

Effect of the intermolecular hydrogen bond conformation on the structure and reactivity of the *p*-cresol(H₂O)(NH₃) van der Waals complex

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The structure and reactivity of *p*-CrOH(NH₃)₂ and *p*-CrOH(H₂O)(NH₃) complexes were studied using mass-resolved one-colour resonance-enhanced multi-photon ionization and laser-induced fluorescence (LIF) spectroscopy together with DFT calculations.

At the excitation energy of this work, the S₁ state of *p*-CrOH(NH₃)₂ shows a sub-nanosecond lifetime, as determined by time-resolved LIF spectra, as a consequence of a hydrogen transfer process that results in NH₄(NH₃) as a reaction product.

Substitution of NH₃ by H₂O closes the reaction channel as evidenced by the absence of excited-state hydrogen transfer (ESHT) reaction products, (H₃O(NH₃) or NH₄(H₂O)) and results in a dramatic effect on the S₁ lifetime of the *p*-CrOH(H₂O)(NH₃) complex which rises to (12 ± 2) ns.

According to density functional theory calculations, the most stable isomer of the *p*-CrOH(H₂O)(NH₃) complex is a cyclic structure, in which H₂O acts as the H acceptor of the phenolic OH group (*c*-OH–H₂O–NH₃). However, the ESHT process is energetically disallowed upon electronic excitation.

Introduction

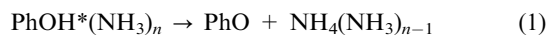
In spite of the very large UV absorption cross-sections of aromatic amino acids like tyrosine, tryptophan and phenylalanine, their fluorescence quantum yields are small, which indicates the presence of efficient non-radiative processes. Phenol (PhOH), which is the chromophore of tyrosine, and its derivatives, such as *p*-cresol (*p*-CrOH), also show similar low fluorescence quantum yields.¹ It is therefore unsurprising that the study of the excited state structure, photophysics and photochemistry of these molecules, as practical models, has attracted the attention of several research groups.^{2,3}

Theoretical and experimental studies suggest that the excited state dynamics of PhOH and *p*-CrOH are governed by a conical intersection (CI) between the ¹ππ* and a ¹πσ* excited state, which is repulsive with respect to the OH bond.^{2–4} Depending on the molecule, the ¹πσ* state can also cross the surface of the ground ¹ππ state, leading to internal conversion (IC).⁴

The fluorescence quantum yield of these molecules is strongly affected by the molecular environment, which makes them ideal candidates to study the effect of the intermolecular interactions on excited state photoinduced processes at a molecular level, using van der Waals complexes.

Hydrogen bonds of the type OH–N, NH–O, OH–O and OH–S are important in many chemical and biological processes, making the excited state dynamics of hydrogen bonded complexes of PhOH or *p*-CrOH with H₂O,^{5–8} NH₃^{9–13} and H₂S⁸ the subject of many studies in the last decade, especially

since the discovery of excited state hydrogen atom transfer (ESHT) in PhOH(NH₃)_{*n*} complexes:^{10,12}



The effect of CH₃ substitution on this process shows contradictory results. While the photodissociation dynamics of bare PhOH² and *p*-CrOH³ are very similar, the lifetime of the S₁ state of the *p*-CrOH(NH₃) complex decreases monotonically upon vibrational excitation,¹³ at variance with the results for PhOH(NH₃) for which vibrational-mode specificity was reported.¹¹ This effect was assigned to the enhancement of the rates of intracuster vibrational energy redistribution (ICVR) as a consequence of coupling between the low frequency modes associated with the CH₃ group in *p*-CrOH with the otherwise relatively isolated intermolecular modes.¹³ Moreover, it has been shown that the rate of O–H bond fission is enhanced when PhOH or *p*-CrOH are hydrogen bonded to NH₃,^{11,13} because this molecule is a good hydrogen acceptor and also because the height of the energy barrier generated by the ππ*/πσ* CI decreases as a consequence of the specific stabilization of the πσ* state by interaction with NH₃.⁴ On the contrary, when PhOH or *p*-CrOH are hydrogen bonded to H₂O, the excited state lifetime increases, since the lower H affinity of water compared with ammonia energetically closes the ESHT channel in the vicinity of the origin of the electronic transition.^{5,6}

The intramolecular ESHT along a hydrogen-bonded solvent wire has also been extensively studied in 7-hydroxyquinoline(NH₃)₃ complexes, where a very fast process takes place.¹⁴ In that system, the solvent wire is connected by terminal hydrogen bonds to the OH and N groups of the chromophore, 7-hydroxyquinoline (7-HQ). Upon electronic excitation, the OH group becomes more acidic and the quinoline N more basic, which drives an ESHT reaction along the solvent wire, equivalent to

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a solvent mediated enol \rightarrow keto tautomerization reaction, resulting in excited 7-ketoquinoline. Substitution of NH_3 by H_2O in the solvent wire in the complex $7\text{-HQ}(\text{NH}_3)_n(\text{H}_2\text{O})_m$, with $n + m = 3$, increases the threshold for ESHT from 200 cm^{-1} for $(n,m) = (3,0)$ to 2000 cm^{-1} for $(n,m) = (0,3)$, with intermediate values of 350 cm^{-1} for $(n,m) = (2,1)$ and 600 cm^{-1} for $(n,m) = (1,2)$.¹⁵ When the NH_3 molecule of the wire is bonded to the OH group, injection of the H atom into the wire occurs by tunnelling through the barrier generated by the $\pi\pi^*/\pi\sigma^*$ CI, as in the case of the intermolecular ESHT. Progress of ESHT along the wire is hindered by the higher barrier imposed by the H_2O molecules and it is almost completely blocked in a pure H_2O wire because the first barrier, of at least of 2000 cm^{-1} , is too high to be overcome.

Recent high-level excited state theoretical calculations¹⁶ on $7\text{-HQ}(\text{NH}_3)_3$ have pointed out that the excited state proton transfer (ESPT) reaction along the hydrogen-bonded ammonia wire is also likely to occur and, therefore, it is still an open question whether ESHT or ESPT is responsible for the enol \rightarrow keto tautomerization reaction. In this work, we investigated the effect of replacing an NH_3 molecule by a H_2O molecule on the intermolecular ESHT of $p\text{-CrOH}(\text{NH}_3)_2$ and $p\text{-CrOH}(\text{H}_2\text{O})(\text{NH}_3)$ complexes, by means of mass-resolved $(1 + 1)$ resonance-enhanced multi-photon ionization (REMPI) and laser-induced fluorescence (LIF) spectroscopy and density functional theory (DFT) calculations. Although in this case the chromophore has only one acid group and there is no possibility of intramolecular ESHT, the rate of the intermolecular reaction, and therefore the lifetime of the excited states, was affected by the presence of the H_2O molecule and the solvent conformation.

Experimental

The apparatus used for REMPI was the same as in a previous work.¹³ It consists of two differentially pumped chambers. The source chamber, pumped with an Edwards 2000 L s^{-1} diffusion pump system, was used to produce the molecular beam by expanding a mixture of He seeded with NH_3 (0.5%) that passed over a reservoir containing $p\text{-CrOH}$ heated to $40\text{--}70 \text{ }^\circ\text{C}$ to increase its vapour pressure. The backing pressure was typically 1–3 bar and it was expanded to vacuum through a $400 \mu\text{m}$ diameter pulsed nozzle (Solenoid General Valve, Series 9). Because of the strong hygroscopic property of $p\text{-CrOH}$, the water present in the samples was high enough for these experiments. However, some experiments were done with controlled added water. Very large clusters were produced under these conditions, which lead to a broad continuum background in the excitation spectra that masks the structured spectra of the smaller complexes.

The molecular beam, collimated by a home-made 4.0 mm diameter skimmer crossed the laser beam at right angle in the ionization chamber. The ions were extracted in a home-made Wiley–McLaren type time-of-flight (TOF) mass spectrometer (46 cm flight length), perpendicular to the molecular beam and laser directions, and entered the drift chamber, where they were detected using a multichannel plate (Del Mar Ventures MCP-MA34). The ionization and drift chambers were both pumped with a 56 L s^{-1} turbomolecular pump (Pfeiffer system).

The TOF mass resolution $R = m/\Delta m = 355$, which was enough to resolve masses (m/z) 142^+ and 143^+ corresponding to $p\text{-CrOH}^+(\text{NH}_3)_2$ and $p\text{-CrOH}^+(\text{H}_2\text{O})(\text{NH}_3)$.

The experimental setup for the LIF experiments has also been described previously.¹⁷ Briefly, a small chamber, evacuated with a Varian 1200 L s^{-1} diffusion pump and provided with two arms with optical baffles to prevent dispersed light, was used to produce the complexes as explained above. The jet was intercepted, at 90° , by the laser beam, at 1.5 cm from the nozzle. The fluorescence was collected by a telescope collinear to the jet and detected by a photomultiplier tube (PMT) (Hamamatsu R636) without any filter.

The LIF and REMPI spectra were measured using a frequency doubled Lumonics (HD500) dye laser (FWHM = 5 ns) operating with a mixture of Rhodamine 590 and 610, pumped by the second harmonic of a Spectra-Physics (Indi-HG) Nd:YAG laser.

The signals from the PMT and the MCP were averaged and digitized by a Tektronik (TDS-3034B) oscilloscope and integrated with a PC. The rise time of the complete detection system was 1 ns .

Quantum chemical calculations were carried out at the DFT level using B3LYP and MPWB1K functionals with the 6-311G++(d,p) basis set, using the GAUSSIAN 03 program package.¹⁸

Results

LIF, REMPI and TOF mass spectra

Fig. 1a shows the LIF spectrum of the species generated in the supersonic co-expansion of $p\text{-CrOH}$, NH_3 and H_2O diluted in He. In addition to the bands that belong to the $p\text{-CrOH}(\text{NH}_3)$ (1 : 1) complex (with the 0_0^0 transition at 34694 cm^{-1}),¹³ two other groups of absorption are observed in the ranges $34500\text{--}34675 \text{ cm}^{-1}$ (group B) and $34775\text{--}34900 \text{ cm}^{-1}$ (group A).

To obtain evidence on the nature of the species responsible for these transitions, one-colour REMPI spectra were recorded monitoring the mass signals $m/z = 125^+$ ($p\text{-CrOH}(\text{NH}_3)$), $m/z = 142^+$ ($p\text{-CrOH}(\text{NH}_3)_2$), $m/z = 35^+$ (NH_4NH_3) and

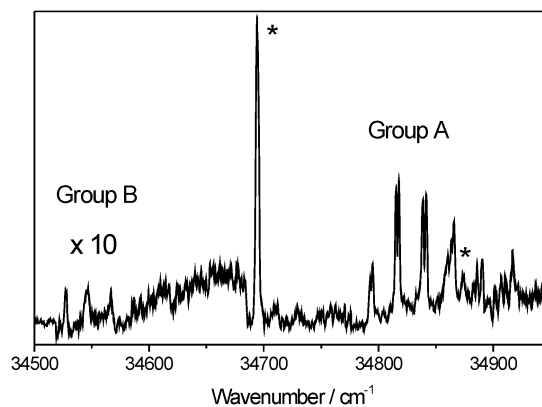


Fig. 1 (a) LIF spectrum of the $p\text{-CrOH}/\text{NH}_3/\text{H}_2\text{O}/\text{He}$ expansion. The vibronic bands marked with (*) correspond to the $p\text{-CrOH}(\text{NH}_3)$ complex (ref. 13).

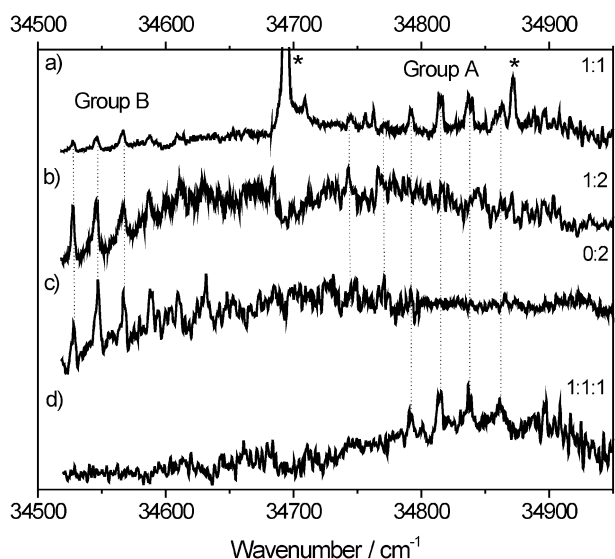


Fig. 2 Mass resolved (1 + 1) REMPI spectra recorded by integrating the masses of: (a) $p\text{-CrOH}^+(\text{NH}_3)$, (b) $p\text{-CrOH}^+(\text{NH}_3)_2$, (c) $\text{NH}_4(\text{NH}_3)$ and (d) $p\text{-CrOH}^+(\text{H}_2\text{O})(\text{NH}_3)$ cations. The vibronic bands marked with (*) in panel (a) have been assigned to the $p\text{-CrOH}(\text{NH}_3)$ complex (ref. 13), the other transitions in this panel come from excitation of larger complexes that evaporate one solvent molecule.

$m/z = 143^+$ ($p\text{-CrOH}(\text{NH}_3)(\text{H}_2\text{O})$). The results are shown in Fig. 2a–d, respectively.

The band at 34527 cm^{-1} (group B) in Fig. 2b shows a progression of 20 cm^{-1} and it was assigned to the 0_0^0 transition of $p\text{-CrOH}(\text{NH}_3)_2$. The structure is complex, possibly as a consequence of transitions from low frequency vibrational modes, as those reported for $\text{PhOH}(\text{NH}_3)_2$.⁹ The broad and unstructured band observed in the range $34743\text{--}34850\text{ cm}^{-1}$, at 216 cm^{-1} from the origin, arises from one quantum of vibrational excitation of the $\sigma(\text{OH}\text{--}\text{NH}_3)$ stretching in the 1 : 2 complex, in agreement with the intermolecular stretching frequency reported for the $\text{F}\text{--}\text{PhOH}(\text{NH}_3)_2$ ¹⁹ and $\text{PhOH}(\text{NH}_3)_2$ ⁹ complexes. The broadening and lack of structure of this band compared with that built on the origin suggests a shortening on the excited state lifetime of the 1 : 2 complex upon vibrational excitation, as expected from previous results on the vibrational dependence of the excited state lifetime of the 1 : 1 complex.¹³

The same transitions are observed at the mass corresponding to $\text{NH}_4^+(\text{NH}_3)$ (Fig. 2c), which is a signature of the occurrence of the ESHT reaction.

Fig. 2d, shows that group A transitions belong to the mixed $p\text{-CrOH}(\text{NH}_3)(\text{H}_2\text{O})$ complex. This spectrum shows a long harmonic progression of a low frequency vibration, ν_1 , at 22.7 cm^{-1} with the origin at 34792 cm^{-1} .

Besides the transitions corresponding to the 1 : 1 complex,¹³ the REMPI spectrum recorded on mass 125^+ (Fig. 2a) also shows transitions from the 1 : 2 and 1 : 1 : 1 complexes, indicating that solvent evaporation takes place from both of them.

Further information is obtained from the TOF mass spectra shown in Fig. 3a, recorded after resonant two photon ionization with the laser tuned at 34527 cm^{-1} (group B) in the upper trace and at 34817 cm^{-1} (group A) in the lower trace, under

the same expansion conditions. A typical mass spectrum recorded under large cluster conditions (10% NH_3/He , at a backing pressure of 3 bar) and after non-resonant two photon ionization (34730 cm^{-1}) is presented in Fig. 3b. These spectra deserve a few comments:

(1) The intensities ratio of the masses $142^+/143^+$ depends strongly on the excitation wavelength (group A or group B transitions) in agreement with the REMPI spectra of Fig. 2.

(2) $p\text{-CrOH}(\text{H}_2\text{O})_m(\text{NH}_3)_n$ clusters are clearly observed for $0 < m + n < 20$, under large clusters conditions.

(3) $\text{NH}_4^+(\text{NH}_3)_{n-1}$ products are observed up to $n = 3$; clusters with $n = 4$ are only weakly observed and those with $n > 4$ are not detected at all, whereas the $p\text{-CrOH}(\text{NH}_3)_n$ precursors are definitively observed up to $n = 20$.

(4) $\text{H}^+(\text{NH}_3)_n(\text{H}_2\text{O})_m$ is only observed for $n = 2$ and $m = 1$, which is barely detected, independent of the excitation wavelength or cluster size distribution.

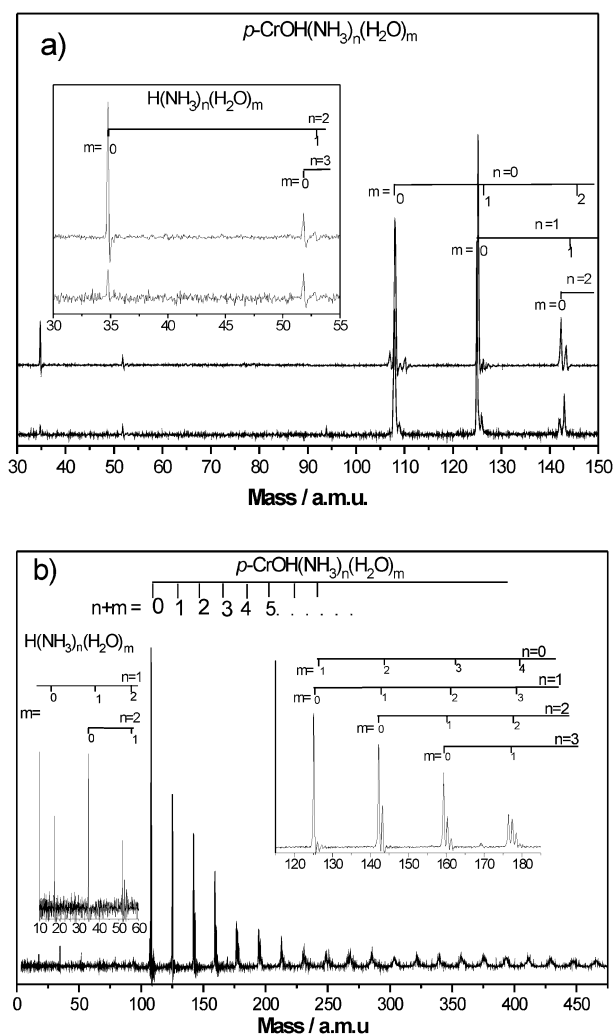


Fig. 3 (a) Time-of-flight (TOF) mass spectra recorded after resonant two photon ionization with the laser tuned at 34527 cm^{-1} (on group B resonance) in the upper trace and 34817 cm^{-1} (on group A resonance) in the lower trace, under the same expansion conditions and (b) with the laser tuned out of resonance at 34730 cm^{-1} under expansion conditions of large cluster formation. The insets in both figures show the region of the $\text{H}^+(\text{NH}_3)_n(\text{H}_2\text{O})_m$ masses.

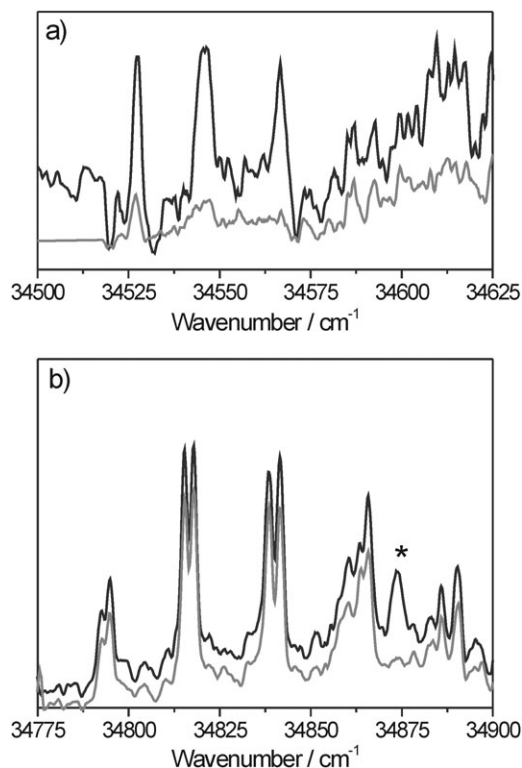


Fig. 4 LIF spectra recorded in the region of (a) group B transitions and (b) group A transitions, integrating the time resolved fluorescence signal in the interval 0–11 ns (black line) and 11–50 ns (light grey line). The vibronic band marked with (*) in panel (b) has been assigned to the *p*-CrOH(NH₃) complex (ref. 13).

Fig. 4 shows the LIF spectra recorded by integrating the time-resolved total fluorescence signal in two different temporal intervals, 0–11 ns (fluorescence during the laser pulse) and 11–50 ns (fluorescence after the laser pulse). These results clearly show that the lifetime of the excited state of the 1 : 1 : 1 complex involved in group A transitions is larger than that of the 1 : 2 complex, which is populated upon excitation of group B transitions. The lifetime of the excited state of the 1 : 1 : 1 complex was determined by time resolved fluorescence as $\tau = (12 \pm 2)$ ns, which is longer than that of the origin of the 1 : 1 complex ($\tau \approx 1$ ns), while the lifetime of the excited state of the 1 : 2 complex was estimated to be $\tau < 1$ ns and comparable with that of the $S_1(\sigma^1)$ of the 1 : 1 complex at 34873 cm^{-1} .¹³ For comparison, the fluorescence lifetime of the $S_1(0^0)$ state of the *p*-CrOH(H₂O) was also measured. The result obtained was $\tau = (15 \pm 2)$ ns, which is larger than the value $\tau = (3.8 \pm 0.5)$ ns obtained from the linewidth of a rotational line,⁶ but identical to that reported for the similar PhOH(H₂O) complex ($\tau = 15$ ns).²⁰

Previous results on the excited state lifetime of PhOH(NH₃)_{1,2} also showed that the lifetime of the $S_1(0_0^0)$ state of the 1 : 2 complex ($\tau = 400$ ps) is comparable to that of the $S_1(\sigma^1)$ state of the 1 : 1 complex ($\tau = 390$ ps).¹¹

Ab initio calculations

To get further insight into the experimental results, the optimized structures and vibrational modes of the ground

electronic state were calculated at the DFT level with the B3LYP functional using the 6-311G++(d,p) basis set. Since the B3LYP functional could provide an incorrect description of the interactions when the dispersive component is significant, the ground state structures were also optimized at the DFT level with the MPWB1K functional, which seems to be appropriate to study dispersion-bound clusters, using the 6-311G++(d,p) basis set.²¹

Normal mode analyses for all the optimized structures, using both functionals, provided the harmonic vibrational frequencies, zero-point vibrational energies (ZPE), binding energies D_e and dissociation energies D_0 .

Calculations with both functionals produced similar results. Therefore, corrections for the basis set superposition error (BSSE) with the full counterpoise method²² yielding D_0^{CPC} , were only applied to the results obtained with the B3LYP functional due to its lower computational cost.

The calculations with the B3LYP functional converged to three stable hydrogen bonded structures that are displayed in Fig. 5a–c together with the intermolecular distances and the angle formed between the *p*-CrOH molecular plane and the H₂O–NH₃ hydrogen-bonded solvent plane. Table 1 shows the calculated values of D_0 , D_0^{CPC} and relative energies (ΔE_0 , ΔE_0^{CPC}) for the three structures. The most stable configuration, shown in Fig. 5a, corresponds to the cyclic structure *c*-OH–H₂O–NH₃, with the OH group of the chromophore acting as a hydrogen donor to the H₂O molecule and as hydrogen acceptor from the NH₃ molecule. Fig. 5b shows another cyclic structure (*c*-OH–NH₃–H₂O) with NH₃ as a hydrogen acceptor of the phenolic OH and H₂O as a hydrogen donor to this moiety, which is slightly higher in energy ($\Delta E_0^{\text{CPC}} = 53 \text{ cm}^{-1}$ or $\Delta E_0 = 143 \text{ cm}^{-1}$). The calculated energy difference between both cyclic structures is too small ($53\text{--}143 \text{ cm}^{-1}$) and it could be within the error of the calculations. Therefore, the ground states of both cyclic structures were also optimized at the MPWB1K/6-311G++(d,p) level; their dissociation energies, D_0 , and relative energies, ΔE_0 , were also calculated with this functional including the ZPE. The results, presented in Table 1, show that both functionals, without BBSE corrections, place the *c*-OH–NH₃–H₂O structure 111 cm^{-1} (MPWB1K) and 143 cm^{-1} (B3LYP) above the *c*-OH–H₂O–NH₃ structure.

Finally, the value of energy of the open structure *o*-OH–NH₃–H₂O (Fig. 5c) lies more than 400 cm^{-1} (MPWB1K) and 600 cm^{-1} (B3LYP) above the energy of the *c*-OH–H₂O–NH₃ structure, in agreement with results on PhOH(NH₃)₂ and F–PhOH(NH₃)₂ complexes.^{9,19}

Discussion

The experimental data obtained from the REMPI spectrum (Fig. 2d) allows for an unequivocal assignment of group A transitions in the range $34800\text{--}34875 \text{ cm}^{-1}$ to the mixed 1 : 1 : 1 complex.

The LIF spectrum of the 1 : 1 : 1 complex in the region of the $0_0^0 + n\nu_1$ progression shows, in more detail (Fig. 4b), that each band is split in two components whose spacing increases with energy, indicating the existence of a tunneling motion through the torsional barrier generated by the hindered rotation of the

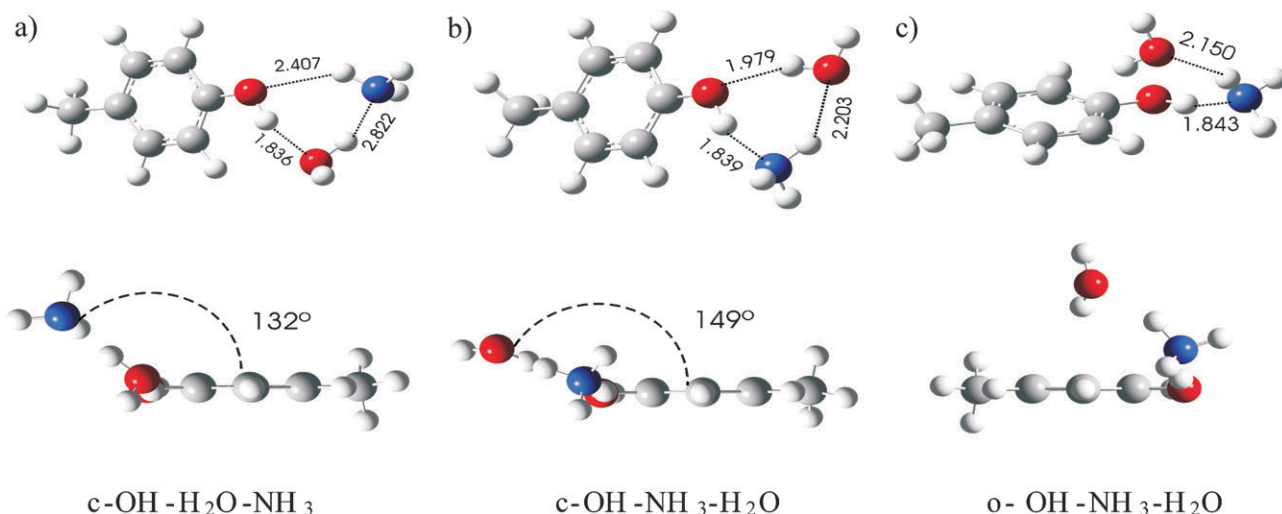
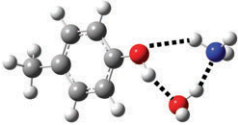
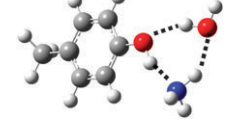
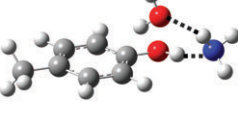


Fig. 5 The optimized structures of the *p*-CrOH(H₂O)(NH₃) complex obtained at the DFT/B3LYP (6-311G++(d,p)) level of theory. (a) *c*-OH-H₂O-NH₃, (b) *c*-OH-NH₃-H₂O and (c) *o*-OH-NH₃-H₂O.

Table 1 Calculated ground state dissociation energies (D_0) including zero point vibrational energy (ZPVE) and corrected for basis set superposition error (BSSE) (D_0^{CPC}), and relative energies (ΔE) of the isomers from the most stable structure (*c*-OH-H₂O-NH₃) corrected for ZPVE (ΔE_0) and BSSE (ΔE_0^{CPC}). All the calculations were performed at the DFT level of theory with the B3LYP or MPWB1K functionals with the 6-311G++(p,d) basis set

Structure	B3LYP		MPWB1K			
	D_0/cm^{-1}	$\Delta E_0/\text{cm}^{-1}$	$D_0^{\text{CPC}}/\text{cm}^{-1}$	$\Delta E_0^{\text{CPC}}/\text{cm}^{-1}$	D_0/cm^{-1}	$\Delta E_0/\text{cm}^{-1}$
<i>c</i> -OH-H ₂ O-NH ₃ 	4603	0	4076	0	4829	0
<i>c</i> -OH-NH ₃ -H ₂ O 	4460	143	4023	53	4718	111
<i>o</i> -OH-NH ₃ -H ₂ O 	3935	668	3457	619	4380	449

NH₃ or H₂O moieties in the complex, as observed in the PhOH(NH₃)₂ complex.⁹ In principle, the splitting could also arise from a hot band contribution or from the presence of different isomers. The former can be excluded, because the intensity ratio of the split bands does not depend on the expansion conditions and temperature of the jet. Also, the lifetime measured from each transition yielded a single value, within the experimental error, suggesting that the S₁ state is the same for all the transitions observed and therefore that only one isomer is involved. This interpretation is not conclusive, however, and spectral hole burning experiments should be performed in order to further clarify this point.

Regarding the structure of the complex, theoretical calculations show the existence of three different ground state structures (Fig. 5), whose energies span over 600 cm⁻¹. Unfortunately, the ground state intermolecular vibrational frequencies calculated at the DFT/B3LYP level for the three structures are very similar, which precludes an unambiguous assignment of the observed transitions to any of them.

In order to obtain more information on the structure of the complex, it is therefore necessary to analyse the experimental data obtained on its lifetime and reactivity, in the light of the information available for other complexes involving *p*-CrOH.^{6,13}

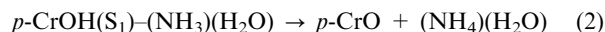
In the first place, the excited state lifetime of the mixed complex ($\tau = 12$ ns) is larger than those of bare *p*-CrOH ($\tau = 1.6$ ns)⁶ and *p*-CrOH(NH₃) ($\tau \approx 1$ ns), but similar to that of the *p*-CrOH(H₂O) complex ($\tau = 15$ ns). This suggests a configuration and reactivity similar to *p*-CrOH(H₂O); that is, a structure where the H atom of the OH group of *p*-CrOH directly interacts with H₂O but not with NH₃ and with a long lifetime that arises as a consequence of the inability of the ESHT to occur at the excitation energy of this work, similar to *p*-CrOH(H₂O).

In addition, further evidence that the ESHT process could be blocked arises from the mass spectra (Fig. 3), where the signal at $m/z = 36^+$, corresponding to the reaction product of the ESHT to NH₃, (H₂O)(NH₄)⁺, is absent. It is known that (NH₄)(H₂O) is a long lived species²³ and it should be easily detected under the present experimental conditions. This indicates that *p*-CrOH is directly bound to H₂O and not to NH₃.

The isomeric reaction product, (NH₃)(H₃O), that should originate from the ESHT to H₂O, could not be detected either. This can be considered either as an indication that this channel is not open, or that the (NH₃)(H₃O) complex does not live long enough to be detected. As there is no evidence of the existence of that complex in the literature, a choice between both alternatives cannot be made. However, the lack of this product is in agreement with the long lifetime of the 1:1:1 complex, and with the fact that *p*-CrOH is directly bound to H₂O, as discussed above.

Additional support for these conclusions comes from an analysis of the energetic of the process.

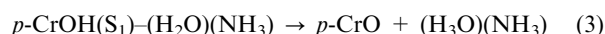
For the *c*-OH-NH₃-H₂O structure, the ESHT process would take place according to:



Considering that, in bare *p*-CrOH, the thermodynamic threshold for the OH dissociation is 29 320 cm⁻¹,³ that the H + NH₃ → NH₄ reaction is quasi-isoenergetic (-242 cm⁻¹),²⁴ that the binding energy NH₄-H₂O is 2749 cm⁻¹,²³ and that the dissociation energy of *p*-CrOH-NH₃-H₂O, (*p*-CrOH-NH₃-H₂O → *p*-CrOH + NH₃ + H₂O) was calculated to be 4023-4460 cm⁻¹ at the DFT/B3LYP level (Table 1), the thermodynamic threshold for reaction (2) is 30 352-30 789 cm⁻¹. This value is 4003-4440 cm⁻¹ below the 0₀⁰ transition for the mixed cluster.

Therefore, the reaction is energetically allowed and, as a consequence, the S₁ state of the 1:1:1 complex should be short lived. Also, the (NH₄)(H₂O) product should be observed at $m/z = 36^+$, upon ionization with a 34 792 cm⁻¹ energy photon, since the ionization potential (IP) of this product is 32 822 cm⁻¹.²³

On the other hand, for the structure *c*-OH-H₂O-NH₃ the ESHT process should take place according to:



In this case, H₂O has a low hydrogen affinity and calculations place the H₃O radical 6450 cm⁻¹ above the H + H₂O limit.²⁵ The *p*-CrOH-H₂O-NH₃ dissociation energy (*p*-CrOH-H₂O-NH₃ → *p*-CrOH + H₂O + NH₃) was calculated to be 4076-4603 cm⁻¹ at the DFT/B3LYP level (Table 1) and

assuming that the (H₃O)(NH₃) binding energy is similar to that of (NH₄)(H₂O) or (NH₄)(NH₃) (2749 cm⁻¹),²³ the thermodynamic threshold for reaction (3) should be 37 097-37 624 cm⁻¹, which is 2305-2832 cm⁻¹ above the 0₀⁰ transition of the mixed cluster. Therefore, reaction (3) is energetically closed at the excitation energies of this work and, consequently, the lifetime of the S₁ state of the 1:1:1 complex should be long enough for the reaction product to be observed, in agreement with the experimental findings. This result also explains the similarity of the excited state lifetimes with the *p*-CrOH(H₂O) complex.

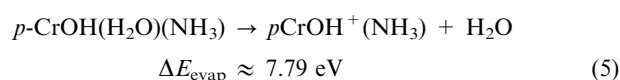
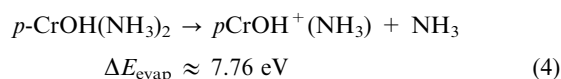
From the discussion above, it is concluded that the *c*-OH-H₂O-NH₃ structure accounts for the experimental observations. It should be noted that in the (H₂O)(NH₃)²⁶ complex, the water molecule acts as a hydrogen donor to the intermolecular hydrogen bond and the ammonia molecule as a hydrogen acceptor and that the solvent structure is kept in the 1:1:1 complex. The solvent structure in turn determines the reactivity and excited state lifetime of the mixed complex.

The presence of other isomers in the molecular beam, especially the *c*-OH-NH₃-H₂O structure, which is very close in energy to the *c*-OH-H₂O-NH₃ structure, cannot be excluded to the light of the present results. It is possible that the former isomer reacts too fast to be detected in a nano-second experiment, thus performing the same experiment with picosecond lasers would help to disentangle this point. Nevertheless, it should be recalled that the (NH₄)(H₂O) reaction product has not been observed either.

The fact that the spectral signatures of the 1:1:1 and 1:2 complexes are also observed in the mass of the *p*-CrOH⁺(NH₃) cation ($m/z = 125^+$), indicates that evaporation of a solvent molecule (H₂O and NH₃ respectively) takes place either in the excited or in the ionic state.

Since excitation to the S₁ state of both complexes is in the vicinity of the 0₀⁰ transition, evaporation in this state is not expected because there is no excess energy to overcome the barrier for this process which, in fact, is endothermic at these excitation energies. Thus, evaporation should take place in the ionic state as observed in similar hydrogen bonded complexes.^{7,9,10,27}

The energy (ΔE_{evap}) required by the 1:1:1 and 1:2 complexes for solvent evaporation in their ionic states can be estimated considering the following known thermodynamic values. The IP of PhOH (8.50 eV)²⁸ is 0.33 eV above the IP of *p*-CrOH (8.17 eV)²⁹ and a similar difference is expected for the PhOH(NH₃) and *p*-CrOH(NH₃) complexes. Since the IP of the former complex is 7.85 eV,³⁰ it renders an estimated value of 7.52 eV for the IP of the later complex. Similar dissociation energies are expected for the ground states of PhOH(NH₃) ($D_0 = 0.3$ eV)⁹ and *p*-CrOH(NH₃) and for PhOH(NH₃)₂ ($D_0 = 0.54$ eV)⁹ and *p*-CrOH(NH₃)₂, whereas the dissociation energy ($D_0 = 0.57$ eV) for the 1:1:1 (*c*-OH-H₂O-NH₃) complex is taken from Table 1. These values lead to:



When the laser was tuned to the 0_0^0 transition of each complex, the energies deposited by the two photon absorption were $69\,584\text{ cm}^{-1}$ (8.63 eV) in the 1:1:1 complex and $69\,054\text{ cm}^{-1}$ (8.56 eV) in the 1:2 complex, which are 0.84 and 0.80 eV above the ΔE_{evap} , respectively. Therefore, the evaporation process is energetically allowed in the ionic state, where it consequently takes place.

Conclusions

The structure and reactivity of $p\text{-CrOH}(\text{NH}_3)_2$ and $p\text{-CrOH}(\text{H}_2\text{O})(\text{NH}_3)$ complexes were studied using mass-resolved one-colour REMPI and LIF spectroscopy together with DFT calculations

From the experimental results, it was concluded that the lifetime of the S_1 excited state of solvated $p\text{-CrOH}$ is strongly affected by replacing one NH_3 molecule in the $p\text{-CrOH}(\text{NH}_3)_2$ complex by one H_2O molecule to produce the $p\text{-CrOH}(\text{H}_2\text{O})(\text{NH}_3)$ complex. The S_1 state is short-lived (sub-nanosecond) in the former complex but its lifetime rises to (12 ± 2) ns. This behaviour was ascribed to the intermolecular hydrogen bond structure of the mixed complex.

In the case of the $p\text{-CrOH}(\text{NH}_3)_2$ complex, the ESHT reaction is an open channel and takes place very fast, while in the $p\text{-CrOH}(\text{H}_2\text{O})(\text{NH}_3)$ complex this reaction is strongly dependent on the specific solvent structure.

DFT calculations point to three stable structures for the mixed complex. The most stable is a cyclic intermolecular hydrogen bonded structure in which H_2O acts as the H acceptor of the phenolic OH group ($c\text{-OH}-\text{H}_2\text{O}-\text{NH}_3$). Therefore, upon electronic excitation of the chromophore ($p\text{-CrOH}$) the H atom should be transferred to the H_2O moiety. This reaction, at the excitation energies of this work, is energetically disallowed since H_2O has a low hydrogen affinity.

Finally, the excess energy deposited in the ionic state of the $p\text{-CrOH}(\text{H}_2\text{O})(\text{NH}_3)$ and $p\text{-CrOH}(\text{NH}_3)_2$ complexes by resonant one-colour two-photon ionization is dissipated by evaporation of a solvent molecule in agreement with previous results.^{7,9,10,27}

In addition, these results could also be useful to provide a new interpretation to the transitions observed in the range $35\,800\text{--}35\,900\text{ cm}^{-1}$ in the $\text{PhOH}(\text{NH}_3)$ complex REMPI spectrum,⁹ regarding whether these transitions actually correspond to $\text{PhOH}(\text{H}_2\text{O})(\text{NH}_3)$ instead of to $\text{PhOH}(\text{NH}_3)_2$.

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