a gated boxcar (Stanford Research: SR 250). Laser, nozzle, and boxcar were synchronized by a four-channel digital delay/pulse generator (Stanford Research: DG 535).

## III. RESULTS AND DISCUSSION

### A. Size assignment of *p*-cresol/H<sub>2</sub>O clusters

Figure 1 shows a typical fluorescence excitation spectrum of *p*-cresol/H<sub>2</sub>O associates at several Torr H<sub>2</sub>O concentration. Without mass discrimination the spectrum exhibits the electronic origin and vibronic bands of free *p*-cresol and of *p*-cresol water clusters of different size. In the absence of water only the spectrum of bare *p*-cresol is obtained and the corresponding bands can be assigned. The band most far to the red is the electronic origin of free *p*-

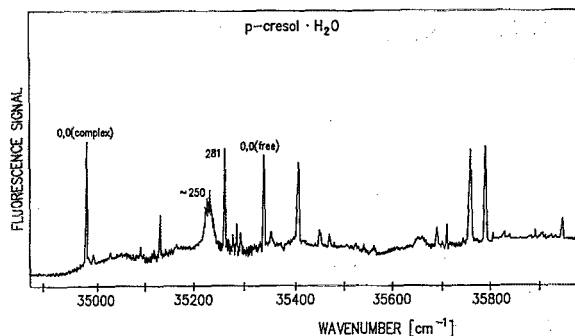


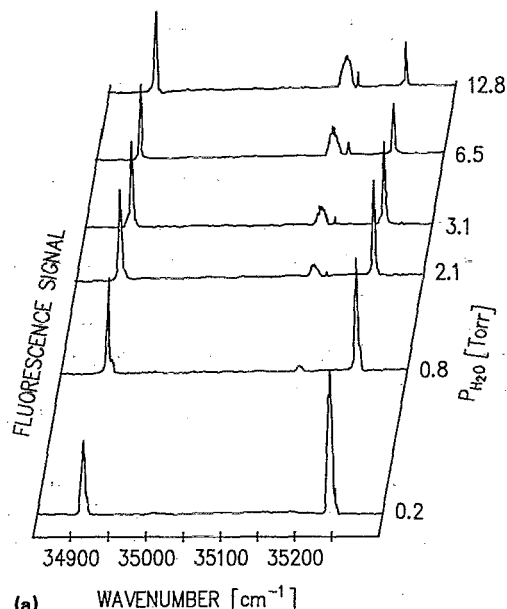
FIG. 1. Fluorescence excitation spectrum of *p*-cresol/H<sub>2</sub>O complexes over a frequency range of 1000 cm<sup>-1</sup>. The electronic origins of free *p*-cresol and of the complex with one water molecule are indicated in the figure. The bands with ~250 cm<sup>-1</sup> and 281 cm<sup>-1</sup> blue shift relative to *p*-cresol (H<sub>2</sub>O)<sub>1</sub>, stem from higher clusters. The mass-resolved REMPI measurements in Fig. 3 show that they arise from *p*-cresol (H<sub>2</sub>O)<sub>2</sub> and *p*-cresol (H<sub>2</sub>O)<sub>3</sub>, respectively. For assignment of the other bands see Ref. 5.

cresol.<sup>5</sup> By adding a very small amount of water, further bands are obtained which are predominantly from *p*-cresol (H<sub>2</sub>O)<sub>1</sub> [c.f. Fig. 2(a)]. Its spectrum is red shifted relative to the spectrum of free *p*-cresol and the band most far to the red is the electronic origin of the complex with one water.

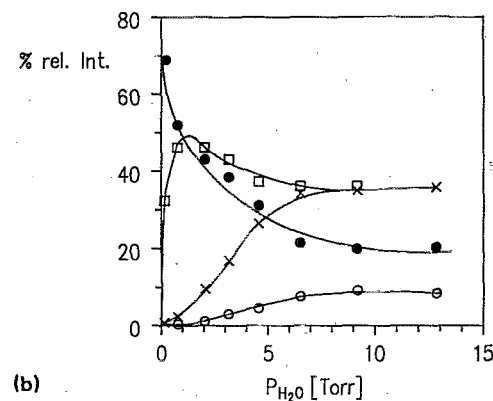
At higher water concentration, further bands arise that are blue shifted by +250 and +281 cm<sup>-1</sup> relative to the origin of *p*-cresol (H<sub>2</sub>O)<sub>1</sub> [c.f., Figs. 1 and 2(a)]. These bands stem from higher clusters, as can be seen from their fast rise with water concentration at high water pressure [c.f., Fig. 2(b)]. From the LIF measurements alone it is hardly possible to assign the bands of larger associates to clusters of definite size. In principle, the reaction order of the corresponding H<sub>2</sub>O association reaction can be determined from the initial rises of curves in Fig. 2(b) (c.f., Table I). However, our experience and the detailed measurements performed show that this method is imprecise and does not allow a discrimination between higher clusters of size  $n > 1$ .<sup>6</sup> The problem with the method is the necessity to measure many points at extremely low solvent concentration where consecutive reactions are not yet important. The defined adjustment of a very low water concentration, however, is exceedingly difficult. It is much better to measure the H<sub>2</sub>O concentration dependence over a large range of water vapor pressures and then simulate these curves kinetically by solving the corresponding master equations. Our results from such calculations based on successive association will be published elsewhere<sup>7</sup> and show clearly that the curve (×) in Fig. 2(b) stems from *p*-cresol (H<sub>2</sub>O)<sub>2</sub> and the later rising curve (○) from *p*-cresol (H<sub>2</sub>O)<sub>3</sub>.

A definite cluster size assignment is possible from mass-resolved resonant ionization measurements. Figure 3 shows the two-photon ionization spectra of *p*-cresol (H<sub>2</sub>O)<sub>*n*</sub> ( $n = 0-3$ ) after  $S_0 - S_1$  ( $\pi-\pi^*$ ) excitation as measured by tuning the boxcar gate to the time-of-flight (mass number) of the individual clusters.

Figure 3(a) shows the REMPI spectrum of free *p*-cresol ( $m/e = 108$ ) seeded in 4 bar of helium between 35 000 and 36 200 cm<sup>-1</sup>. The band at 35 337 cm<sup>-1</sup> is the lowest frequency band of bare *p*-cresol and can be assigned to the elec-



(a) WAVENUMBER [cm<sup>-1</sup>]



(b)

FIG. 2. Dependence of *p*-cresol/H<sub>2</sub>O cluster fluorescence intensity from H<sub>2</sub>O concentration. (a) Part of the fluorescence excitation spectrum of *p*-cresol/H<sub>2</sub>O showing the electronic origins of the clusters and of free *p*-cresol as function of H<sub>2</sub>O partial pressure. (b) Change of the fluorescence intensity of the *p*-cresol/H<sub>2</sub>O cluster electronic origins with H<sub>2</sub>O concentration free. (●) *p*-cresol origin at 35 337 cm<sup>-1</sup>, (□) *p*-cresol (H<sub>2</sub>O)<sub>1</sub> origin at 34 980 cm<sup>-1</sup>, (×) *p*-cresol (H<sub>2</sub>O)<sub>2</sub> origin at 35 230 cm<sup>-1</sup>, (○) *p*-cresol (H<sub>2</sub>O)<sub>3</sub> origin at 35 261 cm<sup>-1</sup>.

tronic origin 0,0 (free). The bands at 35 337 + 419 and +803 cm<sup>-1</sup> can be assigned to the totally symmetric  $a_1$  ( $S_1$ ) state fundamental vibrations  $6a_0^1$  and  $12_0^1$  which are localized mainly in the aromatic ring.<sup>3</sup> The weaker feature at 370 cm<sup>-1</sup> is the  $18b_0^1$  skeletal vibration with  $b_2$  symmetry. The very weak low frequency bands in Fig. 3(a) arise from the hindered internal rotation of the CH<sub>3</sub> group of *p*-cresol and are analyzed elsewhere.<sup>8</sup> The bands generally show efficient rotational cooling with band widths  $< 3.0$  cm<sup>-1</sup> FWHM at 4 bar helium.

Figure 3(b) shows the REMPI spectrum of *p*-cresol (H<sub>2</sub>O)<sub>1</sub> at mass number 126 (108 + 18). The electronic origin 0,0 of the monohydrated *p*-cresol is located at 34 980 cm<sup>-1</sup> with a red shift of 357 cm<sup>-1</sup> relative to bare *p*-cresol. From the complex origin, a vibrational progression starts with a frequency interval of 152 cm<sup>-1</sup>; this is attributable to

TABLE I. Assignment of cluster size  $n$  according to mass analysis and  $H_2O$  concentration dependence.

$\nu$ [ $cm^{-1}$ ]	Assignment	$n$	
		$P_{H_2O}^a$	Mass
349 80	0,0 <i>p</i> -Cr ( $H_2O$ ) <sub>1</sub>	0,4	1
352 30	0,0 <i>p</i> -Cr ( $H_2O$ ) <sub>2</sub>	1,6	2
352 61	0,0 <i>p</i> -Cr ( $H_2O$ ) <sub>3</sub>	1,8	3

<sup>a</sup> According to  $H_2O$  concentration analysis

$$\ln \frac{[p\text{-Cr}(H_2O)_n]}{\sum_{n=0}^3 [p\text{-Cr}(H_2O)_n]} \propto n \ln [H_2O]$$

at low water concentration (little clustering) (Ref. 7).

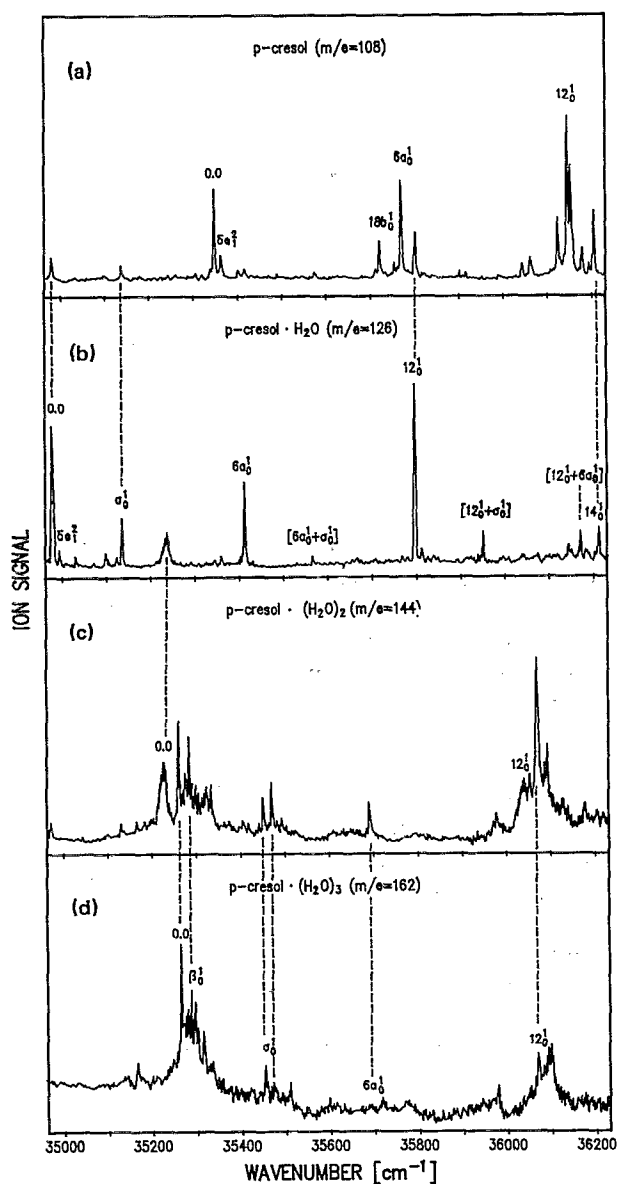


FIG. 3. Mass selected REMPI spectra of *p*-cresol ( $H_2O$ )<sub>0,1,2,3</sub> from excitation of the  $S_0 \rightarrow S_1$  transition. (a) Free *p*-cresol, (b) *p*-cresol ( $H_2O$ )<sub>1</sub>, (c) *p*-cresol ( $H_2O$ )<sub>2</sub>, (d) *p*-cresol ( $H_2O$ )<sub>3</sub>. Corresponding vibronic bands are connected by dashed lines indicating a general fragmentation behavior  $p\text{-cresol}(H_2O)_n^+ \rightarrow p\text{-cresol}(H_2O)_{n-1}^+$ . Experimental conditions are 4 bar Helium, *p*-cresol = 1 Torr and expansion distance  $x/d = 500$ .

the intermolecular stretch vibration  $\sigma_0^1$ . Further bands arise from the intramolecular  $a_1$  ( $S_1$ ) cluster transitions  $6a_0^1$  and  $12_0^1$  as well as from combinations of  $\sigma$  with intramolecular cluster vibrations. Detailed analysis of these bands is performed in Ref. 9.

Figures 3(c) and 3(d) show that the 0,0 bands of *p*-cresol ( $H_2O$ )<sub>2,3</sub> are blue shifted from the origin of *p*-cresol ( $H_2O$ )<sub>1</sub> by 250 and 287  $cm^{-1}$  respectively. These shifts are explained in detail in the next chapter.

Figure 3 shows a distinct fragmentation of *p*-cresol ( $H_2O$ ) <sub>$n$</sub>  to *p*-cresol ( $H_2O$ ) <sub>$n-1$</sub> . Corresponding vibronic bands are connected by dashed lines in Fig. 3, demonstrating this fragmentation behavior. No fragmentation to *p*-cresol ( $H_2O$ ) <sub>$n-2$</sub>  could be detected. This fragmentation behavior is not limited to the 0,0 bands, but is also found after excitation of higher energy vibronic bands, as Fig. 3 shows. Fuke *et al.*<sup>3</sup> performed similar measurements of the phenol/water system and made a different size assignment. They assigned the broad band (shown in this work to belong to the cluster with two water molecules attached) to higher clusters with  $n \geq 4$  and asserted that the band (shown here to belong to  $n = 3$ ) to two different origins with a spacing of 4  $cm^{-1}$ , namely the clusters with 2 and 3  $H_2O$  attached. To clarify this question, the band at 35 261  $cm^{-1}$  of the *p*-cresol/water system was measured carefully many times with low scan velocity of the grating of the dye laser. Within an error  $< \pm 0.5$   $cm^{-1}$  it was established that the band at 35 261  $cm^{-1}$  consists only of one band—the origin of *p*-cresol ( $H_2O$ )<sub>3</sub>. In the same way we remeasured the corresponding band in the very similar phenol/water system and again found only one band here within the same error limits attributable to phenol ( $H_2O$ )<sub>3</sub>. This also corresponds to the assignment made by Lipert and Colson<sup>10</sup> in the phenol/ $H_2O$  system.

A further strong argument for the new assignment is the aforementioned distinct fragmentation behavior. If the broad band really stems from higher clusters  $n \geq 4$ , why do these associates decompose to  $n = 1, 2$  but not to  $n = 3$  (c.f. Figs 3(b), 3(c) and 3(d))? If the  $n = 2$  and  $n = 3$  clusters finally have nearly the same absorption wavelengths why are there fragments from the  $n = 3$  species in the  $n = 2$  spectrum in this wavelength region but not in the  $n = 1$  spectrum (from  $n = 2$  clusters)? Such behavior would strongly contradict the otherwise well-established  $n \rightarrow n - 1$  fragmentation mechanism.

We now turn our attention to bands from higher clusters  $n > 3$  in our *p*-cresol/ $(H_2O)$  spectra. By raising the water vapor pressure up to 20 Torr, we observed a pronounced increase of the background in the region of the 0,0 band of *p*-cresol ( $H_2O$ )<sub>3</sub>. Obviously, higher clusters show absorption in this wavelength region. We could not observe distinguishable sharp peaks in the optical spectrum of the  $n = 4$  cluster. Its ions, however, may decompose readily leading to optical resonances in the crowded  $n = 3$  spectrum.

From this analysis we obtain quite a clear picture of the *p*-cresol/ $(H_2O)$  and phenol/ $H_2O$  systems. The *p*-cresol ( $H_2O$ )<sub>1</sub> spectrum is considerably red shifted relative to free *p*-cresol and shows a number of inter- and intramolecular vibronic bands. The spectrum of *p*-cresol ( $H_2O$ )<sub>2</sub> is blue

shifted relative to *p*-cresol ( $H_2O$ )<sub>1</sub> and shows broad bands, namely the 0,0 and the 12<sub>0</sub><sup>1</sup> band in Fig. 3(c). The *p*-cresol ( $H_2O$ )<sub>3</sub> spectrum is even further blue shifted but still lies at longer wavelengths than free *p*-cresol. It again shows sharp peaks with a great number of low frequency intermolecular bands as well as intramolecular aromatic ring vibrations which are analyzed elsewhere.<sup>9</sup> The higher energy vibronic bands of *p*-cresol ( $H_2O$ )<sub>3</sub> fragment very easily and show more intense peaks at  $n = 2$  than at  $n = 3$ . Generally, an ion pattern is observed which can be explained by a  $n \rightarrow n - 1$  fragmentation behavior.

Higher cluster masses can be observed weakly in the time-of-flight spectra. Their absorption shows as broad background in the vicinity of the *p*-cresol ( $H_2O$ )<sub>3</sub> origin band.

## B. *Ab initio* calculations of cluster structures

*Ab initio* calculations on the Hartree-Fock level were performed on the structures of *p*-cresol ( $H_2O$ )<sub>0-3</sub>. We used the GAUSSIAN 80 program for calculation on a IBM 3090.<sup>11</sup> Due to the size of the molecular systems, the restricted Hartree Fock calculations could be performed only with the minimal STO-3G basis set. This small basis set generally underestimates bond distances and leads to too narrow potential curves.<sup>11</sup> Hence the results, in principle, have only restricted quantitative meaning. In the following however, we show that relative shifts of potential curves in a homologous row of species can be calculated very well by this method.

By extensive geometry optimization we obtained the cluster configurations of *p*-cresol ( $H_2O$ )<sub>*n*</sub> ( $n = 0-3$ ) shown schematically in Fig. 4. In free *p*-cresol the hydroxyl group lies in the plane of the aromatic ring. In the first association step, the water molecule is a proton acceptor. The hydrogen bonding lies in the plane defined by the benzene ring, while the plane of the water molecule orients perpendicular to the ring. The angle between the OO axis and the half angle of the HOH triangle amounts to 50°. This configuration, which is similar to the most stable one of the water dimer, is called translinear.

In the second association step it is energetically more favorable for the water molecule to act as proton donor and form a hydrogen bond to the O atom of the cresol OH group than to cluster with the first water molecule. The second water molecule lies in the plane of the aromatic ring. The H atom not involved in the hydrogen bonding is in transposition to the H-atoms of the first solvent.

In the most stable configuration of *p*-cresol ( $H_2O$ )<sub>3</sub>, the third water molecule associates to the second one and acts as proton donor. Contrary to the O atoms of the first two  $H_2O$ , the oxygen atom of the third  $H_2O$  does not lie in the common plane. Table II shows that the energy gain in the second association step with water acting as proton donor is considerably less than in the first one. The third solvation step, however, is the most effective of all and demonstrates that there are, indeed, stabilizing interactions between the first and the third water molecules. For comparison, calculation of the stabilization energy of the water dimer with the STO-3G basis set yields  $-24.7$  kJ/mol. While the high stabiliza-

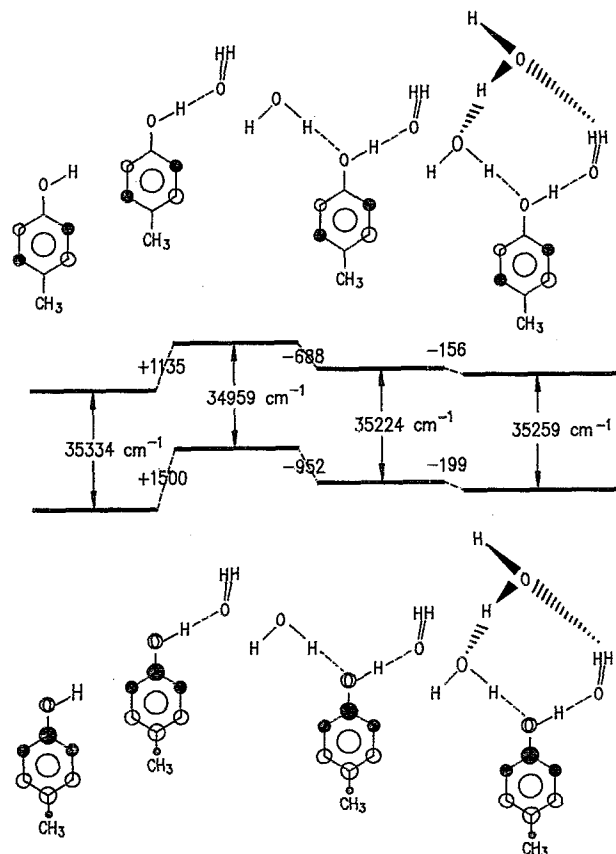


FIG. 4. HOMO/LUMO energetics and MO coefficients in free *p*-cresol and *p*-cresol ( $H_2O$ )<sub>1,2,3</sub> clusters.

tion energy of the first association step can be explained by the considerable acidity of free *p*-cresol, it is evident that the third association step necessitates a second, weaker H bond. A rough guess of the additional stabilization is  $-7.6$  kJ/mol, assuming  $-24.7$  kJ/mol for the H bond of the third  $H_2O$  with the second  $H_2O$ . Altogether, *p*-cresol ( $H_2O$ )<sub>3</sub> can be described by a nonplanar "open cyclic" structure. Further water molecules ( $n > 3$ ) add in the second hydration sphere. We obtained similar results for the phenol ( $H_2O$ )<sub>1,2,3 > 3</sub> cluster structures.

Beside the described cluster structures, other associates of the same mass, but of different configurations, may be formed. For example, one could imagine water as proton donor in *p*-cresol ( $H_2O$ )<sub>1</sub> or the second  $H_2O$  to add to the first one in *p*-cresol ( $H_2O$ )<sub>2</sub>. However, according to our calculations, the structures in Fig. 4 are the most stable ones and probably formed with the highest probability. Furthermore, these structures can be assigned to the important fea-

TABLE II. Hydrogen bond energies of *p*-cresol clusters (STO-3G).

<i>n</i>	1 ( $H_2O$ )	2 ( $H_2O$ )	3 ( $H_2O$ )
$\Delta E_n^a$ [kJ/mol]	-32,0	-23,4	-32,3

<sup>a</sup> According to  $\Delta E_n = E(n) - (E(n-1) + E(H_2O))$ .

tures of the optical spectra, namely the spectral shifts and the vibronic structure in the most direct and unconstrained way, as shown in the following two chapters and in Ref. 9.

Other cluster geometries situated in local minima are probably too unstable to be formed with an appreciable percentage in the jet; they are either destroyed by the measurement conditions or take on so many conformations that no sharp optical resonances are obtained. This may also be the reason; why large *p*-cresol/H<sub>2</sub>O clusters only appear as broad background in the optical spectra. These solvent molecules associate in the second hydration sphere, their perturbation of the *p*-cresol  $\pi$  system is small due to their larger distance from the chromophore and their association and conformation possibilities are manifold, leading to many resonances.

### C. HOMO-LUMO calculations of spectral shifts and bandwidths

Beside the total energy of an energetically optimized cluster geometry, the Hartree-Fock procedure also yields the eigenvalues of the one electron molecular orbitals. The electronic origin bands of the cluster  $S_0 \rightarrow S_1$  excitation, can be considered as arising from the transition of an electron from the HOMO to the LUMO. Although not even approximate absolute transition energies can be expected from this single determinant, minimal basis set procedure, the HOMO-LUMO energy differences describe relative spectral shifts in a "homologous row" of solvent association steps very well. The spectral shifts in Table III show nearly quantitative agreement between experiment and theory with the (0,0)-transition frequency of free *p*-cresol as the only fit parameter. Only the described cluster structures with *p*-cresol acting as proton donor and acceptor in *p*-cresol (H<sub>2</sub>O)<sub>1,2</sub> resp. and an "open cyclic" arrangement for *p*-cresol (H<sub>2</sub>O)<sub>3</sub> yield this satisfactory agreement. Complete neglect of differential overlap/configuration interaction (CNDO/CI) calculations showed even the absolute transition energies to be correct within  $\sim 10\%$ <sup>12</sup> for the cluster structures shown in Fig. 4.

In Sec. III A we pointed out the broadness of the *p*-cresol (H<sub>2</sub>O)<sub>2</sub> electronic origin and its vibronic bands which led to the errors in the work of Fuke and Kaya.<sup>3</sup> In our

TABLE III. Spectral position of the electronic origins of *p*-cresol (solvent) *n* according to experiment and *ab initio* GAUSSIAN 80 calculations (STO-3G basis set).

Species	$\bar{\nu}_{\text{exp}}$ [cm <sup>-1</sup> ]	$\Delta\bar{\nu}_{\text{exp}}$ <sup>a</sup> [cm <sup>-1</sup> ]	$\Delta\bar{\nu}_{\text{calc}}$ <sup>b</sup> [cm <sup>-1</sup> ]
<i>p</i> -cresol	353 37	0	0
<i>p</i> -cresol (H <sub>2</sub> O) <sub>1</sub>	349 80	- 357	- 375
<i>p</i> -cresol (H <sub>2</sub> O) <sub>2</sub>	352 30	- 107	- 110
<i>p</i> -cresol (H <sub>2</sub> O) <sub>3</sub>	352 61	- 76	- 72

<sup>a</sup> Relative to the 0,0 band of free *p*-cresol.

<sup>b</sup> Relative to the calculated electronic transition energy of free *p*-cresol.

calculations we observed that *p*-cresol (H<sub>2</sub>O)<sub>2</sub> is extremely flexible compared to *p*-cresol (H<sub>2</sub>O)<sub>3</sub> with a flat potential especially along the intermolecular coordinate of torsional motion around the OO axis (c.f. Fig. 5). The other motions, namely the intermolecular stretch and bend motions show too stiff electronic potentials to be of importance here. The approximate potential curves of the first electronically excited state along the  $\alpha$  coordinate in Fig. 5 are obtained by adding the HOMO-LUMO energy difference at different angles  $\alpha$  to the electronic ground-state potential energy. The calculations show that along the  $\alpha$  coordinate, the HOMO-LUMO energy difference of *p*-cresol (H<sub>2</sub>O)<sub>2</sub> changes quite strongly compared to the change of the total energy of the electronic ground-state  $S_0$  of the cluster. Figure 5(a) shows this stronger curvature of the  $S_1$  curve in the HOMO-LUMO approximation.

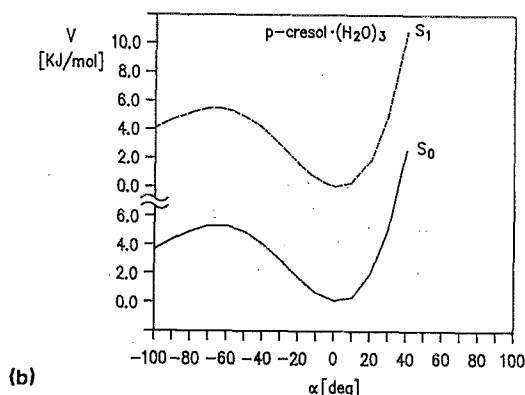
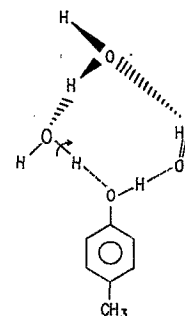
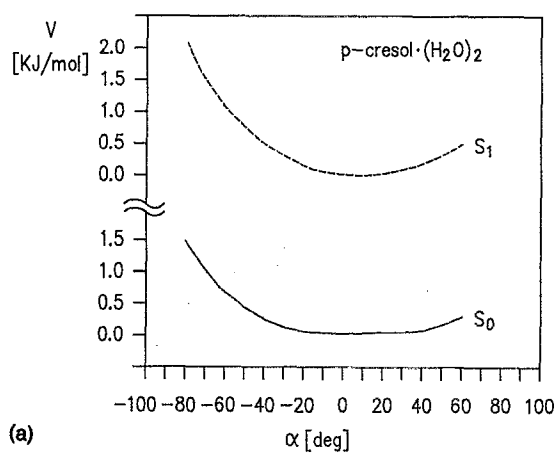


FIG. 5. The dependence of the potential energy of (a) *p*-cresol (H<sub>2</sub>O)<sub>2</sub>, (b) *p*-cresol (H<sub>2</sub>O)<sub>3</sub>, on the torsion angle  $\alpha$  for the electronic ground and excited state in the HOMO/LUMO approximation (STO-3G).

The corresponding potential curves of *p*-cresol (H<sub>2</sub>O)<sub>3</sub> shown in Fig. 5(b) look very different. First of all, the ground-state potential is much stiffer in the vicinity of the equilibrium geometry than the *S*<sub>0</sub> potential of the *n* = 2 cluster. This can be traced back to the open cyclic structure of the *n* = 3 cluster, which is considerably less flexible along the torsional coordinate  $\alpha$  than the open *p*-cresol (H<sub>2</sub>O)<sub>2</sub> geometry. Finally curvature and equilibrium positions of the *n* = 3 *S*<sub>0</sub> and *S*<sub>1</sub> potentials along the  $\alpha$  coordinate are practically the same. The corresponding *n* = 1 torsion potential<sup>13</sup> showed up to be about as stiff as the *n* = 3 potential. Obviously the *n* = 2 torsional potential from H<sub>2</sub>O acting as proton donor is unusually flat allowing large amplitude motion. While a very low frequency of a few cm<sup>-1</sup> would be surprising for the rotation of a single H atom even in a very flat potential well, it may be that the complex structure in the two-water cluster spectrum is due to sequence bands of the torsional vibration and/or hitherto unknown level splittings there.

Lipert and Colson showed in a "persistent hole burning" experiment<sup>14</sup> on phenol (H<sub>2</sub>O)<sub>2</sub> that indeed the broadening is homogeneous in nature and does not result from optical transitions of different isomers. The unusual width and the short singlet state lifetime of phenol (H<sub>2</sub>O)<sub>2</sub> caused Lipert and Colson to propose that the water molecules in the *n* = 2 cluster may be van-der-Waals bonded to the aromatic ring. From the kinetic curves in Fig. 2(b) however, it is more probable that the *n* = 1–3 clusters are formed by successive association, i.e., the *n* = 2 cluster by reaction of H<sub>2</sub>O with hydrogen-bonded *p*-cresol (H<sub>2</sub>O)<sub>1</sub>. Further on the calculated microscopic spectral shifts for H-bonded *n* = 1–3 clusters are in perfect agreement with experiment. The short phenol (H<sub>2</sub>O)<sub>2</sub> singlet state lifetime does not necessarily imply the absence of H bonding as proposed in Ref. 10 but may as well result from the high state density associated with low frequency vibrations leading to faster internal conversion. A more direct argument for a van-der-Waals bonded *n* = 2 cluster is the missing of the usual H-bond stretch vibration in the *n* = 2 phenol- and *p*-cresol cluster spectrum. We are on the way to perform improved 2-color ionization experiments on *p*-cresol (H<sub>2</sub>O)<sub>2</sub> to have a better chance for observation of the weak  $\sigma_0^1$  if existing. At present we, however, cannot completely exclude a van-der-Waals bonding of the *n* = 2 cluster.

#### D. Perturbation treatment of the spectral shifts

Considering the longest wavelength excitation of *p*-cresol and its clusters with water to arise from a HOMO–LUMO transition in the molecular orbital language, we can look more closely at the physical reasons for the observed spectral shifts in Fig. 4. We see that both HOMO and LUMO of the  $\pi$  system are destabilized after addition of the first water molecule acting as proton acceptor or while they are stabilized again after addition of the second and third water acting as proton donors. Now it is well known in simple Hückel theory that electron donating substituents or solvents exert an +*I* effect and destabilize the  $\pi$  system while –*I* substituents stabilize it<sup>15</sup> in agreement with Fig. 4. More quantitatively, in terms of first order perturbation the-

ory, the change in  $\pi$ -system energy of the ground and excited state due to an inductive effect on some center (here the O atom of cresol) is

$$\begin{aligned}\delta E_{\pi} &= q_0^* \delta \alpha_0 \\ \delta E_{\pi}^* &= q_0^* \delta \alpha_0\end{aligned}\quad (1)$$

with  $q_0$  and  $q_0^*$  as O-atom charge order defined by  $\sum b_j C_{jO}^2$  ( $b_j$  = population number,  $C_{jO}$  = O-atom orbital coefficient in the *j*th-MO) and  $\delta \alpha_0$  as change in the Coulomb integral at the oxygen atom which is positive (destabilizing)<sup>12</sup> for +*I* solvent effects and negative (stabilizing) for –*I* solvent effects.<sup>15</sup>

The microscopic shift after addition of the solvent is

$$\begin{aligned}\Delta \delta E_{\pi} &= \delta E_{\pi}^* - \delta E_{\pi} = (q_0^* - q_0) \delta \alpha_0 \\ &= (C_{LO}^2 - C_{HO}^2) \delta \alpha_0\end{aligned}\quad (2)$$

with  $C_{LO}$  and  $C_{HO}$  as LUMO- and HOMO-MO coefficient at the O atom.<sup>13</sup>

Now the  $\pi$ – $\pi^*$  excitation in *p*-cresol is connected with a charge transfer from the oxygen atom to the aromatic ring so that  $q_0^* < q_0$ , c.f. the O-atom MO coefficients in Fig. 4. Hence for +*I* effects with  $\delta \alpha_0 > 0$ , a red shift  $\Delta \delta E_{\pi} < 0$  is expected while for –*I* with  $\delta \alpha_0 < 0$  a blue shift,  $\Delta \delta E_{\pi} > 0$  should result. This agrees with the *ab initio* calculations and the experimental results, if the first water acts as electron donor and the second and third water as electron acceptors. In phenol we again find  $q_0^* < q_0$  and MO shifts in the same directions as in Fig. 4, so that the argument for the observed red and blue shifts is quite analogous.

Table IV shows the change of the Coulomb integral  $\delta \alpha_0$  due to the changes of the inductive effect of the solvents with increasing association. Shown is the change  $\delta \alpha_0$  of *p*-cresol (H<sub>2</sub>O)<sub>*n*</sub> relative to *p*-cresol (H<sub>2</sub>O)<sub>*n*–1</sub>. The table demonstrates the positive inductive effect exerted by the first water molecule acting as electron donor or proton acceptor, respectively. The second water molecule shows a somewhat weaker negative inductive effect acting as electron acceptor or proton donor respectively. The third water molecule is electron acceptor or proton donor, respectively to the second one and exerts only a small –*I* effect on the chromophore due to its larger distance from it.

Beside the *ab initio* calculations, we performed extensive semiempirical CNDO/CI and CNDO calculations of the cluster spectral shifts.<sup>12</sup> We obtained very similar results here. HOMO–LUMO energy changes as well as red and blue

TABLE IV. Change of the Coulomb integral of the chromophore O atom  $\delta \alpha_0$  with increasing association.

	<i>p</i> -cresol (H <sub>2</sub> O) <sub>1</sub>	<i>p</i> -cresol (H <sub>2</sub> O) <sub>2</sub>	<i>p</i> -cresol (H <sub>2</sub> O) <sub>3</sub>
$q_0^* - q_0^a$	– 0,230	– 0,210	– 0,206
$\delta \alpha_0$ [cm <sup>-1</sup> ] <sup>b</sup>	+ 1555	– 1193	– 160

<sup>a</sup> Difference of the O-atom charge density in the excited and ground state.

<sup>b</sup> Change of the O-atom Coulomb integral according to Eq. (3) with microscopic shifts from experiment (Table III) and  $q_0^* - q_0$  from *ab initio* (STO-3G) calculations. Shown is the change of the Coulomb integral  $\delta \alpha_0$  of *p*-cresol (H<sub>2</sub>O)<sub>*n*</sub> relative to *p*-cresol (H<sub>2</sub>O)<sub>*n*–1</sub>. A positive value of  $\delta \alpha_0$  stands for a positive inductive (+*I*) effect, a negative value for a –*I* effect.



spectral shifts as in Fig. 4 were found. In the spectroscopically parametrized CNDO/CI calculations, even the absolute transition energies were quite correct with an error of  $\pm 5\%$  for the *p*-cresol and phenol system. The calculations show that further water molecules do not perturb the *p*-cresol or phenol  $\pi$  system much further because they are hydrogen bonded to the first hydration shell forming the next shell quite distant from the chromophore.

It might be interesting for future investigations if the concept of HOMO—LUMO perturbation treatment can be applied to shifts in electronic spectra of other hydrogen bonded systems as well.

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