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Structure and vibrations of phenol·CH₃OH (CD₃OD) in the electronic ground and excited state, revealed by spectral hole burning and dispersed fluorescence spectroscopy

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The intermolecular vibrations of phenol(CH₃OH)₁ and its deuterated isotopomer *d*-phenol(CD₃OD)₁ were examined by comparing the vibrational frequencies of the electronic ground and excited state with the results of *ab initio* normal mode calculations at the Hartree–Fock level, using the 4-31G* and 6-31G** basis sets. Full energy minimization showed a translinear structure similar to phenol(H₂O)₁ or to the water dimer. Dispersed fluorescence spectra have been recorded via excitation of the electronic cluster origin and several intermolecular vibrational transitions. The Franck–Condon intensity pattern allowed an assignment of the ground state vibrational frequencies to the excited state frequencies, which were examined by resonance enhanced multiphoton ionization and hole burning spectroscopy. The existence of another conformer that possibly absorbs in the region of interest was ruled out by hole burning spectroscopy of the phenol(CH₃OH)₁ cluster. A full assignment of all intermolecular vibrations of this hydrogen bonded cluster in the *S*₀ state could be given for the first time on the basis of *ab initio* calculations and a combination of different spectroscopical methods. © 1995 American Institute of Physics.

I. INTRODUCTION

Hydrogen bonding is responsible for a variety of phenomena in nature and life, from the density anomaly of water, to the determination of protein or DNA structure. The dissociation energy of the hydrogen bond is high enough to facilitate stabilizing effects and surface phenomena, on the other hand it is low enough to be reversible, which is of fundamental importance for biochemical replication mechanisms. Thus a thorough understanding of structure and dynamics of hydrogen bonding between polar solvents and aromatics is of basic interest.

The structure and dynamics of hydrogen bonded clusters of phenol with H₂O,^{1–5} CH₃OH,^{6–10} CH₃CH₂OH,¹¹ and phenol^{12–14} have been carefully investigated spectroscopically and theoretically.^{15,16} In order to study the interaction of one solvent molecule with a solute molecule, all other interactions have to be minimized by isolating the cluster molecules in a supersonic jet expansion. For investigation of the electronic ground state *S*₀ of these clusters, dispersed fluorescence spectroscopy, stimulated emission pumping (SEP),^{17,18} ionization loss stimulated Raman spectroscopy (ILSRS),¹⁹ rotational coherence spectroscopy,¹⁴ and microwave spectroscopy in supersonic jets²⁰ have been performed. Two-color resonantly enhanced multiphoton ionization (REMPI),⁹ laser induced fluorescence (LIF),⁷ and hole burning spectroscopy (SHB)²¹ have been applied to investigate the electronically excited state *S*₁.

In this work we are concerned with the spectroscopy of the phenol(methanol)₁ cluster, extending our experimental investigations of *p*-cresol(methanol)₁ (Refs. 22 and 23) and calculations of the phenol(methanol)₁ cluster.¹⁵ In contrast to

the phenol(H₂O)₁ cluster, with *C*_s symmetry and three totally symmetric intermolecular vibrations out of six, there is no remaining symmetry element in the phenol(CH₃OH)₁ cluster. All intermolecular vibrations should therefore be allowed.

The first work on the phenol(methanol)₁ cluster with supersonic jet spectroscopy was performed by Ito and co-workers.⁶ They used fluorescence excitation spectroscopy for detection of the excited state vibrational frequencies of this cluster. A value of 27 cm⁻¹ for a bending vibration, which was seen in many combinations with other bands, and 175 cm⁻¹ for the stretching vibration was reported. The spectral shift due to complexation was determined to be 415 cm⁻¹.

In a later work⁷ these measurements were extended to the electronic ground state by fluorescence emission spectroscopy, and values of 22 cm⁻¹ (bending vibration) and 162 cm⁻¹ (stretching vibration) were found. The possible existence of different rotational conformers of this cluster was discussed for the first time. In a third paper of this series⁸ Ito and co-workers performed solvent pressure-dependent measurements of the fluorescence intensity of several cluster bands. In addition to the electronic origin of the phenol(methanol)₁ cluster at 35 935 cm⁻¹, a second band at 36 166 cm⁻¹ has been found and assigned to the electronic origin of the phenol(methanol)₂ cluster. The fluorescence excitation spectrum showed rich spectral features in the low frequency region that remained unassigned. A dispersed fluorescence spectrum of the electronic origin of phenol(methanol)₂ stated a vibrational frequency of 192 cm⁻¹ for the stretching vibration.

In order to investigate the phenol(methanol)₁ cluster ion two-color multiphoton ionization (MPI) spectra have been taken by Ito and co-workers.⁹ The ionization potentials for

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the $n=1$ and $n=2$ cluster (uncorrected for the applied extraction field) were found to be 63 350 and 65 300 cm⁻¹, respectively.

A much more precise value for the vertical ionization potential of the phenol(methanol)₁ cluster (63204±4 cm⁻¹) was obtained by Wright *et al.*¹⁰ using ZEKE spectroscopy. In their work, they reported a two-color REMPI spectrum of phenol(methanol)₁ and ZEKE spectra pumped through some of the intermolecular vibrations. They assigned six low frequency transitions at 27, 31.5, 46, 48.5, 55.5, and 176 cm⁻¹ to the six S_1 intermolecular vibrations. We will discuss their assignment later.

Felker and co-workers¹⁹ performed ionization loss stimulated Raman spectroscopy (ILSRS) on several hydrogen bonded clusters, among them the phenol(methanol)₁ cluster. In ILSRS, the depletion of a ground state level by a stimulated Raman process is monitored by resonantly enhanced multiphoton ionization from the ground state. ILSRS is species selective and the resolution is limited only by the laser bandwidth. Unlike stimulated emission pumping, the application of this method is not restricted by small IVR rates in the terminating level, which often limits SEP to a region starting at several hundred wave numbers above the electronic origin. The vibrational shifts of several intramolecular vibrational bands were found to be quite small in most cases.

The appearance of large amplitude motions (e.g., torsion) in hydrogen bonded clusters gives rise to the assumption that different rotational conformers of one cluster size may exist. Prior to any comparison of calculated and experimental vibrational frequencies one has to assure that all low frequency bands appearing in the REMPI-TOF-MS spectrum belong to *one* conformer of this cluster.

REMPI-TOF-MS in principle offers the possibility to distinguish between different cluster sizes.^{24,25} Due to the small dissociation energies of hydrogen bonded clusters, REMPI spectra are often obscured by fragmentation of the mother ion, even under “soft,” two-color excitation conditions. Further REMPI cannot distinguish between cluster ions of the same mass, e.g., conformers.

To the contrary spectral hole burning (SHB) allows differentiation between stable conformers of one cluster.^{26–28} SHB offers the advantage to select transitions, originating from one common vibronic ground state level, and is therefore not only mass but species selective.²⁹ In SHB a ground state vibronic level is depopulated resonantly with a burn laser ω_1 . Several hundred ns after the burn laser pulse, the population of the ground state is analyzed by a probe laser ω_2 , fixed to a strong transition of the cluster. We used LIF²¹ and REMPI³⁰ for detection, while Colson and Lipert²⁷ analyzed the population of the ground state level by REMPI.

Fortunately repopulation of the original level does not occur significantly on the time scale of the experiment. Most of the fluorescence, which is the only fast process to repopulate the electronic ground state, ends up in a manifold of vibrational levels, determined by the Franck–Condon principle.

A pulse energy of 400–800 μ J was sufficient to obtain holes up to 30% of the probe fluorescence signal. Higher

pulse energies lead to an increase of nonresonant signal and therefore have to be avoided.

The most important technique however for obtaining the intermolecular S_0 -vibrational levels, which can be compared with calculations, is dispersed fluorescence spectroscopy. Here we use an optical multichannel analyzer system with a CCD detector for obtaining good quality spectra.

II. EXPERIMENT

The one-color REMPI spectra have been measured in an apparatus similar to that described previously.³¹ It consists of a high-vacuum part, an electromechanically driven pulsed valve (General Valve Iota One, 500 μ m nozzle hole) for skimmed jet expansion ($X/D \approx 130$), a differentially pumped linear time-of-flight (TOF) mass spectrometer, and a Nd-YAG (Lumonics HY 400, 532 nm) pumped, frequency doubled dye laser (Lumonics HD 300), operated with Fluorescein 27.

The pressures in the differentially pumped chambers were 5×10^{-6} mbar (beam off), 1×10^{-4} mbar (beam on) in the expansion chamber, 1×10^{-6} mbar in the ionization chamber, and 1×10^{-7} mbar in the time-of-flight tube. The vacuum in the expansion chamber was maintained by a 3000 ℓ s⁻¹ oil diffusion pump (Leybold DI 3000) and in the other chambers by 1000 ℓ s⁻¹ turbomolecular pumps (Leybold Turbovac 1000).

The apparatus used for spectral hole burning has been described elsewhere.²¹ It again consists of a high-vacuum chamber and a pulsed nozzle (General Valve Iota One, 500 μ m nozzle hole). The fluorescence at a nozzle hole—laser distance $X/D=30$ is collected with a two lens system and detected by a Peltier-cooled photomultiplier (Thorn EMI 9789). The vacuum is maintained by a 2000 ℓ s⁻¹ oil diffusion pump (Edwards), backed by a rotatory pump (Leybold D65B). Pressures are 1×10^{-6} (beam off) and 5×10^{-4} mbar (beam on). The electronic origin of the cluster is probed by an excimer (Lambda Physik EMG 102) pumped, frequency doubled dye laser (Lambda Physik FL 2002). Another excimer (Lambda EMG 200) pumped, frequency doubled dye laser (FI 3002) counterpropagates the probe laser for hole burning. The burn laser is slightly collimated by an $f=1000$ mm lens to a similar size as the probe laser. The spatial distance between burn and probe laser focus is about 0.5 mm, to compensate for the time delay between both lasers. Both lasers and the pulsed nozzle are triggered by a four-channel digital delay generator (Stanford Research DG 535). The delay between burn and probe laser was adjusted to 400–800 ns, while the delay between nozzle-trigger and probe laser was 1.8 ms.

The spectra were taken with 20 mbar CH₃OH or CD₃OD, respectively, and 0.5 mbar phenol, seeded in 4000 mbar He. The photomultiplier signal is averaged with a boxcar integrator (Stanford Research SR250) and recorded by a chart recorder. The fluorescence signal caused by the burn laser is separated from the probe signal by positioning the boxcar gate to the scattered light of the probe laser.

The fluorescence emission spectra were taken in the same vacuum chamber. The emitted fluorescence was collected and focused by a two-lens system on the entrance slit

of a 1 m Czerny–Turner monochromator with an aperture of $f/8.4$ (Jobin Yvon THR 1000). We used a holographic grating (11 cm×11 cm) with 2400 grooves/mm. The resulting linear dispersion $d\lambda/dx$ at 280 nm is 7.2 Å/mm. The fluorescence is imaged on the photocathode of the CCD camera, intensified and recorded on the CCD chip after 15:25 reduction of the image size in an optical fiber taper. With a CCD chip width of 1/3 in. and a pixel size of 23 $\mu\text{m}\times 23\ \mu\text{m}$, a range of 750 cm^{-1} of the emission spectrum can be taken in one mirror position of the monochromator.

The dispersed fluorescence is recorded with 12 bit resolution in first grating order by the intensified slow scan gated CCD camera (LaVision, Flame Star) positioned in the image plane of the monochromator. The resulting two-dimensional array (x =height of the entrance slit; y =dispersion) is averaged over a curved x range, to compensate for errors due to the spherical aberration of the mirrors, cf. Fig. 4. The quality of these spectra compared to previous ones, taken with a scanning monochromator, exit slit, and photomultiplier is enhanced dramatically with respect to resolution and signal/noise. A single fluorescence excitation spectrum was obtained by summing the fluorescence of 200 laser pulses on the CCD chip and subtracting the background stray light (gas pulse off) after 200 laser pulses. 80 of these spectra were averaged to obtain the overall spectra shown in the Figs. 5 and 6.

III. EXPERIMENTAL RESULTS

A. Hole burning spectra of *h*-phenol(CH₃OH)₁

Different cluster sizes and masses can be selected via REMPI in a time-of-flight spectrometer. In the case of different conformers of one cluster and extensive ion fragmentation this method will not lead to reliable results, and SHB will be the method of choice.

A selected vibronic ground state level is resonantly depopulated with a burn laser pulse. The population of this level is probed with laser induced fluorescence, via excitation to a strong transition, originating from the selected level. A reduction of noise from laser energy fluctuations was performed by saturating the observed transition with the probe laser ($>150\ \mu\text{J}$ per pulse).

To achieve the best experimental conditions for resonant depopulation of the electronic ground state, we recorded the hole burning signal as function of the burn laser pulse energy (Fig. 1). The fluorescence intensity without burn laser is defined as 100%. Figure 1 shows that an increase of the burn laser energy results in an increase of the hole burning signal due to the removal of more molecules from the probed state via processes which are irreversible on the time scale of the experiment. At high laser energies $>600\ \mu\text{J}$ these processes are driven to saturation.

At pulse energies above 1.5 mJ the burn (depopulation) process becomes nonresonant, and a bleaching of the entire spectrum is observed.³²

Figure 2 shows the hole burning spectrum of *h*-phenol(CH₃OH)₁ in the region 0–200 cm^{-1} on the blue side of the electronic origin (upper trace) in comparison to the LIF spectrum in the same spectral region (lower trace).

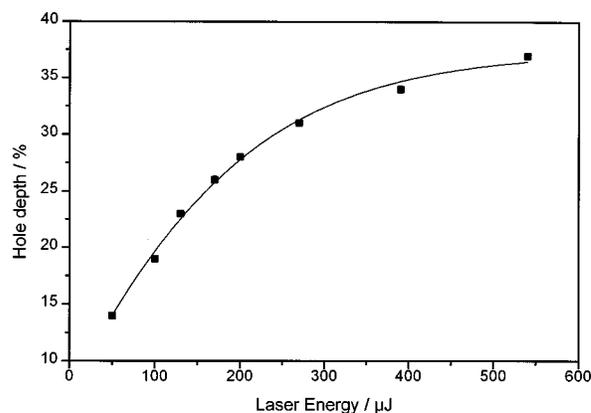


FIG. 1. Dependence of the hole burning signal from burn laser energy.

The $S_1 \leftarrow S_0$ transition was measured at $35\,933 \pm 1\ \text{cm}^{-1}$ in good agreement with the value of Wright *et al.*¹⁰ The probe laser was fixed to the electronic origin of the cluster, while the burn laser was tuned over the region 0–250 cm^{-1} on the blue side of the electronic origin. The most striking feature in the LIF spectrum is the very broad background, superimposed on the resonant phenol(methanol)₁ cluster transitions.

Wright *et al.*¹⁰ observed phenol(methanol)_{*n*} clusters up to $n=10$ in their REMPI spectra, even under moderate expansion conditions. We therefore believe that the background in our LIF spectrum is due to inhomogeneous spectral congestion, caused by the existence of different cluster sizes and isomers. The SHB spectrum supports this opinion. In the case of inhomogeneous broadening, distinct holes can be burned into the distribution, what is indeed observed in the SHB spectrum in Fig. 2. Only those transitions which share a common ground state level with the probed transition are detected by SHB. The broad background due to clusters of different sizes or conformers therefore totally vanishes in the hole burning spectrum. Obviously only one transition (marked with an asterisk) in this spectral region, appears in the LIF spectrum, which does not match with a corresponding band in the SHB spectrum. All other transitions can safely be assigned to vibrations of *one conformer* of *h*-phenol(CH₃OH)₁. By comparison with the phenol(H₂O)₁ spectrum, it was obvious that the transition in question in the LIF spectrum is the electronic origin of the phenol(H₂O)₁ cluster, and stems from water traces in the phenol sample or in the carrier gas. The complete absence of this transition in the hole burning spectrum illustrates again the selectivity of this method even when using a non-mass-selective detection method as LIF.

A closer look on a single rovibronic band reveals a narrower bandwidth in the SHB spectrum, compared with the typical bandwidth in a LIF or REMPI spectrum. This narrowing effect is due to the selective probe of a rotational subensemble in the rovibronic cluster band with a laser bandwidth considerably smaller than the full width at half-maximum of the respective electronic band.³²

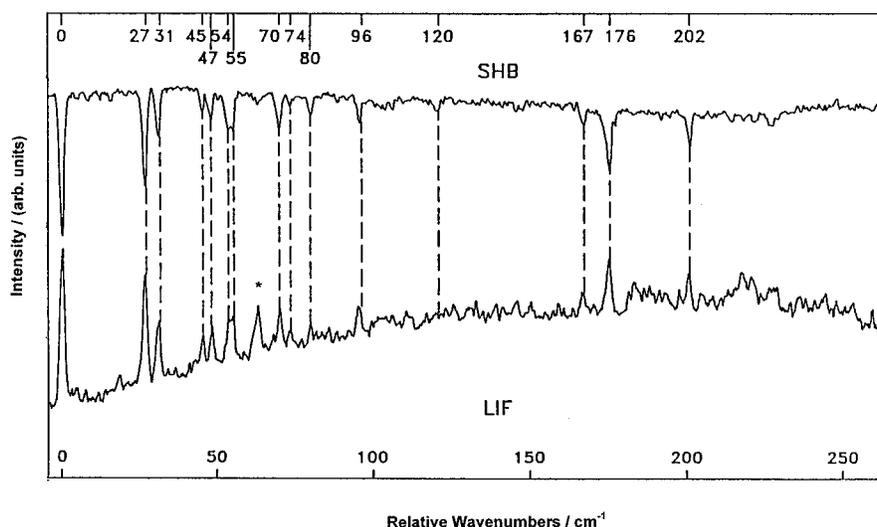


FIG. 2. Hole burning spectrum of *h*-phenol(CH₃OH)₁ in the range 0–200 cm⁻¹ blue to the electronic origin of this cluster. The 0,0 band was the analyzed transition. The band marked with an asterisk belongs to phenol(H₂O)₁. Accuracy of band positions: ±1 cm⁻¹.

B. REMPI spectra of *d*-phenol(CD₃OD)₁

Assignment of experimental frequencies to normal modes is generally easier if other isotopomers of the investigated cluster are used. Due to the acidity of the phenolic H atom, it can easily be exchanged by deuterium. *d*-phenol(CD₃OD)₁ is produced by heating phenol with a threefold excess of CD₃OD for 10 min, drying the mixture, and repeating this procedure four times. A statistical H↔D exchange should result in a *d*-phenol purity >99%. The content of undeuterated phenol in the sample was determined to be less than 3% by taking a NMR spectrum of the sample.

The 1+1 one-color REMPI spectrum of *d*-phenol(CD₃OD)₁ was measured in the apparatus described above. The *S*₁←*S*₀ transition was measured at 35 951 cm⁻¹, with a blueshift of 18 cm⁻¹ relative to the electronic origin of *h*-phenol(CH₃OH)₁ (see Fig. 3).

Table I gives a survey of the *S*₁ frequencies of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁. Some bands remained unassigned, and are probably due to mixed isotopomers.

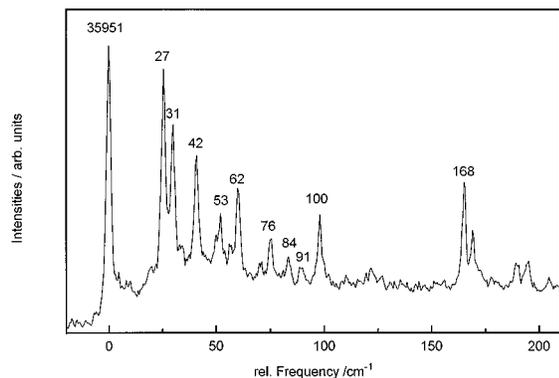


FIG. 3. REMPI spectrum of *d*-phenol(CD₃OD)₁. Bands marked with an asterisk are due to the mixed isotopomers *d*-phenol(CD₃OH)₁ and *h*-phenol(CD₃OD)₁. Accuracy of band positions: ±1 cm⁻¹.

The assignments given in Table I will be discussed extensively in Sec. IV.

C. Dispersed fluorescence spectra of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁

In order to assign the experimental frequencies to specific normal mode vibrations, the SHB (*S*₁) frequencies have to be associated with vibrational frequencies in the electronic ground state, which can be compared directly with the results of *ab initio* normal mode analysis. Fluorescence spectra have been taken by imaging the fluorescence on the entrance slit of a 1 m monochromator and viewing the dispersed fluorescence with an intensified gated CCD camera in the exit image plane. Figure 4 shows the dispersed fluorescence of the electronic origin 0,0 of *d*-phenol(CD₃OD)₁, directly recorded with the CCD camera.

The curvature of each image of the entrance slit is due to spherical aberration of the mirrors used. This spherical aberration is normally reduced by limitation of the entrance slit height. Computer-based processing of the images allows an intensity integration along the curved profile. Compared to a simple reduction of slit height the S/N ratio could be improved with this method by a factor of 3 at the same spectral resolution.

Figures 5(a) and 5(b) show the fluorescence emission spectra of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁, pumped through the electronic origin 0,0 of each cluster. Both spectra have been taken with an entrance slit width of 40 μm (3 cm⁻¹ resolution).

The inserts in Fig. 5 show an intensity expanded part of the low frequency region. Table II displays the experimental vibrational frequencies and intensities for the electronic ground state of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁ and a preliminary assignment to fundamentals, overtones, and combination bands. All bands shown in these spectra

TABLE I. Excited state (S_1) frequencies and intensities of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁.

<i>h</i> -Ph(CH ₃ OH)			<i>d</i> -Ph(CD ₃ OD)		
Rel. freq. (cm ⁻¹) ^a	Rel. Int.	Assignment ^c	Rel. freq. (cm ⁻¹) ^{a,b}	Rel. Int.	Assignment ^c
0(35933)	1	0,0	0(35951)	1	0,0
27	0.69	1	27	0.78	1
31	0.40	2	31	0.68	2
45	0.17	3	42	0.53	3
47	0.21	4	53	0.32	4
54	0.26	1+1	62	0.42	1+1
55	0.29	1+2	76	0.22	1+1+1
70	0.31	1+3	84	0.18	1+4(3+3)
74	0.08	1+4	91	0.11	...
80	0.14	1+1+1	100	0.25	5
96	0.20	5	168	0.58	6
120	0.10	1+5	171	0.44	...
167	0.16	1+3+5			
176	0.33	6			
202	0.29	1+6			

^aAccuracy in band position ± 0.5 cm⁻¹.

^bWave numbers are relative to the electronic origin of *d*-phenol(CD₃OD)₁. Negative wave numbers are due to another isotopomer, not to hot bands.

^cAssignments as described in Sec. IV.

will be assigned in Sec. IV to specific modes on the basis of *ab initio* normal mode analysis. Clearly the most intense band is the electronic origin, due to a small S_0 - S_1 potential shift. The prominent bands at 155 cm⁻¹ in *d*-phenol(CD₃OD)₁ and at 162 cm⁻¹ in *h*-phenol(CH₃OH)₁ show a quite harmonic progression, which can be seen up to the second overtone of this vibration. This band has been reported earlier by Abe *et al.*⁷ for *h*-phenol(CH₃OH)₁ to lie at 162 cm⁻¹ and has been assigned to the intermolecular stretching vibration. A second prominent band at 22 cm⁻¹ is in coincidence with our experimental observation and was assigned to a not further specified "bending vibration." Another strong transition appears at 35 cm⁻¹. The very characteristic intensity pattern can be recognized in combination with the 162 cm⁻¹ band as well as with the intramolecular vibration $6a_1$ at 538 cm⁻¹.

In order to associate the excited state frequencies with ground state vibrations, dispersed fluorescence spectra of

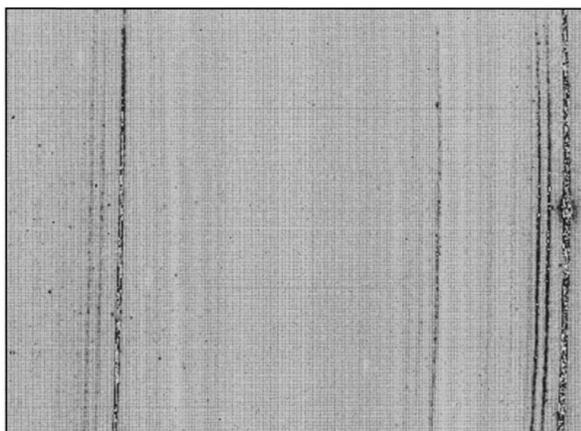


FIG. 4. Dispersed fluorescence spectrum of *d*-phenol(CD₃OD)₁ recorded by the CCD chip of an intensified slow scan camera. The curvature of the lines is due to spherical aberration of the mirrors.

several intermolecular vibrations of *h*-phenol(CH₃OH)₁ have been taken. The result is shown in Fig. 6. The first trace (a) shows, for comparison, the dispersed fluorescence spectrum of *h*-phenol(CH₃OH)₁ pumped through the electronic origin. The fluorescence spectra pumped through the bands at 27, 31, and 176 cm⁻¹ are shown beneath. All fluorescence emission spectra are shifted by their relative excitation frequencies, to match the 0 \leftarrow 1 transitions.

The fluorescence emission spectrum obtained from excitation of the vibration 1 at 27 cm⁻¹ is shown in part (b) of Fig. 6. An intensive, quite harmonic progression with 22 cm⁻¹ quanta is observed from transitions 1_0^1 , 1_1^1 , 1_2^1 , 1_3^1 , and 1_4^1 . It appears reasonable to correlate this 22 cm⁻¹ progression in the electronic ground state with the 27 cm⁻¹ vibration in the electronically excited state. In addition, the 55 cm⁻¹ band appears strongly. This transition is also observed, when pumping through the electronic origin. Intense transitions to other coordinates than the excited one give rise to the assumption of appreciable coupling between the corresponding modes. As shown in Fig. 6(c) the most prominent progression at 35, 65, and 93 cm⁻¹, shown in Fig. 6(c), correlates to the pumped 31 cm⁻¹ S_1 vibration exhibiting little anharmonicity of this vibration in the electronic ground state. The transition to the vibrational state at 22 cm⁻¹ has considerable Franck-Condon intensity again. Figure 6(d) shows the fluorescence emission spectrum obtained from excitation of vibration 6 at 176 cm⁻¹. The strongest transition appears at 162 cm⁻¹ and correlates to the pumped 176 cm⁻¹ S_1 vibration.

D. Theoretical results

In order to get reliable assignments of the observed intra- and intermolecular frequencies, a normal mode vibrational analysis of the clusters has to be carried out. *Ab initio* calculations at the Hartree-Fock (HF) level turned out to be useful to describe the low frequency intermolecular vibra-

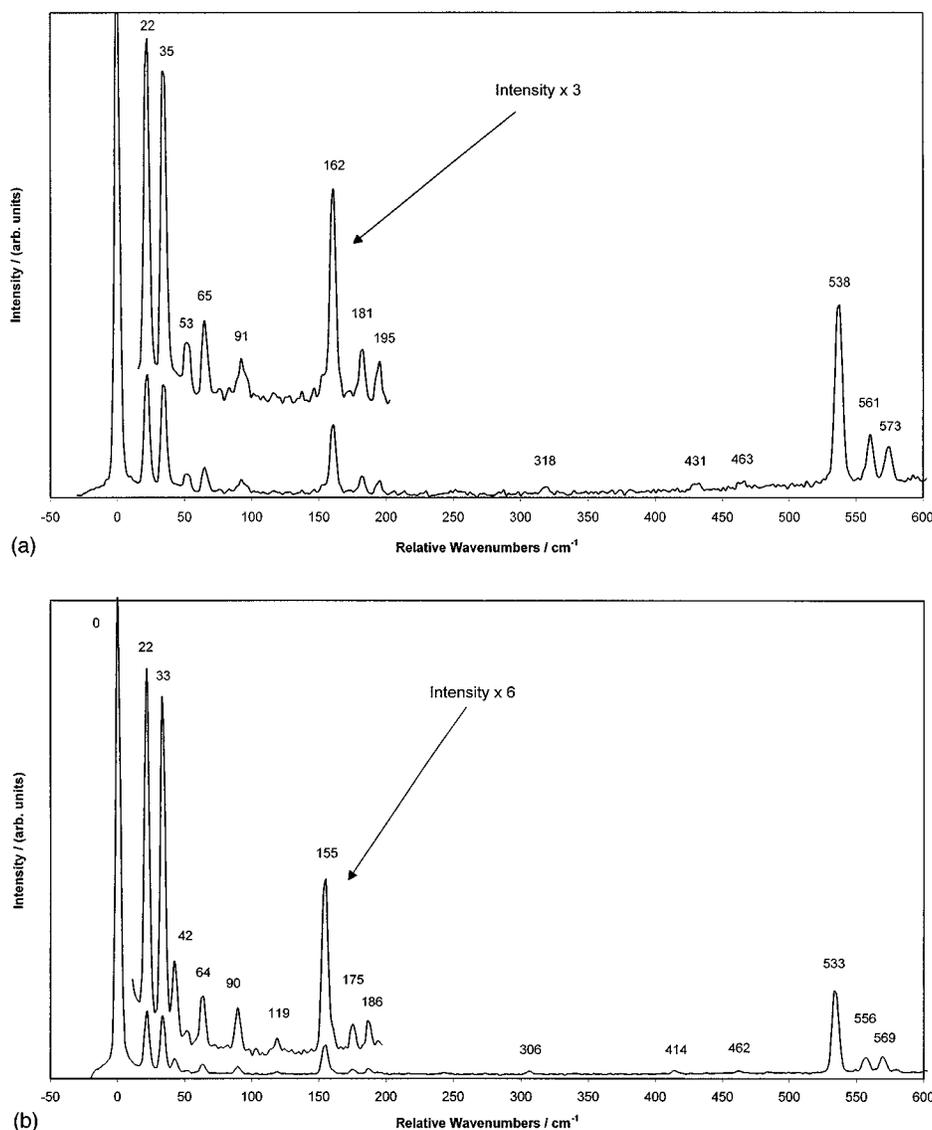


FIG. 5. (a) Dispersed fluorescence spectrum of *h*-phenol(CH₃OH)₁, pumped through the electronic origin. Spectral resolution is 3 cm⁻¹, error in band positions ±2 cm⁻¹. (b) Dispersed fluorescence spectrum of *d*-phenol(CD₃OD)₁, pumped through the electronic origin. Spectral resolution is 3 cm⁻¹, error in band positions ±2 cm⁻¹.

tions of the hydrogen bonded clusters, if both the chosen basis set includes polarization functions⁴ and the vibrations have small anharmonicity.

Complete normal vibrational analyses of hydrogen bonded clusters with H₂O acting as proton acceptor molecule have been carried out on phenol(H₂O)₁ (HF/3-21G, 4-31G, 4-31G*, 6-31G**, 6-311++G**, and MP2/6-31G** basis),^{4,15} naphthol(H₂O)₁ (6-31G** basis),³³ and phenol(H₂O)₂ (6-31G** basis).³⁴ In the case of phenol(CH₃OH)₁, the structures and vibrations of phenol, methanol, and of phenol(CH₃OH)₁ were calculated at the 4-31G* (Ref. 15) and 6-31G** level using the GAUSSIAN 92 program. For the fully optimized minimum energy structures normal coordinate calculations were carried out. The vibrational eigenvalues were calculated using force constants taken from the analytical second derivatives of the SCF potential energy surface.

In the minimum energy structure of phenol(CH₃OH)₁ the

hydrogen bonding arrangement is *trans*-linear, as for *p*-cresol(H₂O)₁,³¹ phenol(H₂O)₁,⁴ naphthol(H₂O)₁,³³ and the water dimer.^{35,36} The structural parameters of this cluster calculated at the 4-31G* and 6-31G** level are given in Table III (cf. Fig. 7). The angles Θ_1 , Δ , φ , Θ_2 obtained for the two basis sets are nearly identical, the angle β differs only by 2.2° and the O···O distance calculated at the 4-31G* level is only 0.014 Å shorter than the corresponding distance calculated at the 6-31G** level. These results are similar to those obtained for the phenol(H₂O)₁ cluster using the 4-31G* and 6-31G** basis sets.¹⁵

The HF stabilization energy, calculated as the difference between the total SCF energy of the Ph(CH₃OH)₁ cluster and the corresponding energy (D_e) of the fully optimized structures of phenol and methanol is 2547 cm⁻¹ (30.5 kJ/mol, 6-31G** basis set). The stabilization energy including zero-point vibrational energy contributions (D_0) is 2094 cm⁻¹ (25.1 kJ/mol). The ZPE energy contribution was calculated

TABLE II. Ground state (S_0) vibrational frequencies and intensities of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁.

<i>h</i> -Phenol(CH ₃ OH) ₁ Rel. freq. (cm ⁻¹) ^b	Rel. Int.	Possible assignment ^a	<i>d</i> -Phenol(CD ₃ OD) ₁ Rel. freq. (cm ⁻¹) ^b	Rel. Int.	Possible assignment ^a
0(35 933)	1	0,0	0(35 951)	1	0,0
22	0.21	1	22	0.15	1
35	0.20	2	33	0.14	2
55	0.04	3	42	0.03	3
65	0.05	4	64	0.02	4
91	0.02	5	90	0.02	5
162	0.14	6	155	0.07	6
181	0.03	1+6	175	0.01	1+6
195	0.02	2+6	186	0.01	2+6
318	0.01	6+6	306	0.01	6+6
431	0.01	ν_{18b}	414	0.01	ν_{18b}
463	0.01	6+6+6	462	0.01	6+6+6
538	0.46	ν_{6a}	533	0.31	ν_{6a}
561	0.10	$\nu_{6a}+1$	556	0.06	$\nu_{6a}+1$
573	0.08	$\nu_{6a}+2$	569	0.05	$\nu_{6a}+2$
630	0.02	ν_{6b}			

^aThe full assignment will be given in Sec. III D by comparison with calculated frequencies.

^bError in band positions ± 2 cm⁻¹.

using the unscaled harmonic vibrational frequencies of methanol, phenol, and the Ph(methanol) cluster. If the correlation energy contribution calculated at the MP2/6-31G** level (at HF optimized geometries of phenol, methanol, and

Ph(methanol) is taken into account the stabilization energy increases by 855 cm⁻¹. In order to estimate the basis set superposition error (BSSE) the full counterpoise procedure of Boys and Bernardi was applied.³⁷ The calculated total BSSE [BSSE(HF)=453 cm⁻¹; BSSE(MP2)=453 cm⁻¹] and the MP2 correlation contribution (855 cm⁻¹) are of the same order, as in the case of the Ph(H₂O) cluster. Taking MP2 and BSSE contributions into account stabilization energies of 2495 cm⁻¹ (D_e) and 2042 cm⁻¹ (D_0) are obtained. The stabilization energy D_0 is 189 cm⁻¹ higher than the corresponding value of Ph(H₂O)₁ calculated at the same level of theory.³³ This result is reasonable, since methanol acts as a stronger H-bonding acceptor molecule than the water molecule due to the inductive effect of the methyl group.

The six intermolecular vibrations, which arise from the complexation of phenol and methanol, are shown in Fig. 8.

In the case of the phenol(H₂O) and naphthol(H₂O) cluster, the σ and β_2 vibrations of the deuterated clusters^{4,33} show a

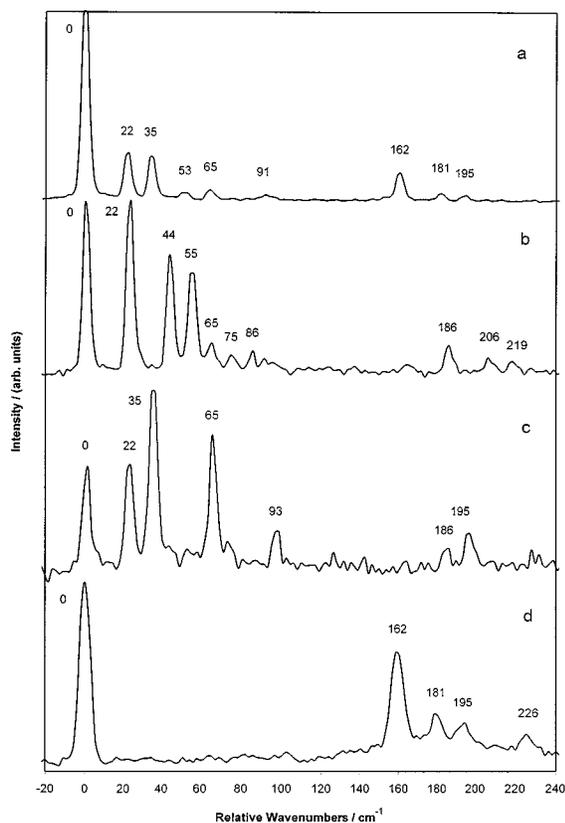


FIG. 6. (a)–(d) Fluorescence emission spectra of *h*-phenol(CH₃OH)₁, obtained by pumping the electronic origin (a) and the intermolecular vibrations at 27 cm⁻¹ (b), 31 cm⁻¹ (c), and 176 cm⁻¹ (d). The absolute frequency scales are shifted to show the concerned 0→1 transition at the same frequency. Spectral resolution is 3 cm⁻¹.

TABLE III. Structural parameters of uncomplexed phenol and methanol and *h*-phenol(CH₃OH)₁ computed with the 4-31G* and the 6-31G** basis sets.

	<i>h</i> -Phenol(CH ₃ OH) ₁ 4-31G*	<i>h</i> -Phenol(CH ₃ OH) ₁ 6-31G**	Phenol, methanol 6-31G**
r_1 (Å)	1.344	1.344	1.352
r_2 (Å)	0.954	0.949	0.943
R (Å)	2.877	2.891	...
r_3 (Å)	1.407	1.407	1.398
r_4 (Å)	0.948	0.942	0.947
θ_1 (deg)	111.33	111.64	110.93
Δ (deg)	117.75	117.71	117.43
φ (deg)	3.03	3.50	...
β (deg)	140.97	143.2	...
θ_2 (deg)	110.11	110.36	105.97
A (MHz)	3810.0	3785.7	...
B (MHz)	6953.5	691.3	...
C (MHz)	608.9	605.9	...

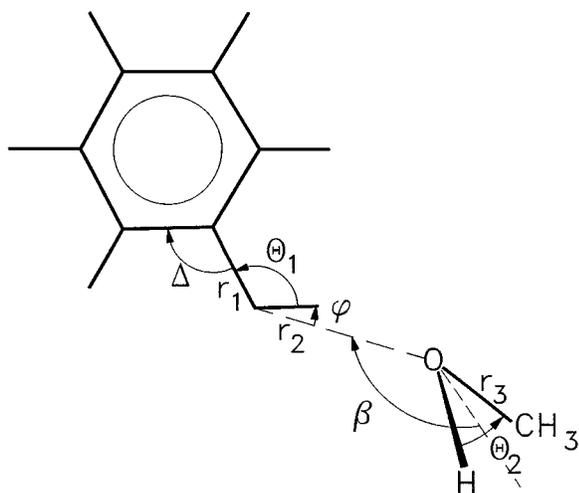


FIG. 7. Calculated geometry and structural parameters of the phenol(CH₃OH)₁ cluster.

strong mode mixing. Concerning the phenol(methanol) cluster no mode mixing occurs due to deuteration. The unscaled intermolecular frequencies of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁ calculated at the 4-31G* and 6-31G** level are listed in Table IV. The corresponding frequencies obtained for the two basis sets differ by less than 5%. The same result was obtained for the frequencies of the normal vibrations of phenol(H₂O)₁ using the 4-31G* and 6-31G** basis sets. These results and the agreement of calculated and experimental frequencies support the reliability of the performed HF *ab initio* calculations.

An assignment of the intermolecular vibrations can be achieved, if we compare these vibrations with the translational and rotational motions of the free methanol. The first three vibrations listed in Table IV correlate with the rotations of the free methanol along the *c*, *b*, and *a* axis of inertia, respectively.

According to the nomenclature of Schütz *et al.*⁴ these

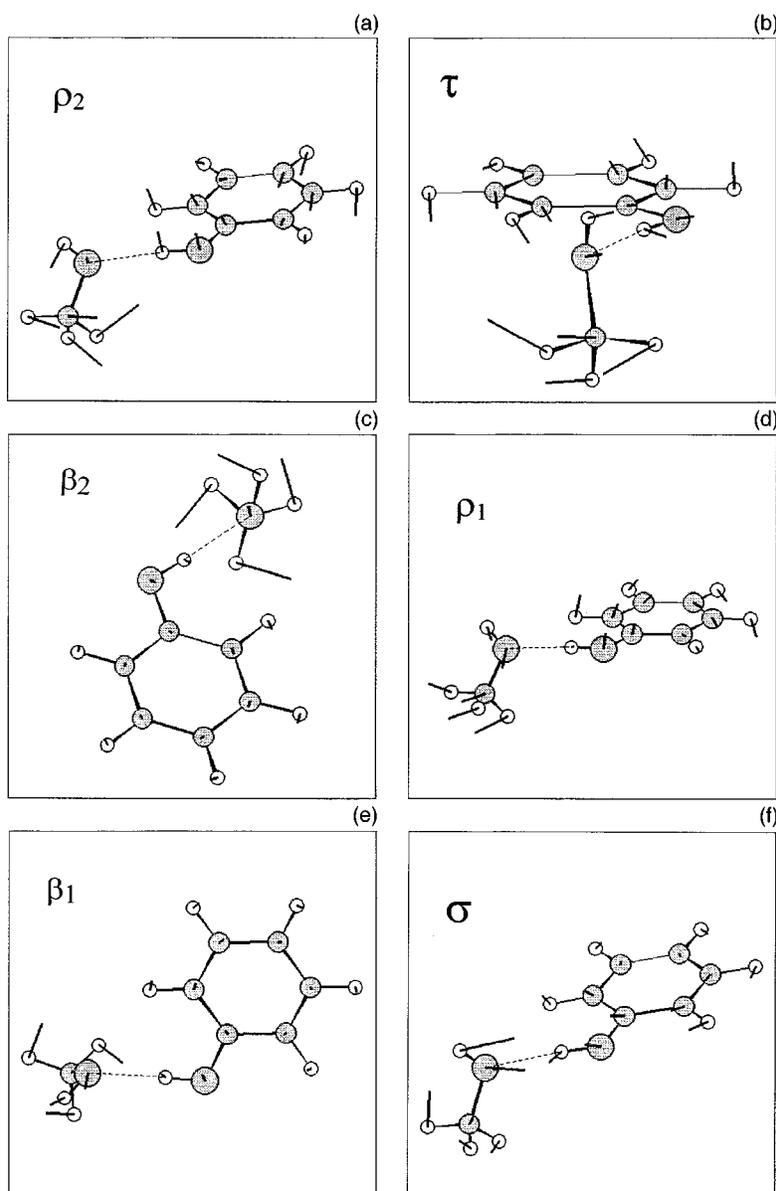


FIG. 8. Intermolecular vibrations of the the phenol(CH₃OH)₁ cluster.

TABLE IV. Computed vibrational frequencies, force constants, and reduced masses for the intermolecular vibrations of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁.

Cluster/ assignment	Frequency (cm ⁻¹) 4-31G*	Frequency (cm ⁻¹) 6-31G**	Force constant (N m)	Reduced mass (amu)
<i>h</i> -phenol(CH ₃ OH) ₁				
ρ_2	17.4	17.3	0.05	3.17
τ	30.7	30.2	0.17	3.11
β_2	56.7	54.6	0.24	1.34
ρ_1	71.6	70.3	1.34	4.62
β_1	94.8	90.4	1.09	2.21
σ	165.0	158.1	7.35	4.99
<i>d</i> -phenol(CD ₃ OD) ₁				
ρ_2	15.8	15.8	0.06	3.93
τ	28.1	27.8	0.17	3.78
β_2	43.0	41.4	0.23	2.24
ρ_1	68.5	67.1	1.44	5.43
β_1	84.0	80.8	1.69	4.38
σ	156.3	149.7	7.48	5.66

vibrations are assigned to the ρ_2 , τ , β_2 mode (rocking, torsion, and wagging mode). The stretching vibration σ and the β_1 and ρ_1 mode correspond to the translations in x , y , and z direction of the free methanol (x direction: direction of the O···O bond; z direction: perpendicular to the phenol ring; y direction: perpendicular to x and z direction). In the case of normal modes with low vibrational eigenvalues and low reduced masses, it is necessary to describe vibrational transitions using large vibrational amplitudes, i.e., large elongations relative to the equilibrium bond length and angles. Anharmonic corrections have to be taken into account in this case. Because of the low reduced mass of the β_2 mode a harmonic description of this vibration may be inappropriate. However, previous calculations on the anharmonicity of the β_2 mode have not shown any significant shift.¹⁵ If we consider that in the case of *d*-phenol(CD₃OD)₁ only the β_2 mode shows a significant shift due to deuteration (24%), the assignment of this vibration seems to be unambiguous, cf.

TABLE V. Comparison of experimental S_0 and S_1 vibrational frequencies with the results of *ab initio* calculations for *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁.

<i>h</i> -Phenol(CH ₃ OH) ₁				
Assignment	4-31 G*	6-31 G*	Expt. S_0	Expt. S_1
0_0^0	0	0	0	0
ρ_2	17.4	17.3	22	27
τ	30.7	30.2	35	31
β_2	56.7	54.6	55	45
ρ_1	71.6	70.3	65	47
β_1	94.8	90.4	91	96
σ	165.0	158.1	162	176
<i>d</i> -Phenol(CD ₃ OD) ₁				
0_0^0	0	0	0	0
ρ_2	15.8	15.8	22	27
τ	28.1	27.8	33	31
β_2	43.0	41.4	42	42
ρ_1	68.5	67.1	64	62
β_1	84.0	80.8	90	100
σ	156.3	149.7	155	168

Table VI. Due to the large reduced masses of the σ and ρ_1 mode, harmonic descriptions of these vibrations should be appropriate. Further, the frequencies predicted for the ρ_2 , τ , and β_1 vibrations are probably of the correct magnitude. A more detailed description and discussion of the intermolecular and intramolecular vibrations is given elsewhere.¹⁵

IV. DISCUSSION

An assignment of all experimental intermolecular vibrations in the S_0 state on the basis of these computational and experimental results is now straightforward. We assign the bands at 22, 35, 55, 65, 91, and 162 cm⁻¹ in *h*-phenol(CH₃OH)₁ and at 22, 33, 42, 64, 90, and 155 cm⁻¹ in *d*-phenol(CD₃OD)₁ to the six fundamental vibrations in the S_0 state. All other bands can be attributed to combination bands of these vibrations (Table II). The experimental S_0 values are in good agreement with the calculated ones. The deviation is smaller than 5% in the case of the 4-31G* and the 6-31G** basis, cf. Table V. The only band which has a large isotopic shift (0.75 calculated with 4-31G*) is the wagging vibration β_2 , in good agreement with the experimental value of 0.78, cf. Table VI. The assignment of the 55 cm⁻¹ band (S_0) to the wagging vibration β_2 is thus secured by two facts: The good coincidence between experimental and computational results, and the agreement between measured and calculated isotopic ratios.

TABLE VI. Isotope ratios of the intermolecular vibrations of *h*-phenol(CH₃OH)₁ and *d*-phenol(CD₃OD)₁.

S_0 D/H (cm ⁻¹)	D/H Expt.	D/H calculated ^a
22/22	1	0.94
33/35	0.94	0.90
42/55	0.76	0.75
64/65	0.98	0.95
90/91	0.98	0.92
155/162	0.95	0.94

^aFor details see Sec. III D.

When exciting the 27 cm⁻¹ (*S*₁) band, a strong, quite harmonic progression with 22 cm⁻¹ is found in the dispersed fluorescence spectrum. The band at 27 cm⁻¹ in the fluorescence excitation spectrum therefore corresponds to the ground state rocking vibration ρ_2 . A strong progression with slight anharmonicity is found at 35 cm⁻¹ when the 31 cm⁻¹ *S*₁ band is excited. This shows that the band at 31 cm⁻¹ in the *S*₁ state belongs to the torsional motion τ in the *S*₀ ground state.

The corresponding *S*₀ frequency of the stretching vibration at 162 cm⁻¹ is increased to 176 cm⁻¹ in the *S*₁ state, indicating an increase in hydrogen bond strength upon electronic excitation in the same order of magnitude as in the Phenol/water cluster.

The assignment of the remaining *S*₁ frequencies is not as clear yet. A quick comparison of *S*₀ and *S*₁ frequencies would give rise to the assumption, that the 55 cm⁻¹ band in the electronic ground state corresponds to 45 cm⁻¹ in the electronically excited state, 65 to 70 cm⁻¹ and 91 to 96 cm⁻¹ (assignment 1).

This assignment however does not explain the appearance of the two bands at 45 and 47 cm⁻¹ in Fig. 2. These bands cannot be explained as combination bands or overtones, and have therefore been assigned as fundamental vibrations by Wright *et al.*¹⁰ If the vibrational frequencies in the *S*₁ state keep at least the same order as in the electronic ground state, the 45 cm⁻¹ band corresponds to the β_2 vibration and 47 cm⁻¹ to ρ_1 . The band at 55 cm⁻¹ was assigned to the fifth intermolecular vibration in Ref. 10. The calculated value for this vibration is 94.8 cm⁻¹ in the *S*₀ state, while the experimental *S*₀ frequency is 91 cm⁻¹. A deviation of 36 cm⁻¹ between the *S*₀ and *S*₁ state seems very unreasonable, because this would demand a large geometry change upon electronic excitation in merely *one* vibrational coordinate. The assignment of the 55 cm⁻¹ band to the combination of the ρ_2 (27 cm⁻¹) and τ (31 cm⁻¹) vibrations seems more reliable.

Thus the transition at 96 cm⁻¹ can tentatively be assigned to the remaining intermolecular vibration β_1 . The bands at 55, 70, 74, 120, and 202 cm⁻¹ are described as combinations of the strong ρ_2 transition at 27 cm⁻¹ with all other intermolecular vibrations. The bands at 54 and 80 cm⁻¹ are the first and second overtone of the ρ_2 vibration in assignment 2, which is shown in Tables I and V.

On the other hand a decrease in vibrational frequency of 18 cm⁻¹ for the ρ_1 vibration is quite large and can hardly be explained by geometry changes upon electronic excitation. To the contrary the vibration of the deuterated cluster does not show a comparable shift after electronic excitation.

Additionally the frequency of the ρ_1 vibration in the *S*₁ state of *d*-phenol(CD₃OD)₁ is considerably larger than in the nondeuterated species, which is unreasonable. There are no problems with assignment 1 in this regard. Hence the assignment of the β_2 and ρ_1 vibrations in the *S*₁ state of *h*-phenol(CH₃OH)₁ still remains an open question.

V. CONCLUSIONS

In the present work REMPI, SHB, and dispersed fluorescence spectroscopy of *h*-phenol(CH₃OH)₁ and

d-phenol(CD₃OD)₁ was performed in the range 0–250 cm⁻¹ on the blue side of the electronic origin of the respective cluster. The intermolecular frequencies obtained from the measurements were compared with the results from *ab initio* based normal mode analysis. An unambiguous assignment of the low frequency transitions to distinct intermolecular vibrations of the cluster can only be given if the existence of transitions, belonging to another species, can be ruled out. Hole burning spectroscopy shows, that in the investigated spectral region no other conformer of the phenol(CH₃OH)₁ cluster absorbs. A straightforward assignment of the *S*₀ intermolecular bands of both clusters could therefore be given with the help of *ab initio* based normal mode calculations, isotopic substitution, and good quality dispersed emission spectra from state selectively excited clusters.

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