Effect of the vibrational excitation on the non-radiative deactivation rate of the S_1 state of p-cresol(NH$_3$) complex

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ABSTRACT

The effect of the CH$_3$ group on the lifetime of the S_1 state of the p-cresol(NH$_3$) complex was investigated by means of REMPI, LIF, DF spectroscopy and *ab initio* calculations.

At variance with PhOH(NH$_3$) for which vibrational-mode specificity was reported, the lifetime of the S_1 state of the p-cresol(NH$_3$) complex decreases monotonically upon vibrational excitation indicating that randomization of energy takes place at low excitation energy. This result is analyzed as the consequence of a stronger coupling of the complex intermolecular modes with those of the CH$_3$ group.

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1. Introduction

Amino acids are among the most important biological molecules. Some of them, such as aromatic amino acids like tyrosine, tryptophan and phenylalanine have very large UV absorption cross-sections and constitute the chromophores of proteins. Absorption of UV photons by tyrosine in the range 240–290 nm corresponds to the photoexcitation of phenol (PhOH), its chromophore, to the $S_1(\pi\pi^*)$ excited-state [1]. For this reason, the structures and reactivity of PhOH and its molecular complexes with a number of solvent molecules (H$_2$O [2], NH$_3$ [3,4], diethyl ether [5], several amines [6], etc.) have been the subject of many detailed studies, intended to provide a better understanding of the photochemical and photophysical properties of tyrosine.

A prominent reaction was found in the excited-state of the PhOH(NH$_3$)$_n$ complexes, where H atom transfer (ESHT) occurs [4,7,8]:

$$\text{PhOH}^*(\text{NH}_3)_n \rightarrow \text{PhO} + \text{NH}_4(\text{NH}_3)_{n-1} \qquad (1)$$
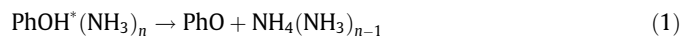
Several studies have shown the importance of this ESHT channel in the S_1 state of many aromatic molecules with O–H and/or N–H substitution [9–13] whose deactivation rate is governed by a conical intersection (CI) between the excited $^1\pi\pi^*$ and a $^1\pi\sigma^*$ excited-state repulsive with respect to the OH/NH bond [14]. Depending on the system the $^1\pi\sigma^*$ state can also cross the ground $^1\pi\pi$ state [14].

The lifetime of the S_1 state of the PhOH(NH$_3$) complex decreases monotonically with increasing vibrational energy when intramolecular PhOH modes are excited [15]. However, the lifetime is shorter upon excitation of the intermolecular stretching (σ) mode than of other intramolecular modes with higher vibrational energies, showing the presence of vibrational-mode selectivity in the reaction rate. The authors suggested that ESHT is responsible for the deactivation of the S_1 states, because the σ mode involves the reaction coordinates of this process [15]. They also suggested that the ESHT reaction occurs by tunneling through the potential barrier created by the conical intersection (CI) of the $\pi\pi^*/\pi\sigma^*$ potential energy surfaces (PESs) [15].

On the other hand, Nix et al. [16] suggested that when the bare PhOH molecule is excited below the crossing area of the CI of the $\pi\pi^*/\pi\sigma^*$ PESs, the O–H bond fission takes place through an internal conversion (IC) to high vibrational levels of the ground state and subsequent coupling to the lowest dissociation asymptote *via* the $\pi\pi/\pi\sigma^*$ CI at extended $R_{\text{O–H}}$. The $\pi\pi/\pi\sigma^*$ coupling was assumed to occur faster than energy randomization in the ground state.

The spectroscopic study on thyrosine in the gas phase is difficult. However, studies on the chromophore of thyrosine, PhOH and its substituted derivatives provided detailed information on the excited-state dynamics [17–25].

Methyl substitution in PhOH introduces a modest perturbation to its nuclear framework, so that it should have little influence on the coupling between the $\pi\pi^*$ and $\pi\sigma^*$ PESs, in agreement with the arguments of King et al. who reported that the O–H bond fission in bare p-cresol [25] is very similar to that in bare PhOH [16]. However, in the molecular complex the dynamics might be affected if the additional density of states provided by the low frequency motions associated with the CH$_3$ group in p-cresol favours the coupling with the otherwise relatively isolated intermolecular modes, enhancing the rates of intracluster vibrational energy distribution (ICVR).

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In order to analyze this effect on the dynamics of the non-radiative processes of the excited-state, to the light of the mode specificity found for the PhOH(NH$_3$) complex [15] we now report a study of the dependence of the non-radiative deactivation rate of the S$_1$ state of the p-cresol(NH$_3$) complex on the excess vibrational energy.

2. Experimental

The set-up for the laser induced fluorescence (LIF) experiments has been described previously [26]. Briefly, the vacuum chamber was evacuated with a Varian 1200 L/s diffusion pump system. The resonance-enhanced multi-photon ionization (REMPI) experiments were performed in two differentially pumped chambers separated by a 4.0 mm diameter skimmer. The expansion chamber was evacuated with an Edwards 2000 L/s diffusion pump system while the ionization chamber was evacuated with a turbomolecular pump Pfeifeer 56 L/s system.

The p-cresol(NH$_3$) complexes were produced by expanding a mixture of He seeded with NH$_3$ (1.5%) and passing over a reservoir containing p-cresol heated to 40–70 °C to obtain enough vapour pressure. The backing pressure was typically 1–3 bar and it was expanded to vacuum through a 400 μm diameter pulsed nozzle (Solenoid General Valve, Serie 9).

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. For the LIF experiments the fluorescence from the clusters was detected by a photomultiplier tube (PMT) (Hammamatsu R636) without any filter. Dispersed Fluorescence (DF) spectra were recorded using a monochromator (McPherson, f = 30 cm) as dispersive element. In the case of the REMPI experiments the ions were detected with a 46 cm home-made TOFMS provided with a microchannel plate (Del Mar Ventures MCP-MA34). 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.

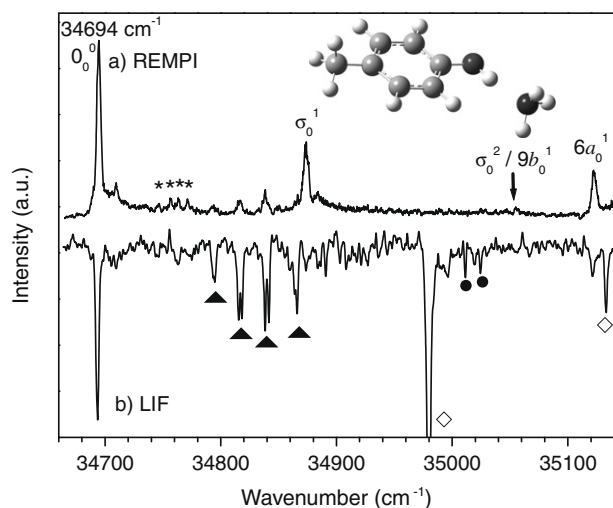Quantum chemical calculations were carried out at the MP2 level with the 6-31G++(d,p) basis set, using the GAUSSIAN 03 program package to obtain the structure and harmonic vibrational frequencies of the ground electronic state (S$_0$).

3. Results and discussion

Fig. 1 shows the REMPI (1+1) (a) and the LIF (b) spectra recorded by integrating the mass corresponding to the [p-cresol(NH$_3$)]$^+$ complex and the total fluorescence in the range 34 660–35 140 cm^{-1}, respectively. In addition to the transitions of the p-cresol(NH$_3$) complex observed in the REMPI spectrum, several transitions from other species are also observed in the LIF spectrum, due to the lack of mass selection. Thus, the transitions at 34 980 cm^{-1} and 35 132 cm^{-1} were assigned to the p-cresol(H$_2$O) [20] complex while those at 35 012 cm^{-1} and 35 025 cm^{-1} belong to the (p-cresol)$_2$ complex [20].

The general spectral features are in agreement with those reported in the literature for PhOH(NH$_3$) [3] and p-fluorphenol(NH$_3$) [10] complexes. These data along with those of the bare p-cresol

Table 1
Experimental vibrational frequencies of the excited (S$_1$) state of the p-cresol(NH$_3$) complex. The frequencies are relative to the 0^0 transition (34 694 cm^{-1}).

S$_1$ state	
Experimental REMPI[a] Frequency (cm^{-1})	Assignment
52	(β^1) Out of plane bending
62	(τ^1) NH$_3$ torsion around the OH...NH$_3$ axis
69	(τ^1) NH$_3$ torsion around the OH...NH$_3$ axis
77	(τ^1) (C–CH$_3$) torsion
179	(σ^1) OH...NH$_3$ stretching
360	σ^2 or $9b^1$ or $16a^1$
428	$6a^1$
608	$6a^1 + \sigma^1$
814	1^1

[a] Frequency accuracy is ±0.5 cm^{-1}.

Table 2
Experimental and theoretical vibrational frequencies of the ground state (S$_0$) of the p-cresol(NH$_3$) complex.

S$_0$ state		
Experimental DF[a] Frequency (cm^{-1})	Calculated MP2/631G++(d,p)	
	Scaled Frequency (cm^{-1})	Assignment
Intermolecular vibrations		
28	17	(β) Out of plane bending
46	52	(τ) NH$_3$ torsion around the OH...NH$_3$ axis
59	62	(τ) NH$_3$ torsion around the OH...NH$_3$ axis
163	177	(σ) OH...NH$_3$ stretching
273	247	(ω) Wagging
312	326	(β) In plane bending
Intramolecular vibrations[b] and combination bands		
80	85	τ (C–CH$_3$) torsion
138–150	133	11^1 (C–CH$_3$) out of plane bending
375	383	$16a_1$
454	459	$6a_1$
607		$6a_1 + \sigma_1$
636	638	$6b_1$
728	734	$10a_1$
824	832	1_1
873	864	$17a_1$
984		$1_1 + \sigma_1$

[a] Frequency accuracy is ±7 cm^{-1}.
[b] The assignment of the intermolecular bands was mainly based on the assignment of the vibrations of PhOH(S$_0$). Refs. [27,28].

Fig. 1. (a) REMPI and (b) LIF spectra of the p-cresol(NH$_3$) complex. The origin band is observed at 34 694 cm^{-1}. The vibronic bands marked with (*) correspond to low vibrational modes of the 1:1 complex. Additional bands in the LIF spectrum correspond to (▲) p-cresol(Solv)$_2$ also present in the REMPI spectrum indicating solvent evaporation process in the ionic state, (◇) p-cresol(H$_2$O) and (●) (p-cresol)$_2$, which are also present in the expansion mixture. Inserted is the calculated (MP2/6-31G^{++}(d,p)) structure of the 1:1 complex in the S$_0$ state.
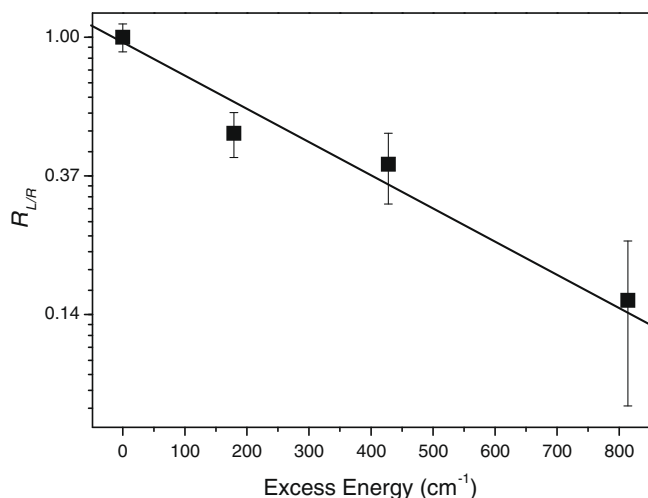
Fig. 2. Measured LIF/REMPI intensity ratios ($R_{L/R}$) for four bands of the *p*-cresol(NH₃) complex as a function of the vibrational excess energy in the S₁ excited-state. The solid line is for guidance.

Table 3
Ratios $R_{L/R}$ of the spectral intensities LIF/REMPI for the three main bands of the *p*-cresol(NH₃) complex.

State	Excess energy (cm^{-1})	$R_{L/R}$
0^0	0	1.0 ± 0.1
σ^1	179	0.50 ± 0.08
$6a^1$	428	0.4 ± 0.1
1^1	814	0.15 ± 0.08

[17–20,23] and PhOH [27,28] molecules provided the basis for the assignment of the intra and intermolecular vibrations (Table 1).

The most intense band peaked at 34 694 cm^{-1} was assigned to the S₁ ← S₀ origin. The band at 428 cm^{-1} from the origin was assigned to the fundamental transition of the intramolecular vibrational-mode $6a^1$ (in-plane ring deformation) in the S₁ state. The transition at 179 cm^{-1} from the origin was assigned to the intermolecular stretching vibration (σ^1) calculated as 177 cm^{-1} in the S₀ state. The weak band at 360 cm^{-1} from the origin could result from the σ_0^2 transition or from the in-plane C–OH bending ($9b^1$) mode observed at 373 cm^{-1} in the bare molecule [23], or from the $16a^1$ mode predicted at 383 cm^{-1} in the ground state (Table 2). A band at 608 cm^{-1} from the origin (not shown in Fig. 1) was also observed and associated to the ($6a^1 + \sigma^1$) vibrational excitation.

The three lowest frequencies at 52 cm^{-1}, 62 cm^{-1} and 69 cm^{-1} from the origin (marked with stars in Fig. 1) were tentatively assigned to the bending (β) and torsion (τ) modes of the NH₃ moiety around the intermolecular hydrogen bond by comparison with the spectrum of the PhOH(NH₃) complex [3] and the ground state calculations (Table 2). The transition at 77 cm^{-1} from the origin was assigned to the C–CH₃ torsion by comparison with the ground state calculations (85 cm^{-1}).

A series of bands between 90 cm^{-1} and 150 cm^{-1} from the origin (marked with ▲ in Fig. 1) with a 22 cm^{-1} progression arise from larger complexes that evaporate one solvent molecule in the ionic state and will be discussed in a forthcoming publication.

The DF spectra obtained by pumping the 0^0 and $0^0 + 179$ cm^{-1} bands of the 1:1 complex are reported in Table 2 together with the calculated frequencies for the S₀ state, scaled by a factor 0.971. The general agreement between the experimental and calculated frequencies of the S₀ state supports the assignment of the vibrational modes. Several low frequency bands (below 200 cm^{-1}) were observed in the DF spectra, corresponding to intermolecular and intramolecular vibrations associated to the CH₃ moiety and their combinations.

The vibrational energy dependence of the S₁ state lifetime was determined from the ratios of the intensities LIF/REMPI ($R_{L/R}$) of the three main transitions (0_0^0, σ_0^1 and $6a_0^1$) (Fig. 1) and that for the 1_0^1 band (814 cm^{-1} from the origin) of the *p*-cresol(NH₃) complex.

Fig. 2 shows the vibrational energy dependence of the $R_{L/R}$ that are normalized to the 0_0^0 transition. The ratios are also summarized in Table 3. The errors informed account for the standard deviation of three set of measurements and several quantification criteria. The remarkable energy/ν-dependence of $R_{L/R}$ evidences a shortening of the S₁ state lifetime upon vibrational excitation [29].

To prove this assumption the LIF spectra for the four transitions were recorded by integrating the time resolved total fluorescence signal in two different intervals, 0–11 ns (fluorescence during the laser pulse) and 11–22 ns (fluorescence after the laser pulse). From the results, shown in Fig. 3, it is apparent that the S₁($\sigma^1/6a^1/1^1$) states are almost completely deactivated during the laser pulse, while the deactivation of the S₁(0^0) state is completed after the laser pulse.

Regarding the nature of the non-radiative decay process of the S₁ state, it is well characterized that in the PhOH(NH₃) complex it proceeds through ESHT reaction [4,7,8,11,15]. Therefore, due to the similarity between the hydrogen bonded structures of PhOH(NH₃) and *p*-cresol(NH₃) complexes, this channel is also expected to be the responsible for the deactivation of the S₁ state
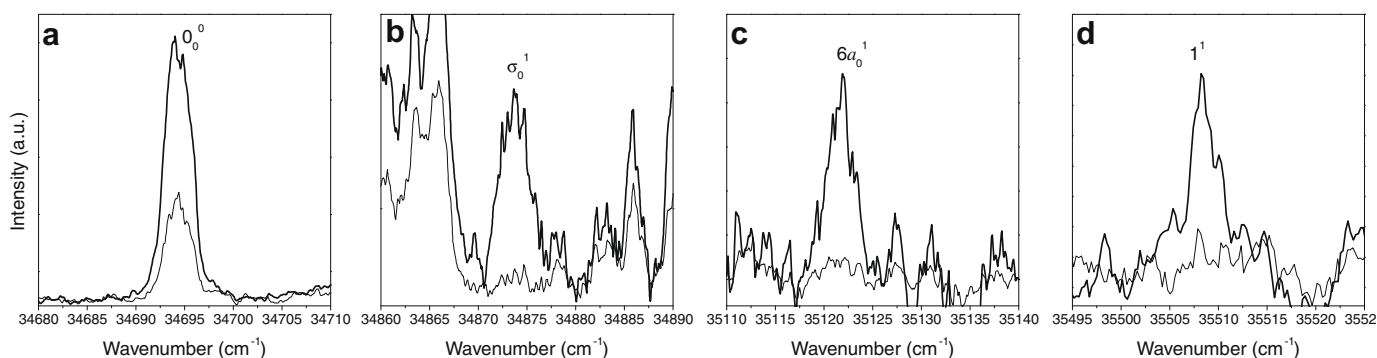

Fig. 3. Excitation LIF spectra of the 1:1 complex recorded in the spectral region of the (a) 0_0^0, (b) σ_0^1, (c) $6a_0^1$ and (d) 1^1 bands: (▬▬) spectra recorded integrating the time resolved fluorescence signal in the interval 0–11 ns; (—) spectra recorded integrating the time resolved fluorescence signal in the interval 11–22 ns. In panel (c) both spectra were corrected by subtracting the background corresponding to the *p*-cresol(H₂O) complex.

in the latter. Additional evidence about the occurrence of ESHT comes from the observation of the 0_0^0 transition of the 1:1 complex in the mass of the NH_4^+ [4,7,8,11,15].

The lifetime of the S_1 state of $PhOH(NH_3)$ is shorter upon excitation to 182 cm^{-1} (σ^1) than to 486 cm^{-1} ($6a^1$) [15]. These results indicate a vibrational-mode specific enhancement of the reaction rate constant, associated with excitation of the intermolecular vibration which is linked to the reaction coordinate of the ESHT process [15]. In contrast, the lifetime of the S_1 state of p-cresol(NH_3) decreases monotonically with the excess vibrational energy. This result implies that CH_3 substitution produces an efficient ICVR which favours a statistical behaviour of the deactivation process.

Studies of the photodissociation of bare PhOH [16] and p-cresol [25] at moderate excitation energies showed similar behaviours for both molecules, indicating that an increase of the density of states is not enough *per se* to produce any noticeable effect on the intramolecular energy redistribution (IVR) rate.

On the contrary in the p-cresol(NH_3) complex the CH_3 group increases the density of states at energy values comparable to those of the low frequency intermolecular vibrations. This allow for an efficient coupling of the inter and intramolecular vibrations and the energy deposited to the σ mode can be distributed through fast randomization at variance with the case of the $PhOH(NH_3)$ complex for which it necessarily remains localized in the ESHT reaction coordinate.

7-Azaindol(MeOH)$_2$ is another example in which the density of states is a key factor that determines the microscopic mechanism of the deactivation process [30]. In this system the excited-state proton/hydrogen transfer reaction occurs in a vibrational-mode specific fashion at vibrational energies lower than 600 cm^{-1}, but the reaction changes to statistical at higher excess energies (>600 cm^{-1}) due to an increased density of states.

4. Conclusions

The effect of the CH_3 group on the lifetime of the S_1 state of the p-cresol(NH_3) complex was investigated by means of REMPI, LIF, DF spectroscopy and *ab initio* calculations.

A comparison of the LIF intensities of four transitions with those of the REMPI spectrum suggests that the lifetime of the S_1 state is shortened upon vibrational excitation due to the presence of a non-radiative decay process, probably ESHT as in the case of $PhOH(NH_3)$. At variance with $PhOH(NH_3)$ for which vibrational-mode specificity was reported, the lifetime of the S_1 state of the p-cresol(NH_3) complex decreases monotonically upon vibrational excitation indicating that randomization of energy takes place at low excitation energies. The presence of the CH_3 group introduces low frequency modes and thus an increased density of states at low values of energy compared with PhOH that facilitates the coupling of the intermolecular modes with those of the p-cresol moiety.

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