

Vibrational spectroscopy of size-assigned *p*-cresol/H₂O-clusters in the S₀ and S₁ state

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Vibrational spectra of supersonically cooled complexes of *p*-cresol with H₂O and CH₃OH were analysed by mass-resolved two-photon ionisation, dispersed fluorescence and stimulated emission, detected by two-colour ionisation dip. In *p*-cresol·(H₂O)₁ progressions of the intermolecular cluster stretch vibration and its combination bands with intramolecular cluster vibrations were observed with similar frequencies in the S₀ and S₁ state. In *p*-cresol·(H₂O)₃ and *p*-cresol·(CH₃OH)₁, further intense intermolecular bands arise, namely the hydrogen-bridge bending and torsion vibration. This can be attributed to the lower symmetry of these clusters. Ab initio quantum chemical calculations show *p*-cresol·(H₂O)₃ to have a higher H-bond stretch frequency than *p*-cresol·(H₂O)₁ because its (unsymmetric) cyclic structure is more rigid.

1. Introduction

The development of sensitive, high-resolution laser spectroscopic methods over recent years in combination with adiabatic cooling in supersonic expansions has yielded much information on electronically excited states of clusters and their intra- and inter-molecular vibrations. Relatively little is known about the vibrational states of the electronic ground state of clusters. Only the ground state information, however, can be compared with ab initio calculations of cluster potentials and vibrations on the Hartree-Fock level. For (aromatic) organic molecules and clusters with chromophoric groups, dispersed laser fluorescence can be used with no restriction in the attainable vibrational states so long as the Franck-Condon overlap between the specific (ro)-vibronic level in S₁ and S₀ exists. The spectral resolution of the method is, however, limited by the monochromator resolution which is normally a few cm⁻¹ – considerably larger than the laser resolution.

An interesting method for obtaining cluster ground state vibrational frequencies is stimulated emission. Here, two laser colours ω_1 and ω_2 are used to first pump a molecule to a level in S₁ with ω_1 and then dump it with ω_2 via stimulated emission to a selected vibrational level in S₀. High resolution (that

of the laser used) can be achieved here.

Stimulated emission spectroscopy (SEP) of stable molecules has been pioneered by the MIT group [1] who used the dip in the fluorescence from the pumped S₁ level to monitor a SEP resonance. The dip of the ion signal in one-colour multiphoton ionisation was used by Cooper et al. [2] as monitor. Ito and co-workers [3] used the two-colour ionisation dip for monitoring stimulated emission. Here, ω_2 induces stimulated emission and ionisation, while ω_1 is weakened to avoid one-colour ionisation. Temporal and spatial mismatching between the pump and dump laser can be minimised easily here by aligning the dump laser for maximum ion signal. This is automatically the best alignment for the pump/dump ion dip signal also. The alignment is easier to achieve because the two-colour ion signal is larger and has a less noisy baseline than the dip signal and furthermore is independent of the dump laser frequency (as far as $h(\omega_1 + \omega_2) \geq \text{IP}$). The one- and two-colour ionisation dip methods have no problems with scattered light from the dump laser and this is another reason for preferring it to fluorescence dip spectroscopy.

In this paper we report the observation of intermolecular vibrational states of hydrogen-bonded cresol clusters in their electronic ground state by

stimulated emission and dispersed fluorescence spectroscopy. We are especially interested in an exact determination of the hydrogen bond stretch, bend and torsion vibrations and their overtones in the electronic ground state because they yield valuable information about the hydrogen bond potential and can be directly compared to ab initio SCF calculations [4]. We observed intermolecular stretch vibrations of *p*-cresol clusters, with one and three water molecules attached, to lie at considerably different frequencies.

2. Experimental

Complexes of *p*-cresol with H₂O were produced in free supersonic expansions of the sample vapours in 1–5 bar He as carrier gas, using a 10 Hz electromagnetically pulsed, modified petrol injection valve (Bosch 0280150 036) with a gas pulse width of 600 μs fwhm, 0.6 mm nozzle hole and heating facilities up to 80°C. Background pressures were $\approx 1 \times 10^{-6}$ mbar (beam off) and 5×10^{-4} mbar (beam on). The vacuum was maintained by a 2000 l/s diffusion pump (Edwards), backed by a roots/rotatory pump system (Al-catel). The dispersed fluorescence and ion dip spectra were usually taken at about 0.12 mbar *p*-cresol (296 K) and partial pressures of the solvent H₂O between 0.05 and 5 mbar. The solvent pressure was changed by varying its temperature from –25 to 10°C with an ice/NaCl bath or a peltier-driven cryostat.

REMPI spectroscopy was performed in another apparatus by crossing the skimmed jet 75 mm downstream from the nozzle with the frequency-doubled output of an excimer laser (Lambda Physik EMG 150 EST) pumped unfocused dye laser (Lambda Physik FL 2002) with 0.2 cm⁻¹ spectral width (fwhm). The dye coumarin 153 and frequency-doubling crystals (Lambda Physik FL 30 and 31) were used at a laser power of about 150 μJ. Background pressures were 3×10^{-4} , 10^{-5} and 2×10^{-6} mbar (beam on) in the main chamber, the differentially pumped ionisation chamber and the time-of-flight chamber, respectively. Time-of-flight spectra were obtained by averaging the preamplified ion signals from a microchannel plate detector (Galileo Chevron type) with a digital oscilloscope (LeCroy model

9400). The mass resolution was 90 at $m/e=108$. 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 synchronised by a four-channel digital delay/pulse generator (Stanford Research DG 535).

For the dispersed fluorescence measurements, the pump light was fixed to a selected vibronic band and the fluorescence was dispersed by a 30 cm monochromator (McPherson 218) in the first order. The dispersed light was detected by a cooled photomultiplier (Thorn EMI 9789 QB; –30°C) and the photocurrent was averaged by a gated boxcar (Stanford Research SR 250) and recorded by a chart recorder.

For the dump process in the two-colour ionisation dip experiment, another excimer laser pumped (Lambda Physik EMG 200) dye laser (Lambda Physik FL 2002) was used with frequency-doubled light from coumarin 153, rhodamin 6G and sulforhodamin B dyes, depending on the wavelength range to be covered. The two laser beams were aligned coaxially with beam diameters of around 1.5 mm and were triggered to have zero time delay (jitter around ± 5 ns). The intensity of the pump light ω_1 was weakened to avoid the resonant multiphoton ionisation caused by ω_1 alone. Under these conditions spatial and temporal overlap of pump and dump beams could be easily aligned by optimising the large two-colour ionisation signal. The ions produced were drawn to the detector (Cu-Be multiplier) by its electric field and the ion current was averaged by the boxcar system described above.

Laser stability is very important in the two-colour ionisation dip experiments. While a dump pulse of around 300 μJ energy was sufficiently intense to drive the stronger dump transitions into saturation and weak enough to avoid multiphoton nonresonant ionisation, an extremely weak pump pulse of 5–10 μJ energy was used. Hence the two-colour ion dip signal was mainly affected by the pump laser fluctuations. In later experiments, the EMG 200 pumped dye laser was used for the pump process because this system showed smaller intensity fluctuations.

3. Results and discussion

3.1. *p*-cresol·(H₂O)₁

Fig. 1 shows the two-photon ionisation spectra of *p*-cresol·(H₂O)_{*n*} (*n*=0–3) after S₀→S₁ (π–π*) excitation as measured by tuning the boxcar gate to the time-of-flight (mass number) of the individual clusters.

Fig. 1a shows the REMPI spectrum of free *p*-cresol (*m/e*=108) seeded in 4 bar of helium between 35000 and 36200 cm⁻¹. The band at 35337 cm⁻¹ is the lowest-frequency band of bare *p*-cresol and can be assigned to the electronic origin 0,0 (free). The bands at 35334+419 and 35334+803 cm⁻¹ can be assigned to the totally symmetric a₁ (S₁) state fundamental vibrations 6a₀¹ and 12₀¹ which are localised mainly in the aromatic ring [3]. The weaker feature at 370 cm⁻¹ is the 18b₀¹ skeletal vibration with b₂ symmetry. The very weak low-frequency bands in fig. 1a arise from the hindered internal rotation of the CH₃ group of *p*-cresol. The bands generally show efficient rotational cooling with band widths <3.0 cm⁻¹ fwhm at 4 bar helium.

Fig. 1b shows the REMPI spectrum of *p*-cresol·(H₂O)₁ at mass number 126 (108+18). The electronic origin 0,0 of the monohydrated *p*-cresol is located at 34980 cm⁻¹ with a red-shift of 357 cm⁻¹ relative to bare *p*-cresol [5]. From the complex origin, a vibrational progression starts with a frequency interval of 152 cm⁻¹. From the isotope shift of the corresponding band in C₇H₇OD·D₂O and from comparison with ab initio SCF calculations of the cluster potential along the OH...O-coordinate (cf. fig. 4 and table 4 below) we can assign this transition to the intermolecular stretch vibration. The intermolecular stretch frequency was obtained by reducing the problem to the motion of the respective centres of mass. The resulting two-body potential was fitted by a Morse potential. The dispersed fluorescence spectrum from excitation of (0,0) *p*-cresol·(H₂O)₁ shown in fig. 2 indicates a slightly lower frequency for the stretching vibration in the electronic ground state. A progression with 146 cm⁻¹ spacing can be observed starting from the origin as well as from some intramolecular vibrations of the cluster. The fluorescence emission spectrum is governed by these combination bands up to more than 3000 cm⁻¹, cf.

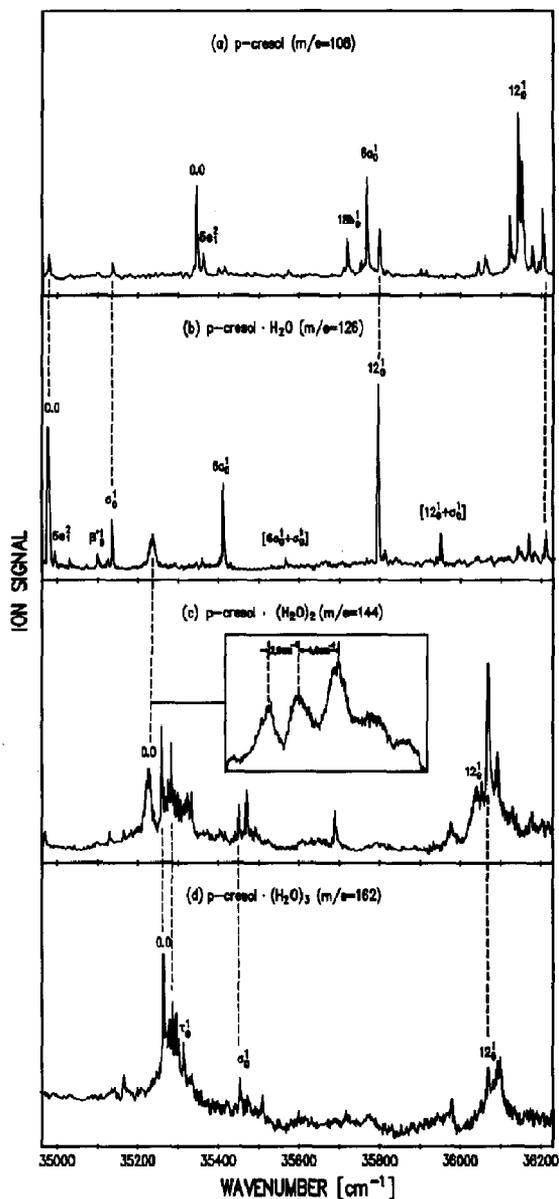


Fig. 1. Mass-selected REMPI spectra of *p*-cresol·(H₂O)_{0,1,2,3} from excitation of the S₀→S₁ transition. (a) Free *p*-cresol, (b) *p*-cresol·(H₂O)₁, (c) *p*-cresol·(H₂O)₂, (d) *p*-cresol·(H₂O)₃. Corresponding vibronic bands are connected by dashed lines indicating a general fragmentation behaviour *p*-cresol·(H₂O)_{*n*}⁺→*p*-cresol·(H₂O)_{*n*-1}⁺. Experimental conditions are 4 bar helium, *p*(H₂O)=1 Torr and expansion distance *x*/*d*=500. The insert in (c) shows the electronic origin of *p*-cresol·(H₂O)₂ at higher spectral resolution.

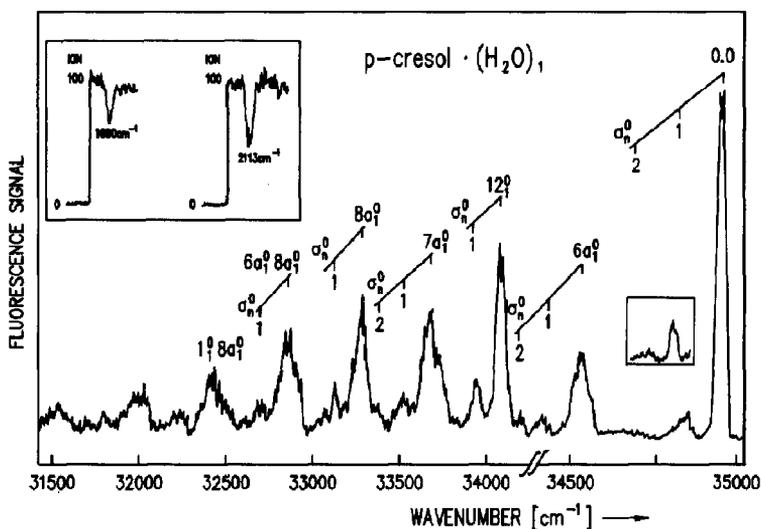


Fig. 2. Dispersed fluorescence spectrum after excitation of (0,0) p -cresol·(H₂O)₁. The spectrum regularly consists of progressions of the intermolecular stretch in the S₀ state σ_n^0 and its combination bands with several intramolecular cluster vibrations. Frequency accuracy is ± 10 cm⁻¹. The insert shows two-colour ionisation dip resonances after pumping the electronic origin of p -cresol·(H₂O)₁. Shown are typical signals at 1690 cm⁻¹ (8a₁⁰) and 2113 cm⁻¹ (6a₁⁰8a₁⁰) leading to ion dips of up to 50%. Frequency accuracy is ± 1 cm⁻¹.

Table 1
Ground (S₀) and excited state (S₁) vibrational frequencies for p -cresol·(H₂O)₁

S ₀		S ₁	Assignment ^{c)}
stim. em. ^{a)} ω (cm ⁻¹)	disp. fluor. ^{b)} ω (cm ⁻¹)	absorption ^{a)} ω (cm ⁻¹)	
0	0	0 (34980)	0,0
146	146	152	σ
291	291	303	2 σ
459	459	427	6a
601	601		6a+ σ
858	858	810	12
999	999	963	12+ σ
1279	1279	1286	7a
1441	1441	1435	7a+ σ
1690	1686	1620	8a
	1838		8a+ σ
2113	2110		6a+8a
2260	2262		6a+8a+ σ
2540	2542		12+8a

^{a)} Accuracy ± 1 cm⁻¹. ^{b)} Accuracy ± 10 cm⁻¹.

^{c)} Only bands which have intensities > 0.2 relative to the origin are given.

table 1. We also observed dispersed fluorescence from excitation of the intermolecular stretch vibration, i.e. (0,0) p -cresol·(H₂O)₁+152 cm⁻¹ (not shown here).

We observed a similar regular vibrational pattern but with the maximum of the Franck–Condon intensities now shifted from X (X represents the respective intramolecular cluster vibration) to $X+\sigma_1^0$. The insert in fig. 2 shows typical two-colour ionisation dip signals after excitation of (0,0) p -cresol·(H₂O)₁ which can be associated with the corresponding bands in the dispersed emission spectrum and assigned as shown in table 1. From the dip spectra quite precise ground state vibrational frequencies can be obtained with an uncertainty of ± 1 cm⁻¹ compared to ± 10 cm⁻¹ in the dispersed emission spectra. Both methods yield a value of 146 cm⁻¹ for the intermolecular stretch vibration. The red-shift of p -cresol·(H₂O)₁ relative to p -cresol shows the hydrogen bond to be stronger in the excited S₁ state than in the electronic ground state. Hence a higher stretch frequency in the S₁ state (152 cm⁻¹) compared to the S₀ state (146 cm⁻¹) is reasonable.

The electronic ground state data for the intermolecular stretch vibration can be compared with ab initio GAUSSIAN 80 calculations with a 4-31G* basis set where a stretch frequency of 175 cm⁻¹ was obtained from the O–O potential curve of the trans-linear configuration of p -cresol·(H₂O)₁ [6]. The agreement with the experimental value of 146 cm⁻¹

is reasonable. As usual the STO-3G potentials along the OO-coordinate is too stiff and this leads to a stretch frequency of 234 cm^{-1} , cf. fig. 4a below and ref. [7]. A more reasonable guess of the cluster stretch frequencies can be obtained by scaling the calculated STO-3G values to the experimental σ_0^1 of the $n=1$ cluster, cf. table 4 below. Further bands in fig. 1b arise from the intramolecular a_1 (S_1) cluster transitions $6a_0^1$ and 12_0^1 as well as from combinations of σ with intramolecular cluster vibrations, cf. table 1. There is a weak low-frequency feature in fig. 1b at 122 cm^{-1} which is absent in the free *p*-cresol spectrum and hence cannot be ascribed to CH_3 -rotation. From its low frequency and the C_s -symmetry of *p*-cresol·(H_2O)₁ the band may stem from the totally symmetric (a') in-plane bend vibration β' , cf. the normal mode analysis of (H_2O)₂ in ref. [8].

In the following we discuss the stimulated emission resonance obtained after excitation of (0,0) *p*-cresol·(H_2O)₁ in more detail. The resonances observed in our first ion dip experiments are presented in table 1 and agree well with the frequencies obtained from the corresponding dispersed fluorescence spectrum. This comparison shows directly that the observed ion dip resonances indeed arise from dumping to the S_0 state of the cluster.

In our experiments we found the very low frequency range $h(\omega_1 - \omega_2) < 300\text{--}400\text{ cm}^{-1}$ of the *p*-cresol·(H_2O)₁ cluster hard to obtain by two-colour ionisation dip spectroscopy. The high intensity of the dump laser can lead to nonresonant multiphoton ionisation of the cluster as background signal if ω_2 is near to ω_1 and $2h\omega_2 > \text{IP}$. Furthermore, the ionisation dip signal generally increases with increasing intramolecular vibrational relaxation (IVR) rate of the dumped vibrational state allowing dipoles of more than 30% which would be the saturation limit in a three-level system. We did indeed observe dipoles up to 50% as shown in fig. 2. The IVR rate, however, increases linearly with the state density of the bath in accordance with Fermi's golden rule and is small at low vibrational energy. Many of the intermolecular cluster vibrations are situated in the range $0\text{--}300\text{ cm}^{-1}$ and may be hard to obtain with ion dip spectroscopy despite the generally high state density of clusters with their low-frequency intermolecular vibrations. In case of cresol, the state density is further enlarged by the low frequency of the hindered in-

ternal rotation of the methyl group (not shown in tables 1, 2, 3 due to their weakness [6]). We have to improve especially our laser stability to cover the most interesting low-frequency range by ion dip measurements. Another possibility is to obtain the intermolecular vibrations from combination bands at higher frequencies.

Two-colour ionisation dipoles cannot be used for de-

Table 2
Ground (S_0) and excited state (S_1) vibrational frequencies for *p*-cresol·(H_2O)₃

S_0 disp. fluor. ^{a)} ω (cm^{-1})	S_1 absorption ^{b)} ω (cm^{-1})	Assignment ^{c)}
0	0 (35261)	0,0
	23	
	32	
74	52	τ
185	187	σ
	210	$\sigma+23$
430	426	6a
610		6a+ σ
830	813	12
1015		12+ σ

^{a)} Accuracy $\pm 10\text{ cm}^{-1}$. ^{b)} Accuracy $\pm 1\text{ cm}^{-1}$.

^{c)} β assigns an intermolecular bending vibration, τ the torsion and σ the stretch vibration. Only bands which have intensities > 0.2 relative to the origin are given.

Table 3
Ground (S_0) and excited state (S_1) vibrational frequencies for *p*-cresol·(CH_3OH)₁

S_0 disp. fluor. ^{a)} ω (cm^{-1})	S_1 absorption ^{b)} ω (cm^{-1})	Assignment ^{c)}
0	0 (34919)	0,0
25	25	β
40	50	$2\times\beta$
70	68	τ
	93	$\tau+\beta$
166	171	σ
	197	$\sigma+\beta$
	241	$\tau+\sigma$
485	426	6a
875	811	12
	836	12+ β

^{a)} Accuracy $\pm 10\text{ cm}^{-1}$. ^{b)} Accuracy $\pm 1\text{ cm}^{-1}$.

^{c)} Only bands which have intensities > 0.2 relative to the origin are given.

tection of SEP of very high vibrational states with $E_{\text{vib}} > 2h\omega_1 - \text{IP}$, because then $h(\omega_1 + \omega_2) < \text{IP}$. In principle one-colour ionisation with an optimised laser alignment from two-colour ionisation is the alternative. This is especially important for vibrational predissociation spectroscopy of hydrogen-bonded clusters. OH stretch vibrations in the range 3500–3800 cm^{-1} for example lie sufficiently above the hydrogen bond energy to induce efficient cluster dissociation but their energy is often $> 2h\omega_1 - \text{IP}$. Hence their SEP excitation can only be detected by a one-colour ion or a fluorescence dip not by the two-colour ion dip.

A rise of the ω_1 power to the one-colour ionisation limit, however, changed our dip signals for the worse so that high-frequency vibrations were not easier to detect. While the absolute ion signal increased drastically, the ion noise at the top of the resonance also increased, whereas the dip did not change much because of its limitations by the power and spatial and temporal characteristics of the dump laser.

3.2. *p*-cresol·(H_2O)₂

Fig. 1c shows the broad bands of the $n=2$ cluster, namely its electronic origin and the intense 12_1^0 band. As pointed out in ref. [5], the blue-shift of the $n=2$ relative to the $n=1$ spectrum can be quantitatively explained with the second H_2O acting as proton do-

nor to the hydroxyl group of *p*-cresol. The insert in fig. 1c shows the 0,0 band of the $n=2$ cluster at low laser scan velocity. The band consists of several broad features spaced by 3–4 cm^{-1} . In a spectral hole burning experiment on the very similar phenol/ H_2O system, Lipert and Colson [9] could show that the unusual width of the $n=2$ cluster bands is homogeneous and does not arise from optical transitions of different isomers. The reason for the unusual width of the $n=2$ cluster band is not clear yet, as discussed in ref. [5]. We could not obtain sufficiently intense dispersed fluorescence spectra for this cluster.

3.3. *p*-cresol·(H_2O)₃ and *p*-cresol·(CH_3OH)₁

Fig. 3 shows the dispersed emission spectrum after excitation of (0,0) *p*-cresol·(H_2O)₃. Starting from the electronic origin of this cluster and from several intramolecular vibrations, a progression with a frequency of 185 cm^{-1} is observed which can be assigned to the intermolecular stretch vibration, cf. table 2. In the REMPI-spectrum in fig. 1d we see a prominent band at 187 cm^{-1} , which is the corresponding intermolecular stretch vibration in the S_1 state, cf. table 2. Neither in the dispersed emission nor in the absorption spectrum of *p*-cresol·(H_2O)₃ did we find indications of an intermolecular stretch attributable to the second water subunit. This stretch vibration may be optically inactive or too weak to be

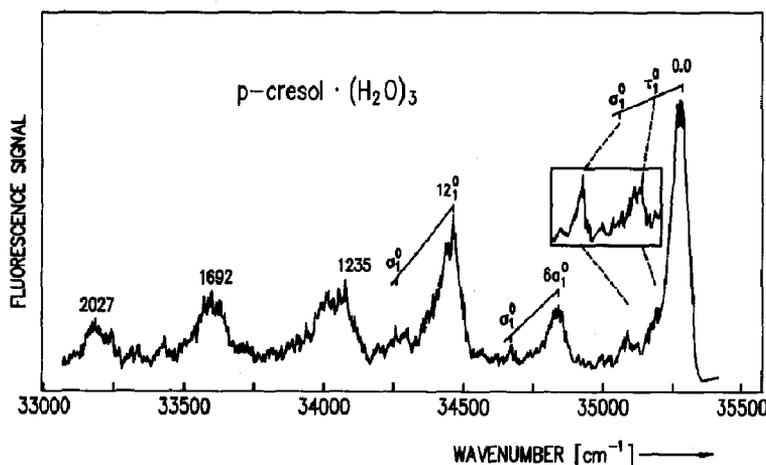


Fig. 3. Dispersed fluorescence spectrum after excitation of (0,0) *p*-cresol·(H_2O)₃. The spectrum consists of transitions from the vibrationless S_1 state to intermolecular cluster vibrations in the electronic ground state τ_1^0 , σ_1^0 and its combination bands with several intermolecular S_0 -cluster vibrations.

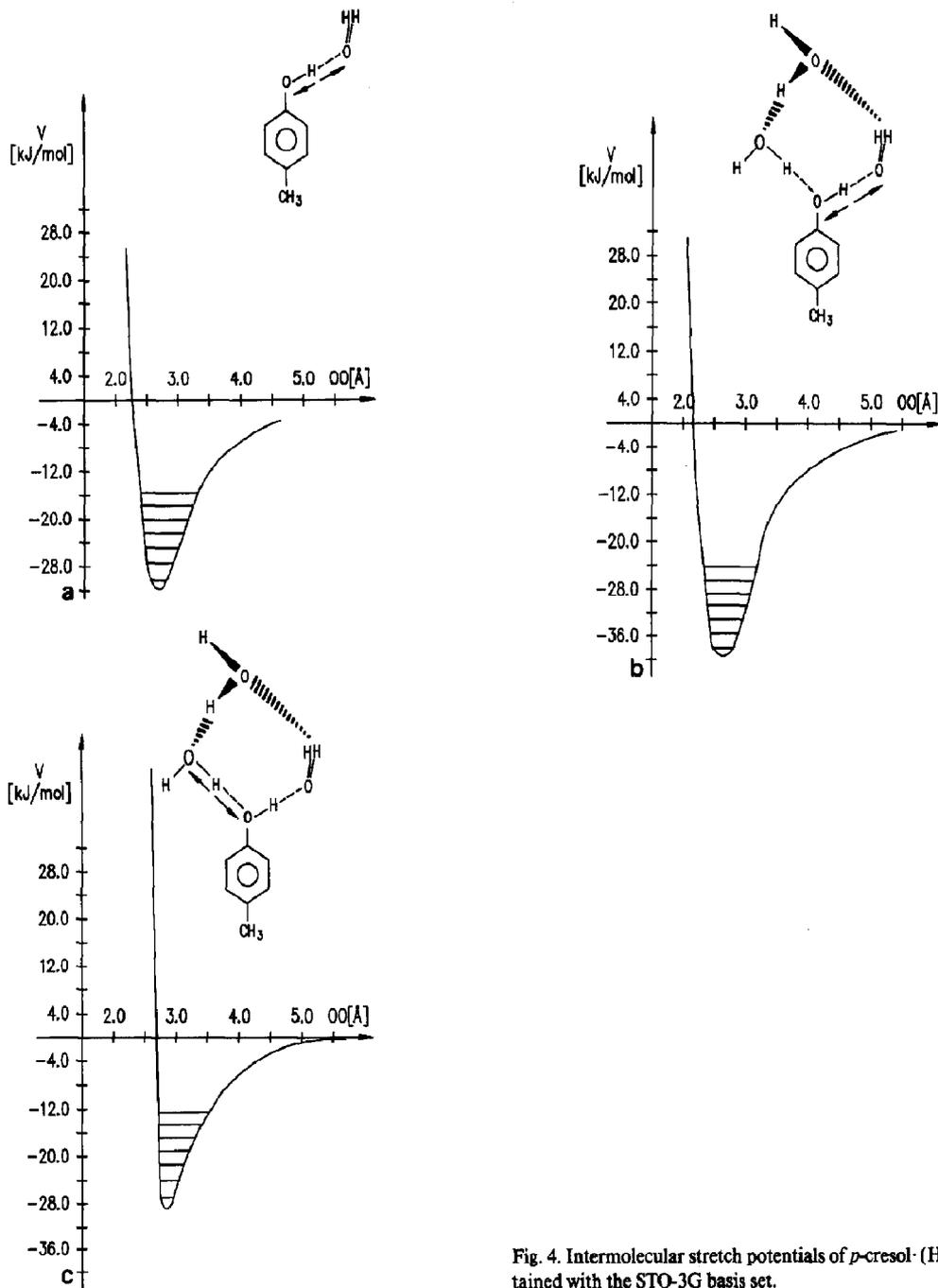


Fig. 4. Intermolecular stretch potentials of *p*-cresol·(H₂O)_{1,3} obtained with the STO-3G basis set.

observable here. Fig. 4c and table 4 show the frequencies which can be expected for the stretch vibration of the second H₂O acting as proton donor. The frequency of the proton donor H₂O in *p*-cresol·(H₂O)₃ was obtained by examination of the

centre of mass motion of the water dimer, relative to the centre of mass of the remaining molecule [10].

It is quite interesting that the stretch frequency in the *n*=3 cluster is considerably higher than in the *n*=1 cluster. As table 4 shows, the scaled STO-3G

Table 4
Ab initio STO-3G intermolecular stretch frequencies of *p*-cresol·(H₂O)_{*n*}, 1,2,3

	<i>n</i> =1		<i>n</i> =2		<i>n</i> =3	
	scaled	unscaled	scaled	unscaled	scaled	unscaled
$\nu_{\text{stretch,A}} \text{ (cm}^{-1}\text{)}^a$	152 (152)	225	148	221	198 (185)	296
$\nu_{\text{stretch,D}} \text{ (cm}^{-1}\text{)}$	-	-	101	150	240	358

^a The subscripts A and D correspond to the H-bond coordinate with H₂O acting as proton acceptor or donor, respectively. The calculated stretch frequencies are scaled to the experimental σ_0^1 of the *n*=1 cluster. Experimental values are in parentheses.

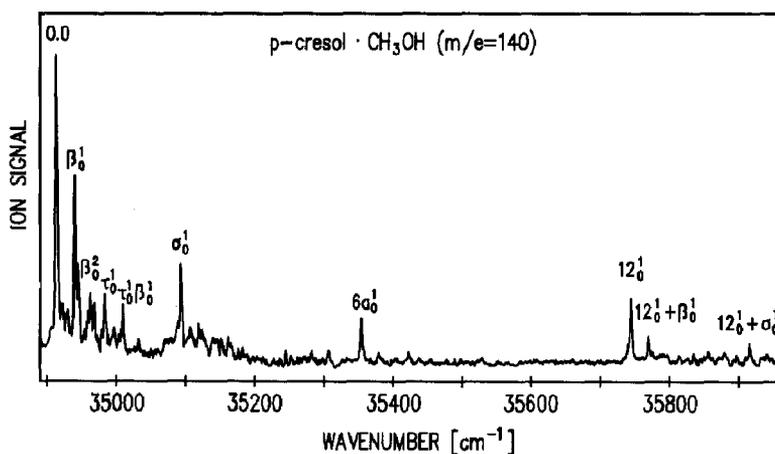


Fig. 5. Mass-selected REMPI spectrum of *p*-cresol·(CH₃OH)₁ over a frequency range of 1000 cm⁻¹. The spectrum consists of transitions β_0^1 , τ_0^1 , σ_0^1 and combination bands with the intramolecular cluster vibrations in the electronic excited state.

stretch frequency is in good agreement with the experimental value. Fig. 4b shows the corresponding cluster potential. The ab initio calculations show that the higher intermolecular stretch frequency (185 cm⁻¹ compared to 146 cm⁻¹) arises from the more rigid OO-potential of the cyclic *n*=3 cluster.

Fig. 1d and table 2 show that the REMPI spectrum of *p*-cresol·(H₂O)₃ contains many low-frequency bands beside the usual intramolecular vibrational transitions, similar to the *p*-cresol·(CH₃OH)₁ in fig. 5. The dispersed emission spectra of *p*-cresol·(H₂O)₃ (fig. 3) and *p*-cresol·(CH₃OH)₁ also contain low-frequency bands not observed in *p*-cresol·(H₂O)_{1,2}. This can be attributed to the lowering of symmetry. While *p*-cresol·(H₂O)_{1,2} still have C_s-symmetry, i.e. the aromatic plane, *p*-cresol·(H₂O)₃ and *p*-cresol·(CH₃OH)₁ have no symmetry anymore.

As shown in figs. 1d, 3, 5 and tables 2, 3 we observe bands at 74 and 70 cm⁻¹ for *p*-cresol·(H₂O)₃

and *p*-cresol·(CH₃OH)₁ in the S₀ state and similar frequencies in the S₁ state. According to quantum chemical calculations of different groups [8] on the translinear water dimer, there is only one vibrational band in the range 70–90 cm⁻¹. This band can be assigned to the torsional motion of the solvent molecule around the hydrogen-bridge axis and is named τ here.

Fig. 5 shows a further low-frequency cluster progression at ≈ 25 cm⁻¹ for *p*-cresol·(CH₃OH)₁ in the S₀ and S₁ state. From its low frequency this band may be assigned to the intermolecular bending motion β of the CH₃OH solvent molecule.

4. Summary

Spectra of the intermolecular H-bond vibrations of *p*-cresol·(H₂O)_{1,2,3} and *p*-cresol·(CH₃OH)₁ in the

S_0 - and S_1 -electronic states were obtained by several laser spectroscopical techniques. The comparison with *ab initio* quantum chemical calculations reveals details of the corresponding parts of the hydrogen bond potentials and points to a cyclic structure of *p*-cresol·(H₂O)₃. Further work will be directed to higher-resolution studies of the rotational envelope of the cluster bands and to improvement of the ion dip technique.

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