

# Vibrational study of the $S_0$ and $S_1$ states of 2-naphthyl-1-ethanol/(water)<sub>2</sub> and 2-naphthyl-1-ethanol/(methanol)<sub>2</sub> complexes by IR/UV double resonance spectroscopy†

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2-naphthyl-1-ethanol/(water)<sub>2</sub> and 2-naphthyl-1-ethanol/(methanol)<sub>2</sub> complexes have been formed in a supersonic expansion and studied by laser induced fluorescence (LIF) and IR/UV double resonance spectroscopy in the region of the O–H stretch. Comparison of the measured frequencies with DFT calculations has led to the attribution of the observed 2-naphthyl-1-ethanol/(water)<sub>2</sub> and 2-naphthyl-1-ethanol/(methanol)<sub>2</sub> complexes to bridged structures. In these structures the solvent dimer is inserted in between the OH group of the chromophore which acts as a hydrogen bond donor, and the electron  $\pi$  system of the aromatic ring. Electronic excitation results in a red shift of all the  $\nu_{OH}$  stretch frequencies.

## Introduction

Solvation of aromatic molecules by water and small size alcohols has recently received much experimental and theoretical attention.<sup>1,2</sup> Spectroscopic studies of gas phase clusters provide a particularly fruitful tool to study the nature of the molecular interactions at play in solvated molecular systems such as van der Waals forces and H bonding. Since the frequencies of the OH or NH stretching modes, together with the breadth and the intensity of the associated transitions, are strongly affected by hydrogen bond formation, IR spectroscopy has been used widely for characterising *intra*- and *intermolecular* hydrogen bonding. Among the most popular systems investigated so far are on the one hand the gas phase benzene/(water)<sub>*n*</sub><sup>3,4</sup> or benzene/(methanol)<sub>*n*</sub><sup>5,6</sup> clusters, where the  $\pi$  electron system provides a template on which the water and methanol aggregates are attached, and on the other hand the phenol/water or phenol/methanol clusters,<sup>7–10</sup> where the acidic OH group of phenol acts as the main binding site for protic solvents.

Aryl alcohols are intermediate chromophores, which possess two different sites of interaction with protic solvents, and their complexes with water or simple alcohols have also been investigated extensively by IR fluorescence or ion dip spectroscopy in the region of the hydride stretch.<sup>11–13</sup> In these molecules the alcoholic OH group can act as a H-bond donor while the aromatic ring provides an acceptor site where a weak OH $\cdots\pi$  interaction can take place. This structural property favours the building of H-bonded networks which involve cooperative effects. The most simple model species for the study of this kind of interaction are benzyl alcohol and its hydrated clusters, which have been studied by the groups of Mikami<sup>11</sup> and Simons<sup>12</sup>. The 1:1 and 1:2 water complexes of 2-phenyl-1-ethanol<sup>14</sup> and 1-phenyl-ethanol<sup>13</sup> have also been investigated for comparison. The IR spectra show that these

systems exhibit very similar fingerprints and reveal the presence of an OH $\cdots\pi$  interaction between the solvent and the aromatic ring. These findings have been rationalised with the help of *ab initio* calculations in terms of bridged structures where the solvent monomers or dimers connect the two sites of the molecule.

We have reported recently the analogous formation of hydrogen-bonded bridges in jet-cooled complexes of the chiral chromophore 2-naphthyl-1-ethanol (NapOH) with methanol.<sup>15</sup> Two isomers of 2-naphthyl-1-ethanol have been characterised together with their associated 1:1 and 1:2 methanol complexes both by LIF excitation and IR-UV dip spectroscopy. The structures of the observed complexes have been assigned on the basis of comparison with DFT(B3LYP) calculations. In the present work we have carried out a similar fluorescence dip study of the water complexes formed with NapOH and compared them with the methanol complexes. Since the monohydrate was not observed experimentally, we concentrate on the 1:2 water and methanol complexes. The IR spectra have also been obtained for the first electronically excited state with the aim of exploring the effect of electronic excitation on the structure of these clusters.

## Methods

### Experimental

The systems under study are formed in a supersonic expansion of helium (2–3 atm). The flow of helium saturated with solvent vapours (water at room temperature and methanol at about 243 K) reaches the oven (363 K) containing the chromophore just prior to the expansion.

The excitation laser is a frequency-doubled dye laser pumped by the second harmonic of a YAG laser (Quanta-Ray). A photomultiplier (Hamamatsu R2059) equipped with a WG320 cut-off filter detects the fluorescence at right angle of the excitation laser and of the molecular beam. The fluorescence excitation spectra are obtained by gating and averaging the signal through a Lecroy 9400 oscilloscope connected to a PC.

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The set-up used for the IR/UV double resonance experiments combines a pulsed jet (General Valve) and two OPOs (BBO for the visible, and LiNbO<sub>3</sub> for the infrared).

The OPO system consists of an original prototype first developed at the Centre Laser Infrarouge d'Orsay (CLIO) and rests on two OPOs synchronously pumped by a pulsed mode-locked Nd:YAG laser (BM Industrie), as described elsewhere.<sup>16</sup> The YAG oscillator is fitted with an intra-cavity non-linear absorber in order to generate trains of 500 ns length (macropulses) consisting of 50 micropulses, at a repetition rate of 20 Hz. The micropulses duration and separation are 12 ps and 10 ns, respectively. The resulting 1.064  $\mu\text{m}$  beam (output power 1.5 W) is split by a beam splitter. Two thirds of the beam are converted to a 355 nm beam which is used to pump the BBO crystal. The signal of the visible OPO is continuously tunable from 440 nm to 700 nm and has a bandwidth of 3  $\text{cm}^{-1}$ . Its output power is about 15 mW at 630 nm. The LiNbO<sub>3</sub>-based OPO is pumped by the remainder of the 1.064  $\mu\text{m}$  beam (500 mW). The idler is tunable from 2.6 to 4  $\mu\text{m}$ . It has a bandwidth of 3  $\text{cm}^{-1}$  (FWHM) and a power of 25 mW at 3  $\mu\text{m}$ .

The IR spectra are recorded with the fluorescence dip technique, a variant of the double resonance technique pioneered by Lee and co-workers<sup>17</sup> and developed by Riehn *et al.*,<sup>18</sup> Tanabe *et al.*,<sup>8</sup> and Pribble *et al.*<sup>3</sup> The fluorescence signal used to monitor the infrared absorption is averaged over the whole macropulse.

Because of the OPO's temporal characteristics, no exact synchronisation between the IR and UV micropulses is required for measuring depletion of species in S<sub>0</sub> or in long lived S<sub>1</sub> states ( $\sim 50$  ns and more). Indeed, each of the 50 micropulses of the IR train reaches S<sub>0</sub> species which can be probed by any of the subsequent UV micropulses before being repopulated. Similarly, an appreciable fraction of a long-lived S<sub>1</sub> population created by a given UV micropulse will survive long enough, before disappearing by energy relaxation processes, to absorb one of the subsequent IR micropulses. The observed spectrum is thereby the superposition of the S<sub>0</sub> and S<sub>1</sub> vibrational spectra. It is however possible to unravel the contributions of S<sub>0</sub> from those of S<sub>1</sub> by setting the IR laser upstream (S<sub>0</sub> spectrum) or downstream (S<sub>1</sub> spectrum) from the UV laser as demonstrated in earlier studies.<sup>19,20</sup>

The 2-naphthyl-1-ethanol (NapOH) chromophore in its pure enantiomeric *R* or *S* forms has been purchased from Aldrich and used without further purification.

## Theoretical

Calculations have been carried out to assist in the analysis of the spectra. They combine a global exploration of a semi empirical potential-energy surface, in which the intramolecular coordinates are kept frozen, and a full *ab initio* geometry optimisation.

Firstly, the interaction energy is described in the framework of the exchange perturbation theory, as a sum of terms analytically written as a function of the intermolecular coordinates.<sup>21,22</sup> The resulting potential-energy surface is explored by simulated annealing,<sup>23,24</sup> followed by a local quasi Newton method. This method has been used widely to calculate the interaction energies in van der Waals complexes.<sup>15,25,26</sup>

The minima obtained thereby serve as starting points for a full optimisation. The geometries and normal-mode vibrational frequencies of the clusters are calculated using the DFT method. The DFT calculations employ the B3LYP functional which has proved to provide a good description of hydrogen-bonded clusters, and the standard 6-31G\*\* basis set. The harmonic vibrational frequencies and IR intensities are calculated using the optimised structures of both the NapOH clusters and (water)<sub>2</sub> or (methanol)<sub>2</sub> fragments of the clusters, for the sake of comparison. The basis set superposition error

(BSSE) is accounted for with the aid of the counterpoise correction of Boys and Bernardi<sup>27</sup> and the zero point energy is included in the binding energy.

The calculations are carried out using the Gaussian98 package.<sup>28</sup>

## Experimental results

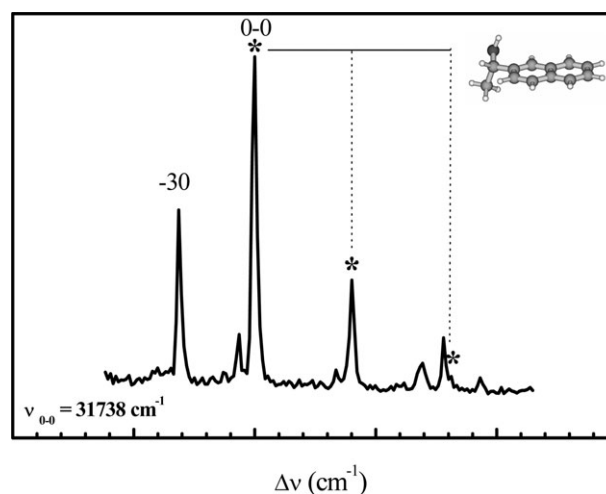
### Electronic spectroscopy

**NapOH/W<sub>2</sub> complex.** Fig. 1 displays the fluorescence excitation spectrum of the NapOH/water (denoted W afterwards) mixture in the region of the 0–0 transition of the chromophore. In the presence of water in the helium flow, a strong red-shifted band appears at  $-30$   $\text{cm}^{-1}$  from the 0–0 transition of the chromophore. The band intensity exhibits a quadratic dependence on the water partial pressure. It has thus been assigned to a complex between NapOH and two molecules of water. A weaker band appears on the low energy wing of the origin band ( $-10$   $\text{cm}^{-1}$ ). This feature may be due to a 1:1 complex. However because of its low intensity the corresponding species has not been investigated further.

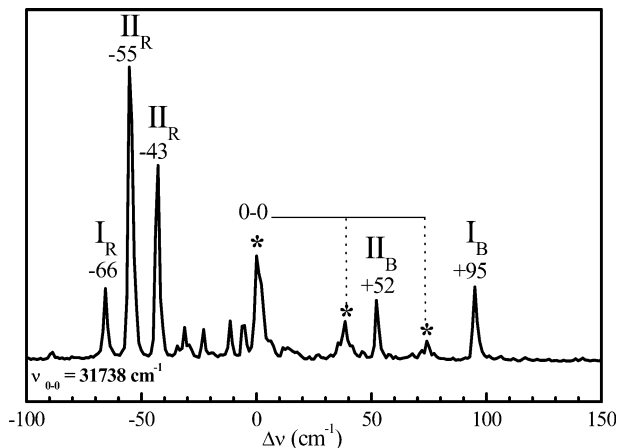
**NapOH/(MeOH)<sub>(n=1,2)</sub> complexes.** The excitation spectrum of the NapOH/methanol (noted MeOH afterwards) complexes has been reported already<sup>15</sup> and is shown in Fig. 2. It exhibits a more complicated pattern than that of the water complex. The main new features appearing on both sides of the NapOH origin transition have been assigned previously on the basis of IR-UV double resonance spectroscopy to two isomeric 1:1 complexes named I<sub>R</sub> at  $-66$   $\text{cm}^{-1}$  and I<sub>B</sub> at  $+95$   $\text{cm}^{-1}$  and to two isomeric 1:2 complexes named II<sub>R</sub> ( $-55$   $\text{cm}^{-1}$  and  $-43$   $\text{cm}^{-1}$ ) and II<sub>B</sub> ( $+52$   $\text{cm}^{-1}$ ). The R and B letters are used to indicate that the corresponding features are shifted to the red and to the blue relative to the main 0–0 transition of the bare molecule, respectively.

### Vibrational spectroscopy

**NapOH/W<sub>2</sub> complex.** The three vibrational spectra, shown in Fig. 3, are obtained for the fluorescence probe set on the NapOH/W<sub>2</sub> band at  $-30$   $\text{cm}^{-1}$  from the transition origin of NapOH and for different relative positions of the IR laser relative to the UV beam. Trace (a) has been obtained when the IR and UV beams are spatially overlapped. The spectrum

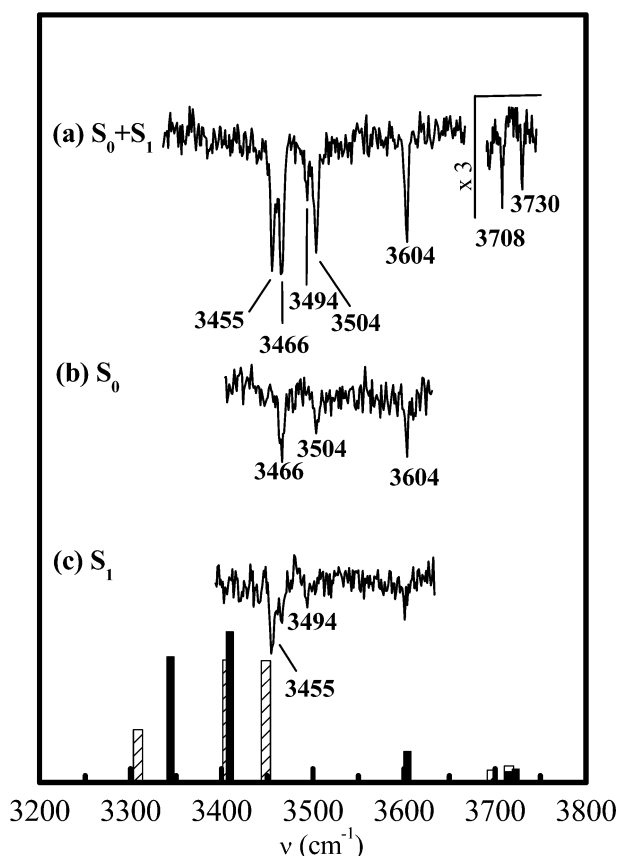


**Fig. 1** LIF excitation spectrum of jet-cooled 2-naphthyl-1-ethanol in the presence of water in the origin region of the S<sub>0</sub>–S<sub>1</sub> transition of NapOH. The energy scale is taken with respect to the 0–0 transition of the chromophore at 31738  $\text{cm}^{-1}$ . The bands due to the bare molecule are labelled with an asterisk. The bare chromophore structure is shown as an insert.



**Fig. 2** LIF excitation spectrum of jet-cooled 2-naphthyl-1-ethanol and its clusters with methanol in the origin region of the  $S_0$ - $S_1$  transition of NapOH.<sup>15</sup> The energy scale is taken with respect to the 0-0 transition of the bare chromophore at 31738  $\text{cm}^{-1}$ . The bands due to the bare molecule are labelled with an asterisk. The bands labelled  $I_R$ ,  $I_B$ ,  $II_R$  and  $II_B$  have been assigned previously to the 1:1 and 1:2 complexes built from the two isomeric forms of NapOH.

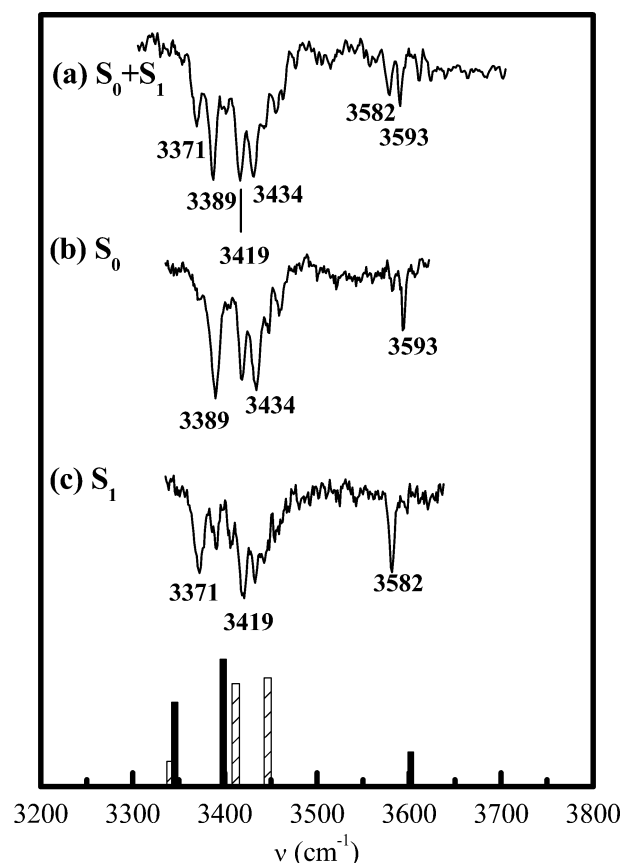
shows three single features at 3604, 3708 and 3730  $\text{cm}^{-1}$  and exhibits in its low-energy region, two doublet structures at 3455/3466, 3494/3504  $\text{cm}^{-1}$ . The spectrum of trace (b) is obtained when the IR beam is shifted upstream from the UV probe, a



**Fig. 3** IR absorption spectra of the NapOH/water 1:2 complex measured by fluorescence dip IR/UV double resonance techniques. The UV probe is fixed on the band at  $-30 \text{ cm}^{-1}$  from the 0-0 transition of NapOH. The  $S_0$  and  $S_1$  IR spectra are resolved by adjusting spatially the relative position of the beams in the interaction zone of the jet. (a) IR and UV beams are superimposed; (b) UV beam is shifted upstream from IR; (c) IR beam is set upstream from UV; the stick diagram shows the computed spectra (DFT B3LYP/6-31G\*\*) obtained by applying a scaling factor of 0.96 to the calculated harmonic frequencies /// for the bridged structure and — for the cyclic one.

scheme which selects the ground state vibrations. It displays three bands appearing at 3466, 3504 and 3604  $\text{cm}^{-1}$ . The total number of ground state  $\nu(\text{OH})$ , including the two OH bands in the 3700  $\text{cm}^{-1}$  region, is five, which supports the attribution of this complex to a 1:2 adduct. Trace (c) is obtained for the opposite configuration of IR and UV beams: the previous bands vanish and the 3455 and 3494  $\text{cm}^{-1}$  remaining bands are thus assigned to vibrations in the  $S_1$  state. Because of their low oscillator strength, the free OH can not be observed when the two lasers are not properly superimposed.

**NapOH/(MeOH)<sub>2</sub> complex.** The vibrational spectra of NapOH/(MeOH)<sub>2</sub> obtained for the probe set on the strong excitation feature at  $-55 \text{ cm}^{-1}$  from the 0-0 transition of the chromophore ( $II_R$ ) are shown in Fig. 4. Trace (a) is obtained for UV and IR beams superimposed and has been reported in a previous paper.<sup>15</sup> As it was mentioned before, each vibrational transition is split into doublets located at 3371/3389  $\text{cm}^{-1}$ , 3419/3434  $\text{cm}^{-1}$  and 3582/3593  $\text{cm}^{-1}$ . The modification of the relative position of the pump and probe beams allows us to lift the ambiguity as to the nature of the observed doublets. When the IR beam is moved upstream from the UV one, three bands (3389, 3434 and 3593  $\text{cm}^{-1}$ ) are predominant as shown in trace (b) and therefore assigned to  $S_0$  vibrations. The opposite effect is observed when the IR beam is shifted downstream from the UV beam (see trace (c)). The three  $S_0$  bands vanish and the three remaining bands at 3371, 3419 and 3582  $\text{cm}^{-1}$  are assigned to  $S_1$  vibrations.



**Fig. 4** IR absorption spectra of the NapOH/methanol 1:2 complex measured by fluorescence dip IR/UV double resonance techniques. The UV probe is fixed on the band  $II_R$  at  $-55 \text{ cm}^{-1}$  from the 0-0 transition of NapOH. The  $S_0$  and  $S_1$  IR spectra are resolved by adjusting spatially the relative position of the beams in the interaction zone of the jet. (a) IR and UV beams are superimposed; (b) UV beam is shifted upstream from IR; (c) IR beam is set upstream from UV; the stick diagram shows the computed spectra (DFT B3LYP/6-31G\*\*) obtained by applying a scaling factor of 0.96 to the calculated harmonic frequencies /// for the bridged structure — and for the cyclic one.

### Theoretical results and assignment of the observed frequencies

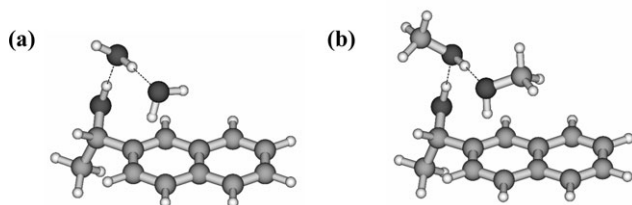
**Isolated subunits.** As described in a previous paper, the NapOH chromophore exists in two isomeric forms.<sup>15</sup> In the present calculations only the form assigned to the most fluorescent species has been considered. The  $\nu_{\text{OH}}$  stretch of NapOH has been calculated at  $3802\text{ cm}^{-1}$  and measured at  $3647\text{ cm}^{-1}$ . In the following, a scaling factor of 0.96 has been applied uniformly to the calculated frequencies. This factor puts into line the experimental and computed frequencies of the bare NapOH  $\nu(\text{OH})$  stretch. Hence the scaled values will appear italicised in brackets in what follows. For the sake of comparison with the OH frequencies in the complexes, the frequencies and intensities of the  $\nu_{\text{OH}}$  stretches of water, methanol,  $\text{W}_2$  and  $(\text{MeOH})_2$  calculated at the same level of theory are also listed in Table 1 together with the experimental data. Both water and methanol dimers consist of a H-donor molecule ( $\text{W}_\text{D}$ ,  $\text{MeOH}_\text{D}$ ) and a H-acceptor part ( $\text{W}_\text{A}$ ,  $\text{MeOH}_\text{A}$ ). The  $\nu_{\text{OH}}$  located on the donor part appear at  $3601\text{ cm}^{-1}$ <sup>29</sup> and  $3574\text{ cm}^{-1}$ ,<sup>30</sup> they are computed at  $3691$  ( $3543$ ) and  $3674$  ( $3527$ )  $\text{cm}^{-1}$  for water and methanol dimers respectively. The  $\text{W}_\text{D}$  moiety shows a free OH at  $3735\text{ cm}^{-1}$  (calculated at  $3880$  ( $3724$ )  $\text{cm}^{-1}$ ) while the  $\text{W}_\text{A}$  part displays two coupled motions which may be correlated

with the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_3$ ) OH stretching modes of the water monomer. The antisymmetric ( $\nu_3$ ) mode has been observed at  $3745\text{ cm}^{-1}$  and the symmetric mode has been estimated at  $3660\text{ cm}^{-1}$  (the computed values are respectively  $3899$  ( $3743$ ) and  $3792$  ( $3640$ )  $\text{cm}^{-1}$ ).

**NapOH complexes.** It has been shown previously that two types of structures, a cyclic and a bridged structure, are expected for complexes formed between an arylalcohol such as benzyl alcohol or 1-phenylethanol and two molecules of water or methanol.<sup>11,13</sup> These structures are also found in the calculated NapOH/ $\text{W}_2$  and NapOH/ $(\text{MeOH})_2$  complexes. The cyclic structure is similar to the free water or methanol trimers.<sup>3,31</sup> The NapOH chromophore and each water or methanol molecule act both as H-bond donor and acceptor and form a three-membered  $\text{OH}\cdots\text{O}$  hydrogen bonded cycle. In the bridged form (Fig. 5), the OH of the chromophore establishes a H bond towards the oxygen of the donor part of the solvent dimer, while its acceptor part interacts with the aromatic cycle through an  $\text{OH}\cdots\pi$  hydrogen bond. In both the cyclic and bridged structures involving the water dimer, two OH groups located on  $\text{W}_\text{D}$  and  $\text{W}_\text{A}$  remain free. As obtained

**Table 1** Experimental and calculated  $\nu_{\text{OH}}$  frequencies and related shifts (in  $\text{cm}^{-1}$ )

Species	Observed $\nu_{\text{OH}}$	Observed shift	Theoretical $\nu_{\text{OH}}$	Theoretical shift	Observed $\nu_{\text{OH}}$ in $\text{S}_1$	Assignment	
W	3652		3801			$\nu_1$ O–H s	
	3756		3915			$\nu_3$ O–H as	
MeOH	3681		3823				
$\text{W}_2$	3601		3691			bonded O–H ( $\text{W}_\text{D}$ )	
	3660		3792			$\nu_1$ free O–H s ( $\text{W}_\text{A}$ )	
	3735		3880			free O–H ( $\text{W}_\text{D}$ )	
	3745		3899			$\nu_3$ free O–H as ( $\text{W}_\text{A}$ )	
$(\text{MeOH})_2$	3574		3674			$\text{MeOH}_\text{D}$	
	3684		3817			$\text{MeOH}_\text{A}$	
NapG1	3647		3802				
Bridged NapOH/ $\text{W}_2$	<b>3466</b>	–181	3483	–319	3455	O–H <sub>NapOH</sub>	} coupled
	<b>3504</b>	–97	3551	–140	3494	O–H ( $\text{W}_\text{D}$ )	
	<b>3604</b>	–56	3754	–38		O–H $\cdots\pi$ ( $\text{W}_\text{A}$ )	} coupled
	<b>3708</b>	–37	3869	–30		Free O–H ( $\text{W}_\text{A}$ )	
	<b>3730</b>	–5	3878	–2		Free O–H ( $\text{W}_\text{D}$ )	
Cyclic NapOH/ $\text{W}_2$	3466	–181	3446	–356	3455	O–H <sub>NapOH</sub>	} coupled
	3504	–156	3548	–244	3494	O–H ( $\text{W}_\text{A}$ )	
	3604	3	3592	–99		O–H ( $\text{W}_\text{D}$ )	} coupled
	3708	–27	3851	–29		Free O–H ( $\text{W}_\text{D}$ )	
	3730	–15	3870	–29		Free O–H ( $\text{W}_\text{A}$ )	
Bridged NapOH/ $(\text{MeOH})_2$ <sup>15</sup>	<b>3389</b>	–258	3485	–317	3371	O–H <sub>NapOH</sub>	} coupled
	<b>3434</b>	–140	3540	–134	3419	O–H( $\text{MeOH}_\text{D}$ )	
	<b>3593</b>	–91	3752	–65	3582	O–H( $\text{MeOH}_\text{A}$ )	
Cyclic NapOH( $\text{MeOH})_2$ <sup>15</sup>	3389	–258	3480	–322	3371	O–H <sub>NapOH</sub>	} coupled
	3434	–250	3554	–263	3419	O–H( $\text{MeOH}_\text{D}$ )	
	3593	19	3590	–84	3582	O–H( $\text{MeOH}_\text{A}$ )	
Bridged PetOH/ $\text{W}_2$ <sup>13</sup>	3458	–189	3475	–327		O–H <sub>PetOH</sub>	} coupled
	3499	–102	3546	–145		O–H ( $\text{W}_\text{D}$ )	
	3594	–66	3757	–35		O–H $\cdots\pi$ ( $\text{W}_\text{A}$ )	} coupled
	3706	–39	3864	–35		Free O–H ( $\text{W}_\text{A}$ )	
	3724	–11	3873	–7		Free O–H ( $\text{W}_\text{D}$ )	
Bridged PetOH/ $(\text{MeOH})_2$ <sup>36</sup>	3376	–271				O–H <sub>PetOH</sub>	} coupled
	3422	–152				O–H( $\text{MeOH}_\text{D}$ )	
	3583	–101				O–H( $\text{MeOH}_\text{A}$ )	



**Fig. 5** Optimised calculated structures of the (a) NapOH/W<sub>2</sub> and (b) NapOH/(MeOH)<sub>2</sub> clusters showing the bridged geometry of the hydrogen bonded chain.

for NapOH/(MeOH)<sub>2</sub>, the binding energy of NapOH/W<sub>2</sub> (corrected for BSSE and including ZPE) is slightly larger for the bridge (10.7 kcal mol<sup>-1</sup>) than for the cycle (9.9 kcal mol<sup>-1</sup>).

The bridged structure can be easily distinguished from the cyclic structure by the presence of a moderately shifted  $\nu_{\text{OH}}$  corresponding to the OH $\cdots\pi$  interaction, in addition to the more shifted OH $\cdots\text{O}$  bands in the 3400–3500 cm<sup>-1</sup> range. As described previously, the NapOH/(MeOH)<sub>2</sub> spectrum displays a strong feature around 3600 cm<sup>-1</sup> which is a clear signature of the bridged structure. The NapOH/W<sub>2</sub> complex exhibits a very similar pattern and can be assigned also to a bridged geometry. This qualitative deduction is corroborated by harmonic frequencies calculations.

**NapOH/W<sub>2</sub>.** The calculated harmonic frequencies are reported in Table 1 and the IR calculated spectrum is shown in Fig. 3 as a stick diagram.

When the scaling factor is taken into account, the calculated free (OH) stretching modes of water (3878 (3723) and 3869 (3714) cm<sup>-1</sup>) are in excellent agreement with the observed values (3730 and 3708 cm<sup>-1</sup>). Moreover, the DFT calculations predict that these two free OH stretching modes are of comparable weak intensity, which is experimentally observed. The  $\pi$ -hydrogen-bonded OH stretch also appears at very similar frequencies in the simulated (3754 (3604) cm<sup>-1</sup>) and experimental spectra (3604 cm<sup>-1</sup>). Again, a frequency assigned to a  $\pi$ -hydrogen-bonded OH stretch leaves no doubt as to the assignment of the observed complex to a bridged complex, as it is not predicted to appear in the spectrum of the cyclic cluster. More discrepancy is observed in the low-energy region of the spectra. The two transitions occurring in this region correspond to the coupled motion of two hydroxy groups engaged in the OH<sub>NapOH</sub> $\cdots$ W<sub>D</sub> and OH<sub>W<sub>D</sub></sub> $\cdots$ W<sub>A</sub> intermolecular H-bonds. They clearly occur at lower frequencies in the simulated spectrum (3551 (3409) and 3483 (3344) cm<sup>-1</sup>) than in the experimental ones (3504 and 3466 cm<sup>-1</sup>). Such a discrepancy is often observed in hydrated clusters,<sup>13,16,32</sup> and persists with more sophisticated calculations. The calculated frequency shifts for the H-bonded OH stretch vibrations is overestimated in benzene/W<sub>3</sub> even at the MP2 level.<sup>4</sup> Similarly, the calculated free OH stretch of the 2-amino-pyridine dihydrate occurs about 60 cm<sup>-1</sup> higher in energy than the experimental value, while the bonded OH group occurs about 40 cm<sup>-1</sup> lower in energy than the experimental value: also in this case, it would not be possible to put into line the experimental and computed free OH stretch vibrations, and the bonded ones, with the same scaling factor.<sup>32</sup> Such a difference probably arises from the anharmonicity of the potential-energy surface, which must be very important in these strongly bonded and coupled systems.

**NapOH/(MeOH)<sub>2</sub>.** As already discussed in a previous article, the NapOH/(MeOH)<sub>2</sub> II<sub>R</sub> complex has also been attributed to the most stable bridged structure.<sup>15</sup> The calculated harmonic frequencies are reported in Table 1 and the IR calculated spectrum is also shown in Fig. 3. The 3485 (3346) cm<sup>-1</sup> and 3540 (3398) cm<sup>-1</sup> calculated frequencies correspond to the

coupled stretches of the hydroxy groups involved in the OH<sub>NapOH</sub> $\cdots$ O<sub>MeOHD</sub> and OH<sub>MeOHD</sub> $\cdots$ O<sub>MeOHA</sub> intermolecular bonds. The highest calculated frequency at 3752 (3602) cm<sup>-1</sup> corresponds to the O–H stretch of the methanol molecule in interaction with the naphthalene ring of the chromophore (OH $\cdots\pi$  interaction). The associated experimental  $\nu_{\text{OH}}$  stretch has been observed at 3593 cm<sup>-1</sup>.

## Discussion

The clusters formed between NapOH and two molecules of water and methanol exhibit a strong structural similarity in their H bonds arrangement. In both cases the solvent dimer is inserted between the OH donating group of the chromophore and the  $\pi$  electron system of the aromatic ring. The comparison between these two systems and other related clusters with similar structures will be examined in the following discussion.

### Comparison between NapOH/W<sub>2</sub> and NapOH/(MeOH)<sub>2</sub>

First we can compare the shifts induced by complexation on the vibrational OH stretches of each of the building entities of the clusters *i.e.* the NapOH chromophore and the water and methanol dimers respectively. Concerning the OH $\cdots\text{O}$  interactions, it has been mentioned before that the donor hydroxy groups of NapOH and W<sub>D</sub> or MeOH<sub>D</sub> are coupled in a kind of “in phase” and “out of phase” motions which are associated with the two lowest calculated  $\nu_{\text{OH}}$  frequencies. However these modes are not totally mixed and the lowest frequency mode has a larger contribution from the NapOH and the other one is more localised on the W<sub>D</sub> or MeOH<sub>D</sub> moiety. Consequently the shifts used further on are given with respect to values in isolated entities: NapOH and W<sub>2</sub> or (MeOH)<sub>2</sub>.

The frequency of the  $\nu_{\text{OH}}$  mode localised on the NapOH chromophore is red shifted by 181 cm<sup>-1</sup> and 258 cm<sup>-1</sup> for the hydrated and methanol clusters while those located on the W<sub>D</sub> and MeOH<sub>D</sub> parts of the solvent dimer are red shifted respectively by 97 cm<sup>-1</sup> and 140 cm<sup>-1</sup>. The moderate shifts of the OH stretches localised on the acceptor part of the water dimer (–56 cm<sup>-1</sup>) and of the methanol dimer (–91 cm<sup>-1</sup>) are associated with OH $\cdots\pi$  bonds. The free OH stretch of the W<sub>A</sub> part undergoes also a red shift of 37 cm<sup>-1</sup> with respect to the  $\nu_3$  value of the free water dimer. As mentioned before, this effect reflects the coupling between the two OH stretching motions localised on the W<sub>A</sub> subunit. Concerning the free OH stretch of the W<sub>D</sub> part in the water dimer, almost no perturbation due to complexation is observed: the experimental frequency is red shifted by 5 cm<sup>-1</sup> in the complex (3730 cm<sup>-1</sup>) when compared to the analogue mode in the isolated water dimer (3735 cm<sup>-1</sup>). From these comparisons several conclusions can be drawn:

First, complexation of NapOH with two molecules of water or methanol induces a large strengthening of the *intra*-solvent dimer hydrogen bond. This cooperative effect manifests itself by the significant red shift of the  $\nu_{\text{OH}}$  assigned to the *intra* dimer OH $\cdots\text{O}$  bond. It is striking to notice that for the NapOH/(MeOH)<sub>2</sub> cluster, this cooperative effect results in a larger shift ( $\Delta\nu = -140$  cm<sup>-1</sup>) than that resulting from the formation of the dimer from the association of two methanol monomers ( $\Delta\nu = -107$  cm<sup>-1</sup>).<sup>30</sup>

Secondly, the red shifts of the O–H frequencies of NapOH/(MeOH)<sub>2</sub> relative to the isolated building entities are larger than those of the hydrated complex. This can be explained by the stronger acidic character of MeOH relative to water and the related larger cooperative effect which takes place in the first system. Indeed, the higher H-bond donating property and the larger H-bond acceptor character of methanol reinforces the hydrogen bond network, which induces a larger frequency red shift of the OH vibrations at play in NapOH/(MeOH)<sub>2</sub> relative to NapOH/W<sub>2</sub>. This difference is also reflected in the

calculated geometry of the two clusters. While the intermolecular distance  $\text{OH}_{\text{D}} \cdots \text{O}_{\text{A}}$  within the solvent dimers is reduced by the same amount (0.13 Å in both systems), the *intra*-dimer  $\angle \text{OH}_{\text{D}} \cdots \text{O}_{\text{A}}$  angle which measures the linearity of the H bond undergoes a different change in the two cases: it opens up from  $160^\circ$  to  $175^\circ$  ( $+15^\circ$ ) in the  $\text{NapOH}/\text{W}_2$  complex and from  $155^\circ$  to  $176^\circ$  ( $+21^\circ$ ) in the  $\text{NapOH}/(\text{MeOH})_2$  complex relative to the isolated dimer. This observation indicates that the solvent dimer geometry is less affected in the case of water than in that of methanol because of weaker interactions and the related smaller cooperative effect.

#### OH $\cdots$ $\pi$ interactions: comparison with aromatic molecule/water or methanol clusters

While both water and methanol tend to form cyclic aggregates when isolated in the gas phase<sup>1</sup> as in rare gas matrices,<sup>33</sup> the solvent clusters behave differently when attached to an aromatic ring. For example, the cyclic geometry of the (water)<sub>3</sub> complex is kept for benzene/W<sub>3</sub> while a  $\pi$  hydrogen-bonded chain like structure is preferred for the benzene/(MeOH)<sub>3</sub> cluster.<sup>34</sup> In the present case, the OH containing flexible side chain of the aromatic chromophore favours the formation of bridged structures, which also involve a chain of three consecutive H bonds both in the case of  $\text{NapOH}/\text{W}_2$  and  $\text{NapOH}/(\text{MeOH})_2$  clusters. It is thus interesting to compare our results on the strength of the OH  $\cdots$   $\pi$  interaction in  $\text{NapOH}/(\text{MeOH})_2$  with those observed in the complexation of a growing number of methanol molecules attached to an aromatic molecule. To our knowledge, no comparative data have been published in the literature for naphthalene as the site of OH  $\cdots$   $\pi$  complexation, but the IR spectra and the corresponding calculations are available for methanol clusters of either benzene or anthracene. When a first methanol molecule is added to the benzene ring, the vibrational frequency shifts by  $-42 \text{ cm}^{-1}$  due to the OH  $\cdots$   $\pi$  interaction. The addition of a second methanol leads to an increase of the shift to  $-76 \text{ cm}^{-1}$  while it amounts to  $-93 \text{ cm}^{-1}$  when the third methanol molecule is added.<sup>6</sup> This last shift is also observed for anthracene/(MeOH)<sub>3</sub><sup>35</sup> and is very close to that observed in  $\text{NapOH}/(\text{MeOH})_2$  that includes also a chain of three OH groups. This comparison indicates that the OH  $\cdots$   $\pi$  hydrogen bond is of similar strength when the methanol cluster is attached to an aromatic ring or in the bridged  $\text{NapOH}/(\text{MeOH})_2$  complex. Therefore, the existence of a covalent link between one of the hydroxy group and the aromatic ring does not seem to influence the OH  $\cdots$   $\pi$  interaction.

#### Comparison between $\text{NapOH}/\text{W}_2$ and $\text{PetOH}/\text{W}_2$

Complexes of 1-phenylethanol (PetOH) with water<sup>13</sup> and methanol<sup>36</sup> have been studied previously. It is interesting to compare the behaviour of the PetOH and NapOH chromophores, which bear the same side chain but differ by the size of their aromatic ring. Both bare PetOH and NapOH display identical O–H stretching frequency:  $\nu_{\text{OH}} = 3647 \text{ cm}^{-1}$  and  $3648 \text{ cm}^{-1}$  in PetOH and NapOH respectively. The experimental OH stretch frequencies of complexes with PetOH and NapOH are compared in Table 1.

The close values of the  $\nu_{\text{OH}}$  frequencies measured for both hydrated NapOH and PetOH confirm that the complexes have the same bridged structure. However the  $\nu_{\text{OH}}$  frequencies in  $\text{PetOH}/\text{W}_2$  are globally more red shifted by a few  $\text{cm}^{-1}$  than in  $\text{NapOH}/\text{W}_2$ . The OH stretch of PetOH is shifted by  $189 \text{ cm}^{-1}$  compared to  $181 \text{ cm}^{-1}$  for NapOH, the OH frequency assigned to the intradimer  $\text{OH}_{\text{WD}} \cdots \text{O}_{\text{WA}}$  hydrogen bond is shifted by  $102 \text{ cm}^{-1}$  ( $97 \text{ cm}^{-1}$  in the case of NapOH), the OH  $\cdots$   $\pi$  interaction results in a red shift of  $66 \text{ cm}^{-1}$  for the associated OH vibration (*vs*  $56 \text{ cm}^{-1}$  in the case of NapOH). Concerning the free OH, that localised on  $\text{W}_{\text{D}}$  presents a shift of  $-39 \text{ cm}^{-1}$

of its vibrational frequency while the last one is red shifted by  $11 \text{ cm}^{-1}$  ( $\Delta\nu = -37$  and  $-5 \text{ cm}^{-1}$  in the  $\text{NapOH}/\text{W}_2$  complex). These results seem to indicate that the interactions governing the formation of the  $\text{PetOH}/\text{W}_2$  complex are slightly stronger than those involved in  $\text{NapOH}/\text{W}_2$  although the differences between IR frequencies are small. This means that the water dimer is more attracted by the benzene ring than by the naphthalene ring. Since the dispersion forces are expected to increase with the size of the aromatic chromophore and thus to be larger for naphthalene, this effect cannot be related to the increased polarisability of naphthalene relative to benzene but is rather explained by the electrostatic interactions which are more localised in the case of small rings due to the limited spatial charge distribution.

The same conclusions can also be drawn when the  $\text{PetOH}/(\text{MeOH})_2$  cluster is considered. The shifts observed for this system are  $-271$ ,  $-152$  and  $-101 \text{ cm}^{-1}$  for the vibration localised on  $\text{PetOH}$ ,  $\text{MeOH}_{\text{D}}$  and  $\text{MeOH}_{\text{A}}$  respectively. In the case of  $\text{NapOH}/(\text{MeOH})_2$  the corresponding values were  $-258$ ,  $-140$  and  $-91 \text{ cm}^{-1}$ . This indicates again that the complex with PetOH is more tightly bound than that with NapOH.

#### OH stretch in the $\text{S}_1$ state

The general trend when going from  $\text{S}_0$  to  $\text{S}_1$  is a small red shift of all the observed OH stretch frequencies as reported in Table 1. In the hydrated complex, the delocalised stretching modes are red shifted by 11 and  $10 \text{ cm}^{-1}$  with respect to the ground-state frequencies. In the  $\text{NapOH}/(\text{MeOH})_2$  complex, larger red shifts have been observed for the delocalised O–H  $\cdots$  O stretching modes (by 18 and  $15 \text{ cm}^{-1}$ ) and a  $11 \text{ cm}^{-1}$  red shift of the OH  $\cdots$   $\pi$  stretch has been measured.

These observations indicate that electronic excitation enhances the hydrogen-bond strength within the hydrogen-bonded chain of the clusters even in the terminal OH  $\cdots$   $\pi$  interaction. The slightly stronger interaction observed in the excited state is in agreement with the red shift of the electronic transition which has been observed for both complexes. Furthermore, it should be mentioned that the small shifts obtained in  $\text{S}_1$  relative to  $\text{S}_0$  show that the complexes under study do not undergo any important modification of their geometry in their excited state. However, a blue shift of the  $\nu_{\text{OH}}$  due to a weakening of the OH  $\cdots$   $\pi$  electrostatic attractive forces in the excited state is usually predicted upon excitation of the aromatic chromophore in  $\pi$  hydrogen bonded clusters.<sup>37</sup> The opposite effect observed in the  $\text{NapOH}/(\text{MeOH})_2$  complex can be related to the balance between dispersive and electrostatic forces which may be in favour of dispersion in the present case. Another explanation may involve cooperative effects along the  $\text{OH}_{\text{NapOH}} \cdots \text{OH}_{\text{MeOH}} \cdots \text{OH}_{\text{MeOHA}} \cdots \pi$  chain which may propagate the enhanced interaction between the terminal  $\text{OH}_{\text{MeOHA}}$  and the aromatic part of the complex and results in the red shifts of the OH stretches in the excited state.

#### Conclusion

In this paper, we have presented a IR/UV double resonance study of the  $\text{NapOH}/(\text{water})_2$  and  $\text{NapOH}/(\text{methanol})_2$  clusters. Comparison of the measured  $\nu_{\text{OH}}$  frequencies with DFT calculations has led to the attribution of the observed species to bridged structures involving the solvent dimer anchored between the OH group of the chromophore which acts as a hydrogen-bond donor and the  $\pi$  electron cloud of the aromatic ring. All the results are in favour of a large implication of cooperative effects in the formation of such complexes and these effects may be even enhanced in the excited state. They depend both on the size of the aromatic ring at play and the acidity of the solvent. Indeed, they are more efficient in the case of PetOH complexed to the methanol dimer than for the

NapOH complexed with the water dimer. It would be interesting to study this system with more acidic alcohols.

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