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Electronic and vibrational spectroscopy of jet-cooled complexes of *o*-cyanophenol

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Abstract

Hydrogen-bonded complexes of *o*-cyanophenol (*o*-CNP) with a series of protic and non-protic solvents have been investigated in supersonic jet by means of laser-induced fluorescence excitation and dispersed emission spectroscopy. All the complexes exhibit a large red shift of the S_0–S_1 transition extending from $-674\,cm^{-1}$ for acetonitrile to $-1321\,cm^{-1}$ for the dimer of methanol. This shift is shown to correlate with the proton affinity of the protic solvents and has been related to the formation of cyclic hydrogen bond networks. For a non-protic solvent such as diethylether, the presence of a strong H bond has been confirmed by the study of the OH stretch using IR–UV double resonance spectroscopy. The low energy intermolecular vibrations observed in the cyclic complexes of *o*-CNP with H_2O and CH_3OH were assigned by comparing the experimental frequencies observed in the S_0 and S_1 states with the results of DFT calculations. The complexes with TEA undergo proton transfer as evidenced from the observation of the fluorescence attributable to the deprotonated form of *o*-CNP.

Keywords: Hydrogen-bonded complexes; Spectroscopy in supersonic jet; Proton transfer

1. Introduction

Because of the presence of the OH group, phenol and its derivatives provide a sensitive probe to study the spectral manifestations of hydrogen bonding on the vibrational and electronic transitions [1]. This property explains the plethora of experimental work performed on the hydrogen-bonded complexes of phenol in molecular beams: the aromatic chromophore permits the use of selective spectroscopic techniques such as fluorescence excitation and emission, resonant two-photon ionisation, zero kinetic energy photoelectron spectroscopy, double resonance UV–UV or IR–UV, etc. which have been extensively applied to characterise jet-cooled clusters of phenol with a large number of small molecules such as water, methanol, ammonia, amines, ethers and carboxylic acids [2–9]. On the other hand, the hydrogen-bonded complexes of phenol can be modelised theoretically by ab initio methods which allow the comparison with experimental data to get a better knowledge of the structure and energetics of hydrogen bonding interactions both in the ground and excited states. Another interest of the spectroscopic study of hydrogen-bonded complexes of phenol rests on its excited state reactivity. Phenol as other hydroxyarenes such as 1- and 2-naphthol are known to undergo a strong increase of their acidity in the excited state and have thus been used as model systems for examining fundamental aspects of photoinduced acid–base reactions. Phenol–ammonia clusters have been in that respect the subject of numerous studies and it has been recently a matter of debate whether H transfer rather than proton transfer takes place from the S_1 state [10].

However, while most of the studies on these hydrogen-bonded complexes have focused until now on the effect of the nature of the solvent, much less attention has been paid to more acidic chromophores as well as to the structure and reactivity of their clusters.

The introduction of an electron withdrawing group such as cyano, NO_2 or sulphonate on the aromatic ring of hydroxyarenes is known to reinforce their acidity both in the ground state and excited states. This property has been used recently to design new compounds named “super” photoacids consisting of 1- and 2-naphthol substituted on the distal ring by one or two CN groups [11]. As a consequence of their strong acidity, the excited state proton transfer (ESPT) from cyanonaphthols to solvents such as alcohols, dimethylformamide and dimethyl sulphoxide was shown to take place in solution as observed from the fluorescence spectra. The behaviour of clusters of the 5-cyano-2-naphthol chromophore

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has also been examined recently in a molecular beam [12]. An efficient ESPT reaction was demonstrated in ammonia and water clusters as was observed in the case of 1-naphthol clusters, but none in the case of methanol and DMSO clusters.

Among the derivatives of phenol, *o*-cyanophenol (*o*-CNP) offers an interesting case, which can be studied both in solution and in the gas phase. First, the ground state gas-phase acidity is larger by 16.2 kcal/mol than that of phenol [13]. The experimental pK_A values show that the three cyanophenols are also more acidic than phenol in solution both in the ground and in the excited state, the *ortho* derivative being the most acidic isomer (p$K_A = 6.97$, p$K_A^* = 0.66$) [14]. Furthermore, both the neutral and anion species emit fluorescence in solution and this property provides a useful diagnostic tool for ESPT reaction. Finally, *o*-CNP bears two neighbouring functional groups which can act as H bond donating and accepting sites and allow the formation of multiple hydrogen bonds with protic solvents or other donor–acceptor molecules.

As an illustration of this property, we have recently carried out a spectroscopic study of jet-cooled *o*-CNP and its 1:1 and 1:2 clusters with water and methanol using laser-induced fluorescence and double UV–IR resonance techniques [15]. As expected because of the stabilising interaction between the OH and CN substituents, only the *cis* conformer of the chromophore has been observed in the jet-cooled conditions. The complexation of *o*-CNP with water and methanol induces both a large red shift of the S_0–S_1 electronic transition and of the ground state OH stretching frequency of *o*-CNP. The IR spectra in the ν(OH) region can be assigned with the help of DFT calculations to a hydrogen-bonded cyclic structure of the complexes and reveal cooperative effects due the multiple H bonds. In the 1:1 complexes, the solvent OH binds as a proton acceptor to the phenol OH and a proton donor to the CN group. The 1:2 complexes involve in a similar way the insertion of the solvent dimer $(\text{water})_2$ or $(\text{methanol})_2$ between the OH and CN substituents of the molecule. No red-shifted fluorescence attributed to the deprotonated form has been evidenced following excitation of any of these clusters.

The scope of this work was to investigate further the isolated complexes of *o*-CNP with various solvents using fluorescence excitation and dispersed emission spectroscopy. Different questions relevant to the microscopic solvation effects were addressed with the aim to compare the properties of *o*-CNP with those of phenol complexes:

- How the presence of proximate donor and acceptor substituents affects the spectroscopic properties of the chromophore when it is complexed with solvents of different nature and polarity (shift of the S_0–S_1 transition, modification of intramolecular vibrational modes)?
- How the cyclic structures found in the previous study on water and methanol complexes manifest themselves in the intermolecular vibrations?
- Finally, what is the effect of the expected enhanced acidity of *o*-CNP relative to phenol and is it possible to observe the proton transfer reaction by detecting the fluorescence attributable to the *o*-cyanophenolate?

2. Methods: experimental and theoretical

The set-up used for fluorescence excitation experiments rests on the laser-induced fluorescence detection of van der Waals complexes formed in a continuous supersonic expansion of helium (2–3 atm) [15]. The complexes are produced from the preheated *o*-CNP sample (60 °C) in the presence of controlled partial vapour pressure of the solvents. They are subsequently excited in the cold region of the jet about 5 mm downstream from the nozzle by means of a frequency-doubled dye laser pumped by the second harmonic of a YAG laser (BM Industrie). The fluorescence is observed at right angle through a WG320 cut-off filter by a Hamamatsu R2059 photomultiplier. The gated and averaged signal is monitored through a PC-controlled Lecroy 9400 oscilloscope.

The IR spectra are recorded with the fluorescence-dip technique, a variante of the double resonance technique pioneered by Riehn et al. [16], Tanabe et al. [17] and Pribble and Zwier [18]. The set-up used for this IR–UV double resonance experiment combines a pulsed jet (general valve) and two 20 Hz OPO lasers (BBO for the visible one, and $LiNbO_3$ for the infrared one).The OPO system consists of an original prototype first developed at the Centre Laser Infrarouge d'Orsay (CLIO) and rests on two OPO lasers synchronously pumped by a pulsed mode-locked Nd:YAG laser, as described elsewhere.

Vibrational analysis has been carried out for the minimised structures of *o*-CNP–water and methanol 1:1 complexes as described in our previous work [15]. We have first combined a model potential with a global optimisation method to explore the intermolecular potential surface by using a semi-empirical method based on the exchange perturbation theory [19]. Then a local optimisation with the DFT method, by means of the Gaussian 98 software package [20], has been performed to determine the fully optimised geometry and the harmonic vibrational frequencies. For the DFT method we have used the combined Becke's three-parameter exchange functional and the gradient-corrected functional of Lee et al. [21] (B3LYP functional) by using the standard cc-pvTZ basis set. The calculated interaction energies and geometries at the B3LYP/cc-pvTZ level are in good agreement with those obtained at the MP2/cc-pvTZ, justifying the use of the DFT method for the systems presented here.

3. Results

3.1. Excitation spectra

The LIF excitation spectra of the bare molecule and its complexes with water and methanol have been reported

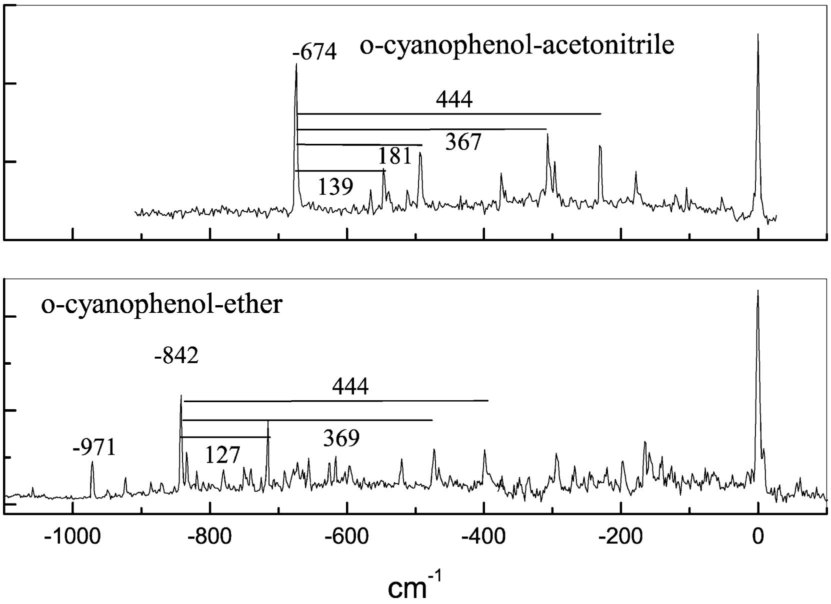

Fig. 1. Fluorescence excitation spectra of *o*-CNP in the presence of CH_3CN and $(C_2H_5)_2O$. The energy scale is relative to the 0–0 transition of the bare chromophore at 33,967 cm^{-1}.

previously [15,22]. The electronic origin of the molecule is located at 33,967 cm^{-1} and the most intense vibronic bands are observed at +129, +370 and +442 cm^{-1} from the 0–0 transition. In the presence of water and methanol, new features corresponding to both the 1:1 and 1:2 complexes have been identified in the spectra. The shifts of the S_0–S_1 transition with respect to the bare molecule are, −787 and −965 cm^{-1}, respectively, for the 1:1 water and methanol complexes and −1071 and −1321 cm^{-1} for the 1:2 clusters. This assignment has been confirmed by IR–UV spectroscopy where the number of observed IR bands in the 3000–3700 cm^{-1} region corresponds to the number of OH oscillators expected for these species.

The excitation spectra obtained with acetonitrile, ether, ammonia, formamide and acetic acid are shown in Figs. 1 and 2 and the shifts of the 0–0 transition are reported in Table 1. All these spectra have in common a large shift extending from −674 cm^{-1} for acetonitrile up to −1321 cm^{-1} for the dimer of methanol. In most of them, the vibronic bands corresponding to the skeletal deformations observed at 370 and 442 cm^{-1} in bare *o*-CNP can be easily recognised. It should be noticed, however, that these features are slightly shifted to higher energy for water, methanol, acetic acid and formamide complexes while they keep the bare molecule value in the case of acetonitrile and diethylether complexes (see Table 2). Based on this vibronic pattern, several origins can be distinguished in some systems: in the complex with diethylether the two bands appearing at −971 and −842 cm^{-1} can be clearly assigned to different origins. The intense band appearing at 129 cm^{-1} for the bare molecule and assigned to the pliers motion of the CN and OH substituents may be still identified in some cases (*o*-CNP–diethylether, *o*-CNP–acetic acid) (see Figs. 1 and 2 and Table 2). Besides the intramolecular deformations of the substituents, several low frequency bands appear in the energy range below 300 cm^{-1} where intermolecular motions are expected for most of the complexes. In the case of the 1:1 water complex, the low frequency vibrational pattern is clearly different from that of the bare molecule. Three main bands are observed at 166, 196 and 206 cm^{-1}. They are shifted by OH/OD isotopic substitution in the *o*-CNPOD–D_2O complex to 117, 181 and 201 cm^{-1}.

3.2. Fluorescence

The dispersed fluorescence resulting from the excitation of the most intense 0–0 transitions of all the complexes

Table 1
Microscopic solvent shifts of the *o*-CNP S_0–S_1 0–0 transition[a]

Solvent	Shift (cm^{-1})	Proton affinity[b] (kJ/mol)	Acidity (kJ/mol)
$(H_2O)_1$	−787	691	1634
$(H_2O)_2$	−1071	815[c]	
$(CH_3OH)_1$	−965	754.3	1597
$(CH_3OH)_2$	−1321	882[c]	
$O(C_2H_5)_2$	−842, −971	828.4	
$HCONH_2$	−1079	822.2	1505
NH_3	−1146, −915	853.6	1691
CH_3CN	−674	779.2	
CH_3COOH	−1129	783.7	1560
(*o*-CNP)$_2$	−1090		1456
TEA		970	

[a] The S_0–S_1 0–0 transition of *o*-CNP is at 33,967 cm^{-1}.

[b] The gas phase proton affinities and acidities are from NIST Web Book.

[c] The proton affinity of water and methanol dimers are those determined by Knockenmuss et al. [36].

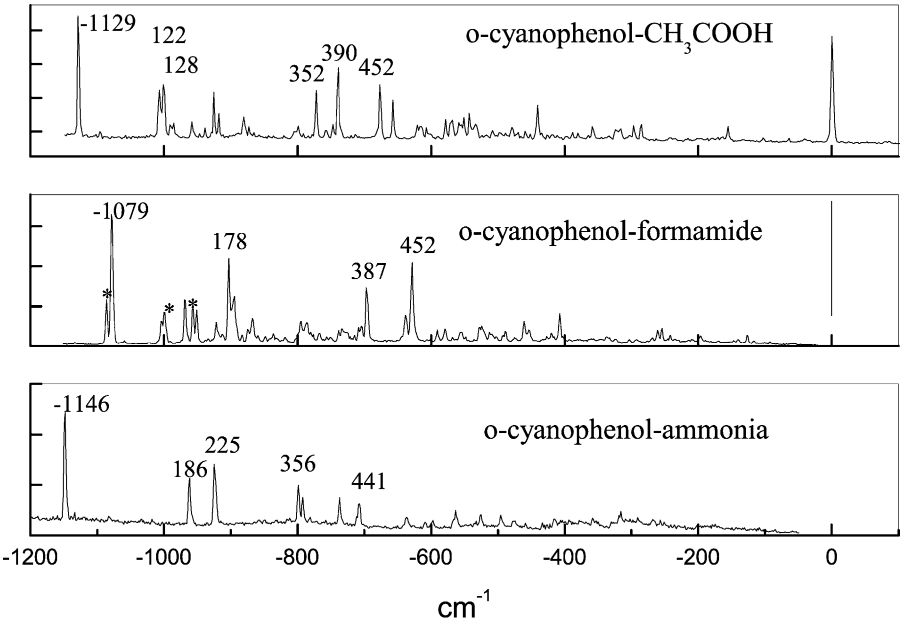

Fig. 2. Fluorescence excitation spectra of *o*-CNP in the presence of CH_3COOH, $HCONH_2$ and NH_3. The energy scale is relative to the 0–0 transition of the bare chromophore. The bands marked with asterisk (∗) in the spectrum of *o*-CNP–formamide complexes correspond to the dimer of *o*-CNP.

is resonant. The emission spectra show above 300 cm^{-1} a global pattern similar to that observed in non-complexed *o*-CNP with the most prominent bands correlating with those found at 382, 462, 853, 1020 and 1316 cm^{-1} for the bare molecule. As typical examples, the dispersed fluorescence obtained by pumping the 0–0 transition of the 1:1 water and CH_3CN complexes are presented in Fig. 3. As observed in the excitation spectra the vibrational pattern below 300 cm^{-1} differs somewhat from that of the bare molecule and depends on the complexing agent. The most active intermolecular frequencies observed in the low frequency region have been listed in Table 2. In the case of the *o*-CNP–water 1:1 complex selective excitation of the three vibronic features at 166, 196 and 206 cm^{-1} has been used to determine their ground state counterparts (observed at 158, 175 and 190 cm^{-1}). It should be noticed that the intermolecular frequencies are larger in

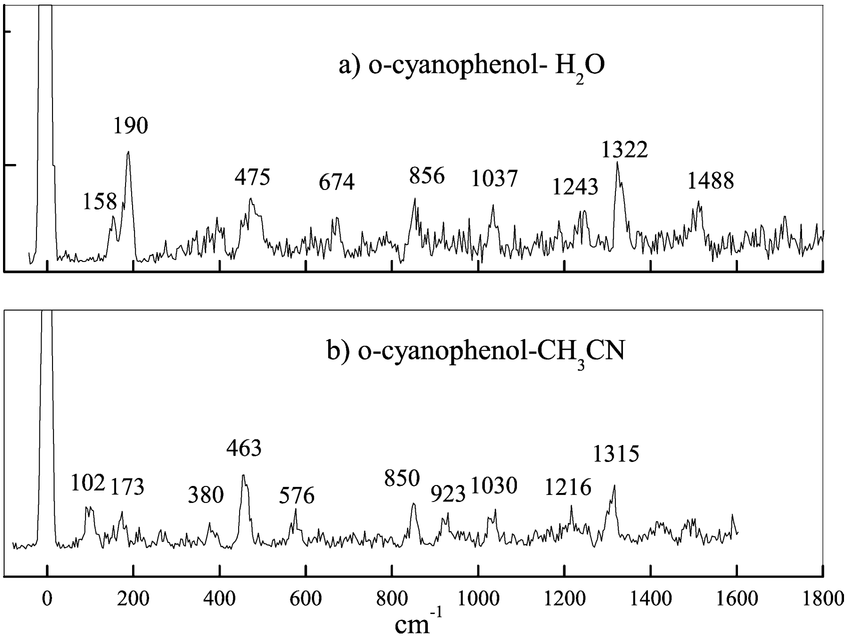

Fig. 3. Dispersed fluorescence spectra from (a) the 1:1 complex of *o*-CNP with water excited at 33,180 cm^{-1} and (b) 1:1 complex of *o*-CNP with CH_3CN excited at 33,293 cm^{-1}. The resolution is ∼25 cm^{-1}.

Table 2
Main vibrations in *o*-CNP complexes

Solvent	S_0	S_1	S_0 (calculated)	
			Cyclic form	Open form
$(H_2O)_1$			139 (sliding)	133
	158	166	219 (τ)	113 (τ)
	175	196	173 (mixed σH-bonds)	
	190	206	201 (mixed σH-bonds)	196 (σ)
	402	387	407 (C–OH bend)	400
	475	453	471	477
$(D_2O)_1$			133 (sliding)	
		117	150 (τ)	
		181	184 (mixed σH-bonds)	
		201	207 (mixed σH-bonds)	
		387	400 (C–OH bend)	
		455	477	
$(H_2O)_2$	157	165	133	
	195		225	
	480		480	
CH_3OH		19	24 (CH_3 rocking)	
	128	105	106 (τ)	
		138	135 (sliding)	
		202	188 ($\sigma OH_{CH_3OH} \cdots NC$)	
	200	225	207 ($\sigma OH_{phenol} \cdots O$)	
		388	408 (C–OH bend)	
		450	476	
CH_3CN	102	127		
	173	180		
	380	367		
	463	444		
$(C_2H_5)_2O$	121	127		
	175			
	392	369		
	478	443		
CH_3COOH		122		
		128		
		390		
		452		
$HCONH_2$		178		
		387		
		458		

the S_1 state than in S_0. This result indicates a tightening of the structures in the excited state.

3.3. IR–UV study of the diethylether complex

The IR–UV dip spectrum of the complexes of *o*-CNP with water and methanol has revealed two types of hydrogen bonds. These results have been interpreted with the help of DFT calculations, in terms of a bridged ground state structure of these species involving both the OH groups of the chromophore and of the solvent. Such a structure cannot take place in the case of diethylether, which bears a single accepting site for complexation with *o*-CNP. In order to characterise the interaction between *o*-CNP and a non-protic solvent, we have thus recorded the IR spectrum in the OH stretch region for the complex of *o*-CNP with diethylether. When the most intense UV transition of the *o*-CNP–diethylether complex is used as a probe, an intense and broad dip at 3155 cm^{-1} (Fig. 4) is observed which can be assigned to the *o*-CNP OH stretch. It is red-shifted by 430 cm^{-1} with respect to the ν(OH) of the *cis* form of the bare chromophore (3585 cm^{-1}). This large shift shows that the *o*-CNP–ether complex is linked through a strong $OH_{o\text{-CNP}}$–$O_{(diethylether)}$ hydrogen bond. The OH frequency of this complex is similar to that observed for the *o*-CNP–CH_3OH 1:1 complex (3165 cm^{-1}).

3.4. Complex with triethylamine in the gas phase

When triethylamine (TEA) is added to *o*-CNP, the shape of the excitation spectrum undergoes a dramatic change. The well-resolved structure observed in the previous cases is replaced by a broad continuum extending over more than 2000 cm^{-1} below the 0–0 transition of the bare chromophore (Fig. 5a). The use of cut-off filters shows that most of the emission is emitted at $\lambda > 345$ nm and is still observed at $\lambda > 375$ nm. The intensity of the emitted fluorescence increases linearly with the partial pressure of TEA. This linear dependence shows that the associated absorption can be attributed to the 1:1 complex. The dispersed fluorescence is also continuous and exhibits a large Stokes shift of about 5000 cm^{-1} with respect to the onset of the excitation (Fig. 5b). It peaks at about 360 nm. This strongly red-shifted emission can be readily assigned to the fluorescence of the anionic form of *o*-CNP by comparison with the spectroscopic data obtained in solution and provides thus evidence for the proton transfer process in the jet-cooled *o*-CNP–TEA 1:1 complex.

3.5. Complexes with TEA in solution

The photophysical behaviour of the *o*-CNP–TEA system in solution is parallel to that observed in the gas phase complex. The first absorption band of *o*-CNP in cyclohexane solution is located between 300 and 280 nm, and the emission spectrum is the mirror image of the absorption. This transition corresponds to the S_0–$S_1(L_b)$ transition. As shown in Fig. 6a, the addition of TEA to the cyclohexane solution induces a significant modification of the absorption spectrum, which is shifted towards the red and presents a tail extending up to 340 nm. This behaviour is characteristic of a ground state equilibrium between the free *o*-CNP and hydrogen-bonded stable complexes. When the excitation is set at 298 nm, two fluorescence bands are observed (Fig. 6b). The band peaking around 310–315 nm is similar to that obtained in the absence of TEA and originates from protonated *o*-CNP, while the second one, peaking at 370 nm, is similar to that observed in alkaline ethanol solutions [23] and is assigned to the deprotonated form. When the excitation wavelength is set either at 310 or 330 nm, only the red fluorescence band appears (Fig. 6d). The fluorescence

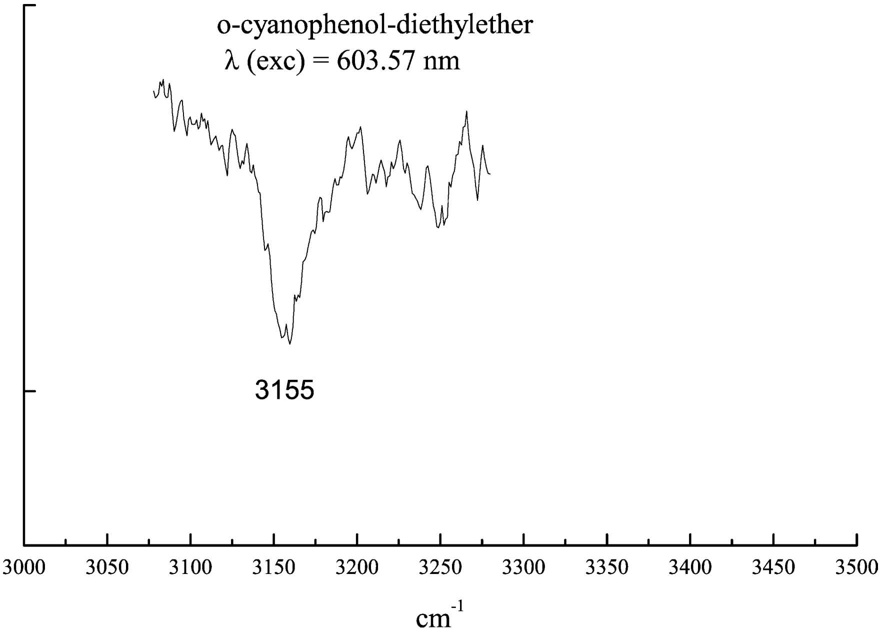

Fig. 4. IR–UV double resonance spectrum of the *o*-CNP–diethylether complex probed at the origin of the S_0–S_1 transition at 33,125 cm^{-1}.

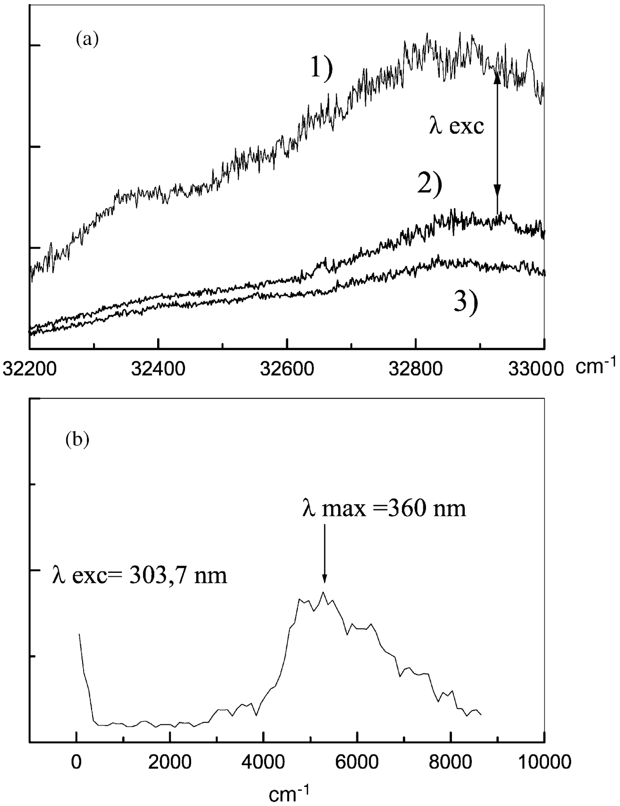

Fig. 5. (a) Fluorescence excitation spectra of jet-cooled *o*-CNP–TEA mixture: (1) fluorescence observed through a WG345 filter, (2) fluorescence observed through a WG375 filter and (3) same as (2) with TEA partial pressure reduced by a factor of 2. (b) Dispersed fluorescence from the *o*-CNP–TEA complex excited at 303.7 nm.

excitation spectra shown in Fig. 6c demonstrate the presence of three absorbing ground state species in the solution. The excitation spectrum of the fluorescence emitted at 310 nm corresponds to the protonated form of *o*-CNP observed in the absence of TEA (maximum at 298 nm). When the fluorescence from the anionic form emitted at 380 nm is detected the excitation spectrum exhibits two excitation bands, the most intense one peaks at 305 nm while the weakest one is maximum around 330 nm and appears as the mirror image of the fluorescence. The relative intensity of the two absorption bands depends on the nature of the solvent. In a solvent of higher polarity than cyclohexane, such as dichloroethane, the absorption band at 330 nm band gets stronger, is slightly shifted to the red and exhibits a similar intensity as the 305 nm band (Fig. 6a). This shows that the two absorption bands responsible for the anionic red fluorescence belong to different ground state species. A similar behaviour has been described in the case of *p*-nitrophenol [24] and has been explained in terms of two equilibria in the ground state involving the neutral hydrogen-bonded species and ionic pair:

$$o\text{-CNP} + \text{TEA} \leftrightarrow o\text{-CNP}\cdots\text{TEA}$$

$$o\text{-CNP}\cdots\text{TEA} \leftrightarrow o\text{-CNPO}^{-}\cdots\text{HTEA}^{+}$$

The 305 nm band can be assigned to the neutral hydrogen-bonded *o*-CNP···TEA species while the second absorption at 330 nm corresponds to the ionic pair *o*-CNPO^{-}···HTEA^{+}, which gets stabilised in a polar medium. The observation of the red-shifted fluorescence from the deprotonated form *o*-CNPO^{-} following excitation either at 330 nm or at 305 nm shows that the proton transfer reaction occurs both in the ground state and in the excited state. This result is in

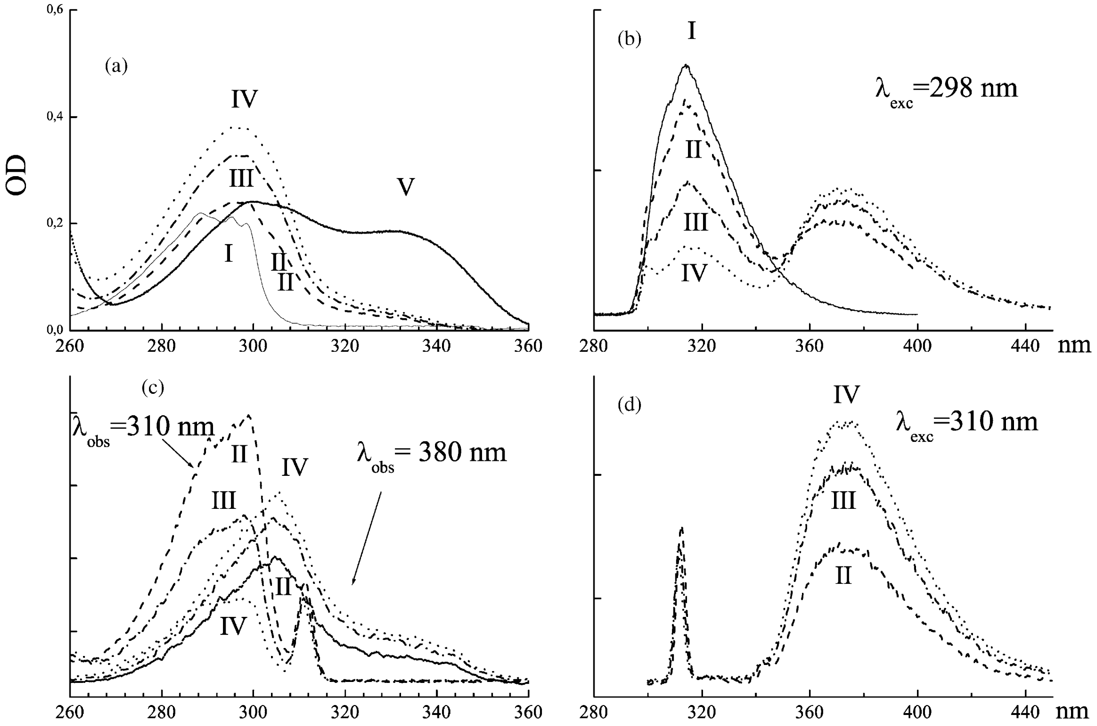

Fig. 6. Solution spectra of *o*-CNP. (a) Absorption of *o*-CNP in cyclohexane ($c = 1.1 \times 10^{-5}$ M/l) in the presence of TEA: (I) $c = 0$, (II) $c = 5 \times 10^{-3}$ M/l, (III) $c = 10^{-2}$ M/l, (IV) $c = 2 \times 10^{-2}$ M/l, (V) in $C_2H_4Cl_2$. (b) Fluorescence spectra of the solutions I, II, III, IV λ(excitation) = 298 nm. (c) Fluorescence excitation spectra (uncorrected) for solutions II, III, IV observed at 310 and 380 nm. (d) Fluorescence spectra of solutions II, III, IV λ(excitation) = 310 nm.

agreement with the significant acidity of *o*-CNP both in S_0 and S_1 as shown by the reported pK_A values [14].

4. Discussion

4.1. Microscopic solvent shift

The most striking effect obtained in this study is the large bathochromic shift of the S_0–S_1 transition of the *o*-CNP chromophore induced by complexation. In the complexes investigated here the shifts are twice as large as those involving the parent phenol molecule (Table 1). This result emphasises the role of the CN substituent in *ortho* position from the acidic OH group in influencing the properties of the phenol chromophore at several levels. First, the cyano substitution increases both the ground state and excited state acidity of phenol because the electron withdrawing CN group helps the delocalisation of the charge away from the oxygen atom in the anion and renders thus the deprotonation reaction more favourable. Second, the CN substituent reinforces the charge transfer character of the intermolecular hydrogen bond between *o*-CNP and electron donors. Third, the presence of adjacent donor and acceptor sites for hydrogen bonding allows the formation of bridged structures.

In a first attempt to rationalise the effect of increasing acidity in the excited state of *o*-CNP, it is interesting to correlate the microscopic solvent shifts with the gas phase proton affinity of the solvent as it has been suggested in the case of hydrogen-bonded phenol and 1-naphthol complexes [5,25]. As shown in Fig. 7, a rather good linear dependence is evidenced for complexes involving protic solvents. However, the experimental data relative to the non-protic compounds (diethylether and acetonitrile) lie out of this curve. Thus according to this behaviour, the solvents can be divided into two groups on the basis of structural considerations: the solvents which are able to act both as proton donor and proton acceptor and thus to form hydrogen-bond bridges with the OH and CN sites of the chromophore exhibit larger shifts than the complexes with solvents bearing a single accepting site which can only involve a single hydrogen bond with the OH group of the chromophore.

In the case of protic solvents, which present both H bond donor and acceptor sites, the “cyclic” structure of the complexes as those demonstrated in the cases of the water and methanol complexes can be responsible for the large microscopic solvent shift [15]. First, a large red shift of the S_0–S_1 transition seems to be a characteristic feature of complexes involving the chelate type structure created by the presence of the two binding sites which is expected to extend the electronic delocalisation. A similar behaviour has been observed in complexes involving chromophores with proximate bonding and accepting sites such as the cyclic 1:2 and 1:3 water complexes of 7-hydroxyquinoline [26,27]. Complexing agents bearing both a H bond donor and acceptor group such

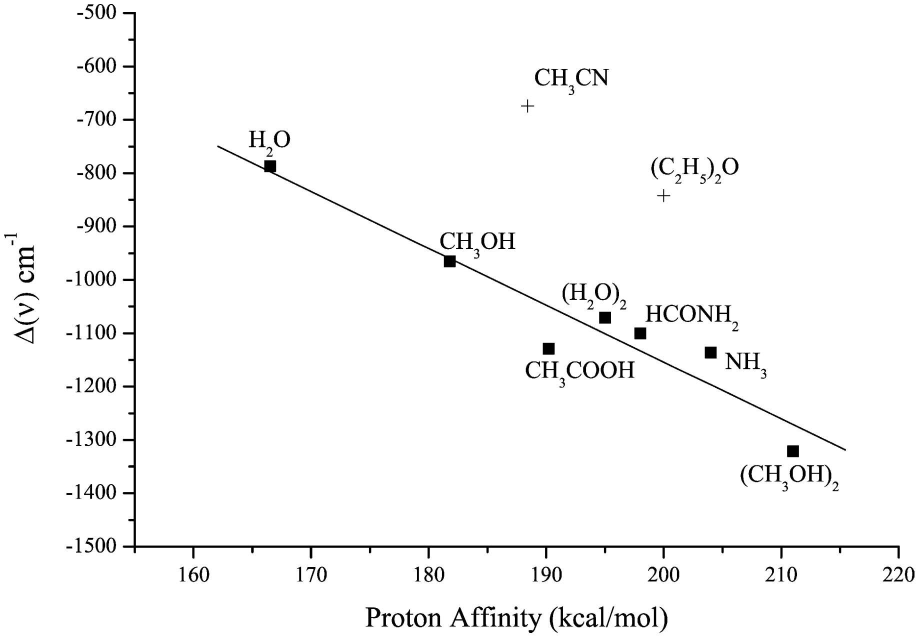

Fig. 7. Spectral red shifts of the S_0–S_1 transition of *o*-CNP complexes as a function of the gas phase proton affinity.

as CH_3COOH and $HCONH_2$ are also able to give rise to cyclic double hydrogen-bonded structures towards the OH and CN groups of *o*-CNP and this would explain the magnitude of the observed shift. Second, cooperativity effects taking place in the double hydrogen-bonded structures reinforce the proton affinity of the solvent-accepting site because of the polarity of the H bond between the solvent and the CN group and this enhanced interaction should manifest itself more significantly in the excited state.

However, the microscopic solvent shifts (842 and 674 cm^{-1}) observed for diethylether and acetonitrile–*o*-CNP complexes are still indicative of a large stabilisation of the excited state with respect to the ground state. For comparison, the shift measured for the phenol–diethylether complex is 431 cm^{-1}. Since no cyclic structure can be formed in these systems, the main interaction of *o*-CNP with these two solvents is expected to be located on the $OH\cdots O_{(diethylether)}$ and $OH\cdots CN_{(acetonitrile)}$ hydrogen bonds. It is thus tempting to attribute the observed red shift mainly to the increase of acidity between S_0 and S_1 state which would be more important in *o*-CNP than in phenol. However, although *o*-CNP exhibits in S_0 and S_1 a larger acidity than phenol, the measured $\Delta pK_A \approx\sim 6$ in water solutions is about the same for *o*-CNP and phenol. In solution, one expects, however, an attenuation of the CN substituent effect because the delocalisation of the negative charge due to the attracting character of the *ortho* CN results in a reduced solvation energy of *o*-cyanophenolate relative to phenolate. The resulting ΔpK_A obtained in solution underestimates the real acidity change in gas phase complexes. Recent ab initio calculations have also concluded to the larger acidity of cyanophenols with respect to phenol [28] but predict that the relative acidity increase between S_1 and S_0 is twice less for *o*-CNP than for phenol. This discrepancy may be due to the fact that the calculations have been performed for the *cis* geometry of *o*-CNP in which the intramolecular hydrogen bond may result in a reduced acidity relative to an open geometry.

The strong red shift of the phenolic ν(OH) stretch of the *o*-CNP–diethylether complex measured by IR–UV dip spectroscopy ($\Delta\nu = -430\,cm^{-1}$) brings an experimental support to the large ground state acidity of *o*-CNP relatively to that of phenol as it has been observed by McMahon and Kebarle [13] and as found in recent calculations [28]. For comparison, the ν(OH) stretch of the phenol–diethylether complex has been determined in solution at 3360 cm^{-1} corresponding to a red shift of 252 cm^{-1} with respect to free phenol ($\nu(OH) = 3612\,cm^{-1}$) [29]. Furthermore, the red shift of the $\nu(OH)_{o\text{-CNP}}$ obtained for the methanol 1:1 complex is close to that of the diethylether-complex indicating a nearly identical hydrogen bond strength in the two species. Since the proton affinity of methanol is significantly lower than that of diethylether (see Table 1), this result illustrates the cooperative effect at play in the bridged structure of the 1:1 methanol complex which enhances the accepting power of the O atom site of CH_3OH.

Another striking point arises from the comparison of the large microscopic solvent shift obtained in the clusters with the relatively small solvatochromism observed in solution [23]. This discrepancy emphasises the fact that the properties of the bulk are strongly different from those of the isolated gas phase and shows that solvation effects should play an important role in determining the solution properties of *o*-CNP. Such a difference between the solvatochromic shifts obtained in pure solvents and in the 1:1 complex has already been observed for 2-naphthol in the presence of protic solvents while non-protic solvents exhibit a similar behaviour in solutions and in the 1:1 complexes [30]. This effect has been explained by the dual role played by the solvent which provides the hydrogen bond accepting site for the acidic chromophore but can act also as a donor to solvate the chromophore via $OH_{solvent}\cdots O_{o\text{-}CNP}$ bonds. This latter interaction induces a blue shift of the S_0–S_1 transition overriding the red shift due to hydrogen bonding from the chromophore to the solvent. A more convincing way to account for the different behaviour between complexes in the gas phase and in solution relies on the solvation effect on the anionic form [13]. As shown by Granucci et al. [28], the anions undergo a larger solvent stabilisation in the ground state than in the excited state resulting in an attenuation of the acidity increase of the protonated form upon excitation, in solution relative to the gas phase. This explanation is valid for protic solvents but may also account for the much larger shift of the S_0–S_1 transition of *o*-CNP observed in isolated hydrogen-bonded complex involving non-protic solvents relative to the bulk solution.

4.2. Low frequency intermolecular vibrations

One of the objectives of this work was to assign the experimentally observed low frequency modes to intermolecular normal modes involving the H bond bridges of the 1:1 water and methanol complexes in order to evidence the spectral manifestations of the cooperative motions between the two partners.

To make such attributions we have compared the ground state and excited state measurements with the harmonic frequencies obtained by DFT B3LYP calculations in the case of 1:1 complexes of *o*-CNP with water and methanol. The eight low frequency normal modes are the composite mixture of the two low intramolecular modes assigned to the out of plane and in plane CN bending vibrations of the bare molecule and the six intermolecular modes originating from the three translations and the three rotations of the free solvent molecules with respect to the chromophore. The results of the calculations are reported in Table 2 for the *cis* *o*-CNP–H_2O, the *cis*-*o*-CNPOD–D_2O, the *cis*-*o*-CNP–CH_3OH and the *trans*-*o*-CNP–H_2O complexes. The representations of the three a' motions involving the deformation of the H bond bridge within the cyclic structure of the 1:1 water complex are also shown in Fig. 8. The vibration found at 139 cm^{-1} for the 1:1 water complex, 133 cm^{-1} for the deuterated species and 135 cm^{-1} for the 1:1 methanol complex involves mainly the relative sliding of the solvent inside the OH and CN pliers of the

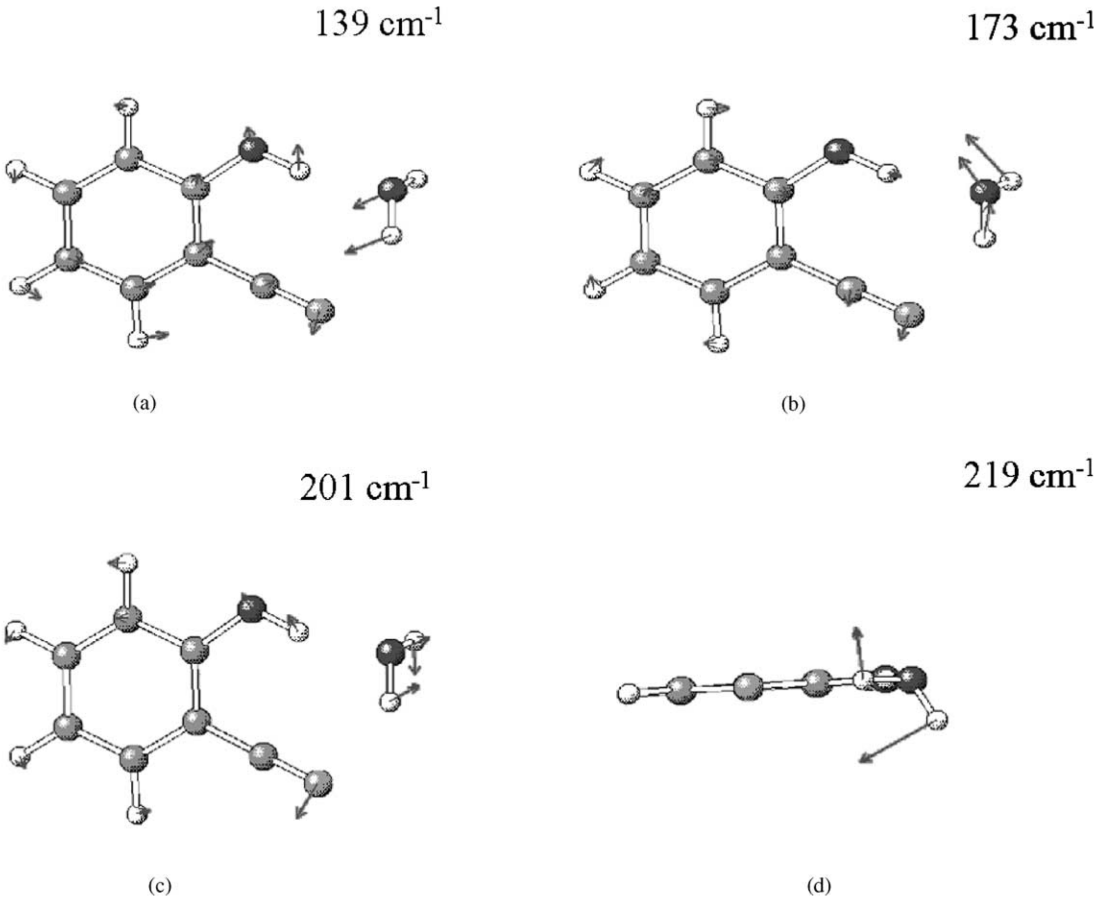

Fig. 8. Intermolecular normal vibrations of *o*-CNP–H_2O 1:1 complex.

o-CNP chromophore. The vibrational mode at 173 cm^{-1} for the monohydrate corresponds also to a translation of H_2O in the plane of the chromophore and can also be represented as a combination of the $OH_{(solvent)}\cdots CN$ and the $OH_{(phenol)}\cdots O$ intermolecular H bond stretches with a minor contribution of the intramolecular CC–N bending. The vibrational mode at 201 cm^{-1} is the major component of the intramolecular CC–N bending and involves also a combination of the two hydrogen bond stretches. The vibrations calculated at 187 and 208 cm^{-1} for the 1:1 methanol complex are more localised than those of the monohydrate and can be assigned dominantly, respectively, to the $OH\cdots CN$ and $OH\cdots O$ stretches. These three modes are not strongly sensitive to the deuteration since their counterparts in *o*-CNP-(OD)–D_2O are found at 133, 184 and 207 cm^{-1}. The most sensitive mode to deuteration in the low frequency region is the out of plane torsion τ of the water molecule with respect to the *o*-CNP plane found at 214 cm^{-1} in the hydrogenated complex and at 150 cm^{-1} in the deuterated one. The most relevant intermolecular vibrations involving the open form of the 1:1 water complex built on the *trans* rotamer of *o*-CNP are also listed in Table 2. The vibrations calculated at 133 and 199 cm^{-1} are assigned to the in plane CC–N bend and the H-bond stretch σ while the torsion τ is at 113 cm^{-1}.

An assignment of the main experimental vibrations can then be proposed on the basis of these computational results according to Table 2. The main bands observed at 175 and 190 cm^{-1} in S_0 (respectively at 196 and 206 cm^{-1} in S_1) in the *o*-CNP monohydrate are assigned to the two coupled in plane stretches of the H bonds in agreement with calculated values at 173 and 201 cm^{-1} (Fig. 8b and c). The assignment of the third most intense vibrational band observed at 158 cm^{-1} in S_0 (166 cm^{-1} in S_1) is more problematic since its experimental value is found higher in energy than the in plane sliding mode calculated at 136 cm^{-1}. Moreover, this vibration is strongly shifted in the excitation spectrum of the deuterated complex (117 cm^{-1}). It must therefore correspond to a hindered rotation. The experimental isotope ratio $\nu_D/\nu_H = 0.70$ is the same as that obtained for the torsion calculated at 219 cm^{-1} (Fig. 8d). However, the experimental frequency is far below the calculated value for this hindered rotation. It has been shown in the case of phenol/H_2O complex that these modes are strongly anharmonic [3] and thus strongly overestimated in the harmonic approximation. A similar explanation should apply here to the 158 cm^{-1} vibration. In the case of the 1:1 methanol complex, an intense low frequency band appears at 210 cm^{-1} in the dispersed emission. It should be assigned to the $OH\cdots O$ stretch calculated at 207 cm^{-1}. In S_1 the 1:1 methanol complex exhibits a much more complex vibrational pattern than the 1:1 water complex due to the presence of the CH_3 group [15]. A tentative attribution of the excited state intermolecular frequencies on the basis of the calculated values is also given in Table 2.

Another point that is worth mentioning concerns the change induced by complexation on the intramolecular modes localised on the CN and OH substituent and particularly the C–OH in plane bending calculated at 392 cm^{-1} and the C–CN bending at 475 cm^{-1}. These two vibrational modes are active both in absorption and emission in the isolated chromophore. While the calculated frequency of the latter mode is not modified by complexation with water and methanol, the C–OH bend frequency undergoes a blue shift of about 18 cm^{-1}. A similar blue shift is observed experimentally in the fluorescence excitation spectra of the complexes involving protic solvents where the band at 370 cm^{-1} is shifted to 387 cm^{-1}.

4.3. Proton transfer reaction

Although the strong hydrogen-bonded systems observed for the *o*-CNP complexes with water and methanol should facilitate the fast proton transfer in the excited state, no evidence was found for any fluorescence attributable to the *o*-cyanophenolate anion. The proton transfer reaction observed in neutral aqueous solution [23] does not occur in small clusters. Proton transfer has also been proved to be hardly observable in water clusters for other hydroxyaromatics such as 1-naphthol [31]. The reason for this discrepancy is still not clear and may rest as suggested by Knochenmuss et al. [31] on dynamic arguments involving solvent motions. Besides, the cyclic structures of the complexes may also explain because of their rigidity the lack of proton transfer. It has to be stressed that, in spite of the strong red shift of their excitation spectra, similar systems involving bifunctional chromophores such as 7-hydroxyquinoline clusters with water and methanol have failed to give rise to the Stokes shifted fluorescence of the tautomeric form observed in condensed phase in the presence of protic solvents [26].

The spectroscopy of the *o*-CNP complex with TEA contrasts strongly with all the other clusters investigated in this study. The excitation of the broad and continuous absorption band leads to the emission of the *o*-cyanophenolate anion. Moreover, the spectroscopic and photophysical properties of the isolated jet-cooled complex reproduces those observed in solution. This system appears to be unique in this regard since no ESPT has been evidenced in the jet-cooled 1:1 complexes of phenol [5], 1-naphthol [25] and 2-naphthol [32] with TEA while it is observed in solution for the two latter compounds [33,34]. Both the enhanced acidity of *o*-CNP in S_0 and in S_1 and the large proton affinity of TEA (232 kcal/mol) [35], which provides a strong accepting base for the acidic proton of the OH group from *o*-CNP are responsible for this behaviour. For comparison, a critical threshold of about 243 kcal/mol was determined for the gas phase proton affinity of the basic partner for the ESPT reaction to take place in the case jet-cooled clusters of 1-naphthol with ammonia or piperidine [36].

The excitation spectra of the *o*-CNP complexes with the solvents used in this study exhibit sharp lines with mirror symmetry relationship to the fluorescence spectra suggesting no strong modification of the geometry of the chromophore upon excitation. This is obviously not the case for the *o*-CNP–TEA complex whose continuous excitation spectrum indicates a dramatic displacement in the equilibrium geometry between S_0 and S_1. Similarly, the occurrence of naphtholate or phenolate type emission appearing for the complexes of 1-naphthol or phenol/$(NH_3)_4$ is accompanied with a sudden broadening of the absorption [5,25]. This behaviour may be interpreted by considering two different hypotheses: either the neutral complex is still the most stable complex in the ground state and the proton transfer takes place without barrier from the initially locally excited $o\text{-CNPOH}^{*}\cdots\text{TEA}$ state to the lowest $o\text{-CNPO}^{-*}\cdots\text{HTEA}^{+}$ ionic pair or the formation of the hydrogen-bonded ion pair $o\text{-CNPO}^{-}\cdots\text{HTEA}^{+}$ has already occurred in the ground state. In the case of the neutral complex, the broadness of the excitation spectrum may be explained by the strong coupling between the two excited species and the high density of states in the excited $o\text{-CNPOH}^{*}\cdots\text{TEA}$ species. In the second hypothesis, the excitation spectrum corresponds to the transition S_0–$S_1(L_a)$ of the hydrogen-bonded *o*-cyanophenolate in the Franck Condon window. Because the negative charge in the anion should be more delocalised in the excited state than in the ground state [28], one can expect a reduced electrostatic interaction along the H bond coordinate. The resulting change of the equilibrium distance between the ionic partners in the ground and excited state would also explain the broadening of the spectrum.

One can have, however, an indication of the feasibility of the proton transfer reaction in the ground and excited states by considering the thermodynamic cycle as suggested first by Chesnovsky [25] in the case of 1-naphthol–$(NH_3)_n$ clustersΔH_{acid} the ionic dissociation enthalpy of the OH bond

$$\begin{tikzcd}
o\text{-CNPOH} + \text{TEA} \arrow[r, "\Delta H_{\text{acid}}"] \arrow[d, "\Delta H_{\text{HB}}"'] & o\text{-CNPO}^{-} + \text{H}^{+} + \text{TEA} \arrow[r, "\text{PA}_{\text{B}}"] & o\text{-CNPO}^{-} + \text{TEAH}^{+} \arrow[d, "\Delta H_{\text{IP}}"] \\
o\text{-CNPOH...TEA} \arrow[rr, "\Delta H_{\text{PT}}"'] & & o\text{-CNPO}^{-}\text{.....}\ \text{TEAH}^{+}
\end{tikzcd}$$

of *o*-CNP has been measured by comparison with phenol $\Delta H_{\text{acid}} = 14.56\,\text{eV}$ [13]. The proton affinity of TEA PA_{B} is 10.16 eV [35]. The interaction energy due to the hydrogen bond in the neutral complex ΔH_{HB} is estimated around 0.3 eV while the stabilisation of the ionic pair ΔH_{IP} can be evaluated by analogy with similar system around 4–4.4 eV. According to these values the enthalpy of the ground state proton transfer ΔH_{PT} should be close to 0 or slightly negative and thus the reaction may take place already in the ground state. The application of the same thermodynamic cycle to the excited reaction shows that the proton transfer should be exothermic by 0.6 eV. Solution data show that the ground state ionic pair is in thermodynamical equilibrium at room temperature even in a non-polar solvent such as cyclohexane with the neutral complex. Both the neutral and ionic pairs give rise to the emission from the deprotonated form upon excitation. The same situation may hold in the isolated complex and explain the shape of the excitation spectrum, which may consist of two overlapping bands originating from both the neutral and ionic complexes in the ground state.

The IR spectrum of *o*-CNP–TEA complex in the region of the OH or NH^{+} stretch would be necessary to investigate in order to get an unambiguous signature between the neutral and ionic ground state structures and pump probe IR–UV experiments are planned in the next future to help to solve this problem. Time resolved experiments would be also useful to evidence the dynamics of the eventual proton transfer in the excited state.

5. Conclusions

We have presented the LIF excitation and dispersed fluorescence spectra for the jet-cooled complexes of *o*-CNP with a variety of solvents. The complexation induces a large bathochromic shift of the S_0–S_1 transition of the chromophore compared to phenol. The observed results can be attributed to the effect of the CN substituent in the *ortho* position from the acidic OH group and can be rationalised in terms of three different types of behaviour:

(1) Protic solvents are expected to give rise to bridge structures connecting the OH and CN groups of the chromophore as previously shown in the case of water and methanol. The cyclic structure of the water and methanol complexes have been confirmed by the study of the low frequency intermolecular vibrations active in the excitation and emission spectra which have been assigned with the help of DFT calculations.

(2) Non-protic solvents bearing a single accepting site such as diethylether and acetonitrile act as weak Lewis bases and form also strong hydrogen-bonded complexes with *o*-CNP as evidenced by the large shift of the phenolic OH stretch in the ground state and that of the S_0–S_1 transition. These results demonstrate the effect of the CN substituent to increase both the ground and excited state acidity of phenol.

(3) Complexes involving a strong base such as TEA lead to the red-shifted emission characteristic of the anionic form in the jet-cooled conditions and in solution. The comparison of the spectroscopic properties of the isolated hydrogen-bonded complexes of *o*-CNP with TEA with the same system in solution show that the proton transfer reaction can take place both in the ground and in the excited state. This system provides thus a unique example to study the mechanism of the acid–base reaction in the isolated gas phase.

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