Photoinduced Proton and Charge Transfers in a Dihydroxynaphthalene Derivative: Chromotropic Acid

Elisabeth Bardez,*,† Valérie Alain,† Émilie Destandau,† Aleksandre Fedorov,‡ and José M. G. Martinho‡

Laboratoire de Chimie Générale, Conservatoire National des Arts et Métiers, 292 rue Saint-Martin, 75003 Paris, and Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires (CNRS UMR 8531), Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94235 Cachan Cedex, France, and Centro de Química-Física Molecular, Instituto Superior Técnico, P-1049-001 Lisboa, Portugal

Received: April 4, 2001; In Final Form: August 14, 2001

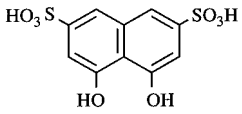
Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid) is a chelating agent whose fluorogenic character has never been explained yet. The excited-state behavior of chromotropic acid itself has never been reported, despite its relationship with naphthols that are well-known photoacids. The present paper is accordingly devoted to a thorough investigation of chromotropic acid emission in aqueous solutions, which revealed its excited-state prototropic behavior in relation with the key role of the ground-state internal H-bond between the two −OH groups (displayed by the very different p*K*values, 5.4 and 15.6). Experiments were carried out in the whole acidity range (8 M $HClO_4$ to 10 M NaOH) using steady-state and time-resolved fluorimetry. In concentrated $HClO_4$, competitive quenching processes occurred, due to $HClO_4$ itself and to water, respectively, but no photoinduced deprotonation was observed. The former quenching was confirmed by studying the emission of 2,6-naphthalenedisulfonic acid in the same media. Photoinduced deprotonation from the first −OH group was only observed in diluted acidic solutions ($[HClO_4] \leq 1$ M), within 500 ps, leading to an intermediate species IS*, which in turn leads to the monoprotonated form HCA^{3-}* within ≈230 ps. The structure of HCA^{3-}* is resonance stabilized by an internal charge transfer. The lifetime of HCA^{3-}* is 2.1 ns. The structure of IS* was tentatively proposed to be an ion pair between H^+ and the hydroxylate form of HCA^{3-}*. The p*K** value of the first −OH group (≈1.8) was deduced from the rate constants. A moderate photoacidity ($\Delta pK \approx -3.6$ p*K* units on excitation) is then displayed. Regarding the second −OH group, its photoinduced deprotonation was never observed, even in strongly basic solutions (1 M ≤ [NaOH] ≤ 10 M), which points out the outstanding stability of HCA^{3-}*. The lifetime of the fully deprotonated form (1.76 ns) could only be measured after direct excitation in 10 M NaOH.

Introduction

Bidentate ligands are compounds whose two complexing functions are generally acido−basic functions. Some of such ligands are fluorogenic reagents, that means that several of their metal chelates are much more fluorescent than the free ligands themselves. Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid, Chart 1) belongs to this class of compounds. Although it is a well-known chelating agent,[1] its fluorogenic character is nevertheless not often reported; most metal determinations using chromotropic acid in fact rely on spectrophotometric methods. Concerning fluorimetric determinations, there are only a few papers, which essentially deal with chelations of boron,[2] beryllium,[3] or aluminum.[4,5] In these studies, analytical methods were developed using the enhancement of fluorescence observed on chelation. However, this phenomenon was not explained, and even less explained was the possible excited-state processes underlying the fluorescence of the free ligand.

Chromotropic acid is a dihydroxynaphthalene derivative. It can therefore be expected to exhibit very different acidic behaviors in the ground and excited states, as many hydroxyaromatic compounds do, for instance, 1-naphthol,[6] 2-naphthol,[7] pyranine,[8,9] etc. In the latter compounds, the hydroxyl group is a much stronger acid in the S_1 excited state than in the ground state, and a proton is photoejected in aqueous solutions, even at acidic pH values. However, in chromotropic acid, two functional groups are present, and one may wonder whether synergistic effects between them occur upon $S_0 \rightarrow S_1$ excitation and how such effects could influence the possible photoinduced deprotonation.

CHART 1



Chromotropic acid

Nevertheless, as far as we are aware, no study of the excited-state behavior of chromotropic acid in aqueous solution has ever been reported yet. The study presented here is, accordingly, undertaken with the objective of clarifying this question. The fluorescence emission of chromotropic acid will be investigated using steady-state and time-resolved fluorimetric measurements, as a function of either acidity in concentrated perchloric

* To whom correspondence should be addressed. E-mail: bardez@cnam.fr.
† CNRS, UMR 8531 (Conservatoire National des Arts et Métiers et ENS de Cachan).
‡ Instituto Superior Técnico.

10.1021/jp0112673 CCC: $20.00
Published on Web 10/19/2001

TABLE 1: Ground-State pK_a Values of Chromotropic Acid

method[a]	ionic strength (M)	pK_4 (H_4CA/H_3CA^-)	pK_3 (H_3CA^-/H_2CA^{2-})	pK_2 (H_2CA^{2-}/HCA^{3-})	pK_1 (HCA^{3-}/CA^{4-})	ref
P/S[b]				5.36 ± 0.01[e]	15.6 ± 0.3	10
P[b]	0.1			5.53	>12.75	11
S[b]	0.1			5.44 ± 0.03	>14	12
P[c]	0.1			5.38 ± 0.01		13
P[d]	0.2			4.99 ± 0.01		14
P[c]	0.1			5.50	13.30	15
P/S[b]		0.61 ± 0.02	0.73 ± 0.03	5.45 ± 0.03[e]	15.5 ± 0.1	16
P[b]	0	0.09 ± 0.11	0.80 ± 0.05	4.61 ± 0.02	12.37 ± 0.05	17
P[c]	0.1			5.35 ± 0.01	13.0	18
P[c]	0.5			5.3	11.8	19

[a] P, potentiometry; S, spectrophotometry. [b] 20 °C. [c] 25 °C. [d] 30 °C. [e] Ionic strength = 0.1 mol L^{-1}.

solutions, or pH in diluted aqueous solutions, or basicity in concentrated sodium hydroxide solutions. The results will allow us to show dissimilar behaviors of the two −OH functions, together with an outstanding stability of the monoprotonated form, even in the excited-state where its structure turns out to be stabilized by intramolecular charge transfer.

Experimental Section

Chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dihydrate) was purchased from Aldrich and twice recrystallized from water−ethanol mixtures. 2,6-Naphthalenedisulfonic acid disodium salt (Aldrich, 97%) was used as received.

Redistilled perchloric acid from Aldrich containing 69.5% $HClO_4$ (purity: 99.999%) was used to prepare the acidic solutions. Every acidic solution was obtained by weighing appropriate amounts of the commercial concentrated $HClO_4$ in volumetric flasks and by addition of water up to the desired volume. Similarly, every concentrated sodium hydroxide (Aldrich, 99.998%) solution was constituted by weighing. Thus, the error on the [$HClO_4$] or [NaOH] concentrations was less than 0.5%. Buffers were from Prolabo (Normadoses). Millipore filtered water (conductivity $< 1 \times 10^{-7}$ Ω^{-1} cm^{-1} at 25 °C) was employed to prepare the solutions.

Most of the solutions of chromotropic acid were prepared by addition of an aliquot of an ethanolic stock solution of purified chromotropic acid (concentration $\geq 6 \times 10^{-4}$ mol L^{-1}) to the desired medium. In every case, the addition of ethanol to the aqueous solution did not exceed 2% v/v. In concentrated basic media, an aqueous stock solution was used instead, because of the impossibility of mixing ethanol and concentrated sodium hydroxide solutions. For every fluorimetric (steady-state and time-resolved) experiment, the final concentration was $(1.19 \pm 0.01) \times 10^{-5}$ mol L^{-1}.

It must be mentioned that alcoholic stock solutions of chromotropic acid, kept in the dark, could be stored without degradation. On the contrary, aqueous stock solutions could not, and fresh solutions must be prepared prior to each experiment. Otherwise, they became yellow as a result of possible photooxidation. Even the diluted aqueous solutions underwent photobleaching because of the excitation light, especially above pH = 4.

Moreover, when studying the fluorescence emission of chromotropic acid, the greatest care had to be taken to avoid contamination by metal ions that are able to form fluorescent complexes with chromotropic acid. Many metal chelates are much more fluorescent than the free ligand, in particular from pH = 4−7. Low concentrations of metal ions, such as 10^{-8}−10^{-7} mol L^{-1}, may induce a significant contribution in the global fluorescence emission, in solutions where the ligand concentration is typically $\approx 10^{-5}$ mol L^{-1}.

UV−vis absorption spectra were recorded on a Kontron Uvikon-940 spectrophotometer. The corrected fluorescence spectra were obtained with a SLM 8000C spectrofluorometer. The excitation wavelength was 316 nm for the acidic and neutral solutions and 350 nm for the concentrated basic ones (isosbestic points). To avoid the decrease of signals due to photodegradation of chromotropic acid under the light source during the recording of the spectra, especially above pH = 4, the solutions were stirred and the excitation bandwidth was not larger than 2 nm. Fluorescence quantum yields were measured using PPO in undegassed cyclohexane as the standard ($\Phi_F = 0.90$).

The fluorescence decay curves were obtained by the single-photon timing technique with picosecond laser excitation. The setup consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (DCM) laser, delivering 3−4 ps pulses (with ca. 40 nJ/pulse) at a frequency of 3.4 MHz. The laser excitation pulse ($\lambda_{exc} = 330$ nm) was recorded slightly away from excitation wavelength with a scattering suspension. Fluorescence was detected through a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm. The detector employed was a Hamamatsu 2809U-01 microchannel plate photomultiplier. The instrument response function had an effective fwhm of 35 ps. The temperature of the samples was 20 °C. The data were analyzed by a nonlinear least-squares method using Globals software (Globals Unlimited, University of Illinois at Urbana−Champaign, Laboratory for Fluorescence Dynamics).

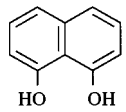
Results and Discussion

Ground-State Acidity Constants. Chromotropic acid possesses four acido−basic functions, i.e., two sulfonic acid functions and two hydroxyl groups. The former functions are known to be strong and ionized in the usual pH range of aqueous solutions. The latter functions are of phenolic type. The fully protonated form will be further denoted H_4CA and the other forms H_3CA^-, H_2CA^{2-}, HCA^{3-}, and CA^{4-} respectively.

Many determinations of the −OH groups pK_a values were carried out.[10−19] On the contrary, only two papers give pK_a values for the $-SO_3H$ functions.[16,17] Most of the published values are collected in Table 1. Concerning the sulfonic groups, even if the two pK_4 values are not in agreement, their strong acidity is confirmed, and they can be considered fully ionized above pH = 1. Consequently, the ionization of the first −OH group occurs from the disulfonate form (H_2CA^{2-}).

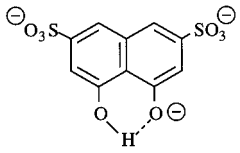
Table 1 shows that the authors generally agree about the acidity constant K_2 of the first −OH function. Most of pK_2 values are lying in the range of 5.3−5.5; that is, p$K_2 = 5.4 \pm$

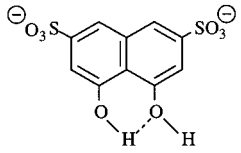
CHART 2



1,8-Dihydroxynaphthalene

CHART 3





0.1 at room temperature. This value is about four pK_a units lower than the pK_a values of phenol or naphthols and one pK_a unit lower than the pK_a value of the first hydroxyl group of 1,8-dihydroxynaphthalene (Chart 2), i.e., 6.36.[18]

The difference between the pK_2 of chromotropic acid and 1,8-dihydroxynaphthalene is accounted for by the presence of the sulfonate groups whose attractive effect usually lowers the pK_a of the −OH group present on the same ring by ca. 1 pK_a unit. Moreover, the pK_a gap between 1,8-dihydroxynaphthalene and phenol or naphthols (≈3 pK units) is usually ascribed to the respective position of the hydroxyl groups, which brings about the strong increase in the mobility of the first leaving proton (see below). What about the second leaving proton?

When looking at Table 1, discrepancies can be noticed concerning the pK_a of the second −OH group, i.e., pK_1(HCA^{3-}/CA^{4-}), according to the experimental determination method, potentiometry, or spectrophotometry. In fact, pK_1 is too large to be determined by potentiometry and must be measured by a spectrophotometric method. The actual value of pK_1 is reported in refs 10 and 16. This value, pK_1 = 15.6 ± 0.3, could be confirmed by us (see below the spectra recorded in strongly basic media). The ground-state monoprotonated form HCA^{3-} is then of utmost stability.

It is worth noting that the corresponding pK_a for 1,8-dihydroxynaphthalene is also very large, reported to be too high to be measured.[18] An internal H-bonded structure is usually assumed to be responsible for the lack of ground-state acidity of the monoprotonated forms for both compounds. Besides, the internal H bond is supposed to be retained in the H_2CA^{2-} species and to cause the mobility of the first −OH proton.[1] Chart 3 shows the structure of HCA^{3-} and H_2CA^{2-}. No other conformers were ever shown to exist.

Absorption Spectra. The absorption spectra were recorded in the whole range of acidity, from 8 M $HClO_4$ to 10 M NaOH. In $HClO_4$ solutions, dilution from 8 mol L^{-1} to pH = 3.4 did not modifiy the absorption spectrum, showing that deprotonation of the sulfonic acid groups has no effect on the spectrum. Then, all of the forms H_4CA, H_3CA^-, and H_2CA^{2-} have the same absorption spectrum (number 1 in Figure 1) with vibronic maxima at 315, 331, and 347 nm.

Figure 1 also shows the spectra of the HCA^{3-} and CA^{4-} forms. The spectrum of the HCA^{3-} form could be recorded in moderately basic solutions, i.e., from pH = 7.4 to 0.1 mol L^{-1} NaOH. It is less structured and red-shifted (λ_{max} = 330, 346, and 360 nm) compared to that obtained in acidic medium. In 10 mol L^{-1} NaOH (concentration corresponding to the saturation at room temperature, H_- = 16.2[20]), the absorption spectrum is supposed to be nearly that of the CA^{4-} form. The vibrational

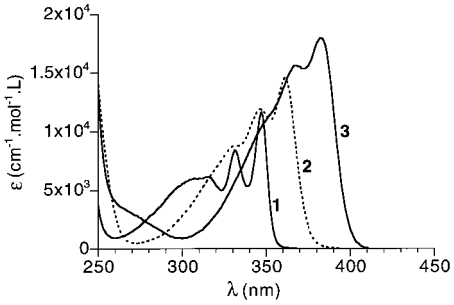


Figure 1. Absorption spectra (expressed by the molar absorption coefficient ϵ) of chromotropic acid. 1: H_2CA^{2-} form (same spectrum as for the H_4CA and H_3CA^- forms). 2: HCA^{3-} form. 3: CA^{4-} form (recorded in 10 M NaOH).

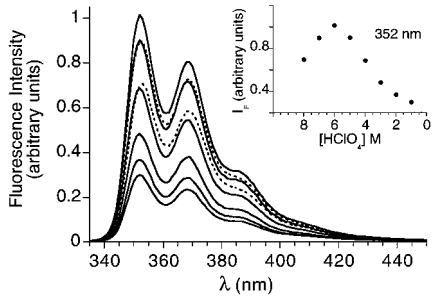


Figure 2. Corrected fluorescence spectra of the H_4CA^* form of chromotropic acid in concentrated $HClO_4$ solutions (λ_{exc} = 316 nm). Dotted lines, from bottom to top: [$HClO_4$] = 8 and 7 M. Solid lines, from top to bottom: [$HClO_4$] = 6, 5, 4, 3, 2, and 1 M. Insert: Evolution of the fluorescence intensity measured at 352 nm as a function of the decreasing [$HClO_4$] values.

structure becomes further blurred, and the red shift increases (λ_{max} = 351, 367, and 382 nm).

Fluorescence Spectra and Time-Resolved Measurements. The fluorescence emission study was carried out in the whole acidity range similar to that for the absorption spectra. The chromotropic acid concentration was the same in every solution (see the Experimental Section). The evolution of the spectra and the time-resolved measurements will be described considering successively three reduced acidity ranges.

Concentrated Perchloric Acid Solutions (1 M ≤ [$HClO_4$] ≤ 8 M). In concentrated perchloric acid solutions, progressively diluted such as [$HClO_4$] decreased from 8 to 1 mol L^{-1}, the shape of the fluorescence spectra obtained on excitation at 316 nm remained strictly the same, but the fluorescence intensities depended on the $HClO_4$ concentration (Figure 2). The wavelengths of the maxima were λ_{max} = 352, 369, and 386 nm. The spectra in the most concentrated perchloric acid solutions ([$HClO_4$] = 8 and 7 mol L^{-1}) were slightly red-shifted (≈1 nm) compared to the other spectra, and an increase in the fluorescence intensity was observed by dilution of perchloric acid from 8 to 6 mol L^{-1}. Then, further dilution led to a continuous decrease that became weaker when approaching [$HClO_4$] = 1 mol L^{-1}. The insert in Figure 2 shows this evolution of the fluorescence intensity at the maximum wavelength 352 nm, upon progressive dilution of the perchloric acid.

In this acidity range, the only species present in the ground-state is the fully protonated H_4CA form. The question is then, Can the evolution of the emission spectra be ascribed to photoinduced deprotonation of the excited H_4CA^* form? However, excited-state deprotonation is expected to lead to another emitting species and to some resulting modification (even slight) of the spectrum shape, which is not observed. Consequently, some medium effects may rather be thought to be responsible of the observed evolution of the spectra.

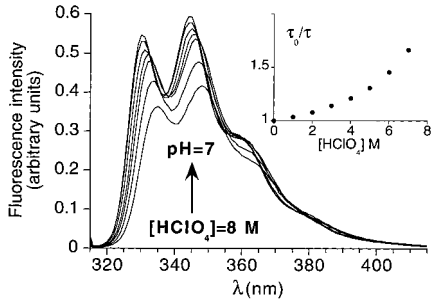


Figure 3. Corrected fluorescence spectra of NDSA as a function of $HClO_4$ concentration. From bottom to top: $[HClO_4] = 8$, 7, 6, 5, 3, and 1 M and buffer pH = 7. Insert: Plot of the ratio τ_0/τ (τ_0 being NDSA lifetime in pH = 7 buffer (where no quenching occurred) and τ the NDSA lifetime in each acidic solution) as a function of $[HClO_4]$. For both experiments: $\lambda_{exc} = 312$ nm.

Considering the increase of the emission intensity when going from 8 to 6 mol L^{-1}, it can be due to the weakening of a quenching process usually attributed to the protonation of the naphthalene ring by the strongly protonating perchloric acid. This hypothesis was checked by studying the behavior of 2,6-naphthalenedisulfonic acid (NDSA) in perchloric acid solutions. Such a quenching was indeed observed, as shown in the fluorescence spectra (Figure 3). The concomitant decreases of the NDSA fluorescence emission and lifetime, when $[HClO_4]$ increased, revealed the existence of a dynamic quenching. However, the plot of the ratio τ_0/τ (τ_0 being NDSA lifetime in pH = 7 buffer, in absence of quenching, and τ being the NDSA lifetime in each acidic solution) as a function of $[HClO_4]$ (see insert in Figure 3) showed a marked departure from Stern−Volmer linearity, especially for the highest acid concentrations. Such a departure from linearity may be due to static quenching often taking place at high concentrations of quencher in addition to dynamic quenching; this results in nonlinearity of the Stern−Volmer plot. However, the variations of τ_0/τ vs $[HClO_4]$ could not be satisfactorily fitted to a second degree polynomial function (expected from a 1:1 association of NDSA with the quencher $HClO_4$) nor to an exponential function (expected from the model of active sphere). In the present case, another reason for nonlinearity can be invoked: the variable $[HClO_4]$ was inadequate for representing the strong protonating power of the concentrated $HClO_4$ solutions, but the use of the Hammett acidity function H_0 as a variable still led also to a similar nonlinearity (not shown). The quenching processes thus turned out to be quite complex, and a better understanding would require further investigations that are out of the scope of the present paper.

By comparison with NDSA, the variations in fluorescence intensity of chromotropic acid upon dilution of $HClO_4$ are quite different. In the case of NDSA, the continuous increase of the fluorescence intensity when $HClO_4$ was diluted from 8 mol L^{-1} until pH = 7 showed a sole process of proton quenching. In the case of chromotropic acid, the increase in the fluorescence intensity from $[HClO_4] = 8$ to 6 mol L^{-1} was followed by a marked decrease occurring below $[HClO_4] = 6$ mol L^{-1}. This behavior may be correlated to the presence of the −OH groups on the naphthalene ring and, consequently, to some additional nonradiative deexcitation pathway when solvation built up an hydrogen bond network around the −OH groups. This interpretation was supported by both quantum yields and decay times measurements.

Thus, for each acid concentration studied in the range $[HClO_4] = 8$ to 1 mol L^{-1}, the quantum yield Φ_F of the H_4CA^* form was measured and the fluorescence decays were recorded; the decays, monitored at 350, 369, 386, and 410 nm, showed similar single exponential decreases at each wavelength. Thus, the H_4CA^* lifetime τ was determined for each perchloric acid concentration. Results are given in Table 2.

TABLE 2: Quantum Yields, Decay Times, and Deexcitation Rate Constants of Chromotropic in Concentrated Acidic Solutions When $HClO_4$ Was Diluted from 8 to 1 mol L^{-1}

$[HClO_4]^a$ (M)	τ^b (ns)	$\Phi_F{}^c$	$k_r/10^8$ $(s^{-1})^d$	$k_{nr}/10^9$ $(s^{-1})^d$
8	1.39	0.13	0.90	0.63
7	1.71	0.17	0.97	0.49
6	1.82	0.18	1.00	0.45
5	1.60	0.16	1.00	0.53
4	1.23	0.12	0.98	0.72
3	0.79	0.085	1.07	1.16
2	0.60	0.060	1.00	1.57
1	0.46[e]	0.053	1.15	2.06

[a] Accuracy < 0.5%. [b] Accuracy = 5%. [c] Accuracy = 8%. [d] Accuracy = 13%. [e] In this case, the decay was better fitted by a sum of three exponentials, rather than by a single exponential (see Table 3). Nevertheless, the 0.46 ns component is predominant (fractional preexponential factor between 0.83 and 0.90).

The radiative and non radiative decay rate constants were then calculated from

$$k_r = \frac{\Phi_F}{\tau} \qquad k_{nr} = \frac{1 - \Phi_F}{\tau}$$

In fact, the radiative rate constant k_r remains constant from $[HClO_4] = 7$ to 1 mol L^{-1}, whereas the non radiative rate constant k_{nr} varies, increasing with dilution for $[HClO_4] < 6$ mol L^{-1} (Table 2). This is consistent with a quenching process due to water, opposite to the quenching due to $HClO_4$. Unfortunately, in such conditions, it appears to be impossible to determine the actual lifetime of the H_4CA^* form, independently of any quenching effect.

From [HClO$_4$] = 1 M to [NaOH] = 0.1 M. The fluorescence spectra recorded from $[HClO_4] = 1$ M (pH ≈ 0) to [NaOH] = 0.1 M were obtained by excitation at 316 nm, i.e., at the isosbestic point wavelength (Figure 4). The studied solutions can be divided into three parts, according to the value of their pH compared to the pK_2 value (p$K_2 = 5.4 \pm 0.1$). For pH = 3.3, the predominant ground-state species is H_2CA^{2-}, whereas it is HCA^{3-} in basic media (buffer pH = 10, NaOH 10^{-3} and 10^{-1} M). When pH increases from 3.9 to 7, the ground-state H_2CA^{2-} form progressively converts into the HCA^{3-} form.

For pH ≤ 3.3, when the only ground-state species was H_2CA^{2-}, a continuous change of the shape of the fluorescence spectra was observed between pH = 0 and 2.9. The variation was pronounced until pH = 2.6 and very small between pH = 2.6 and 2.9. Above pH 2.9, the spectra were invariant until pH = 3.3 (Figure 4A). The bands at 352 and 369 nm progressively decreased, with the lowering of the former band being somewhat more pronounced than that of the latter (Figure 4B). Besides, the band at 386 nm and a new wide band, whose maximum is around 430 nm, began to rise up. This evolution shows that the excited $H_2CA^{2-}*$ form underwent an excited-state transformation, whose apparent dependence on pH became weaker when the pH increased.

Between pH = 3.9 and 7, excitation swung from H_2CA^{2-} to HCA^{3-}. The spectral evolution started again in line with the previous one (Figure 4 parts A and B). At pH = 5.2, the bands at 369 and 386 nm were higher than the band at 352 nm. From pH = 5.6 to 7, the bands at 369 and 386 nm progressively disappeared, whereas the broad band with $\lambda_{max} = 430$ nm grew up.

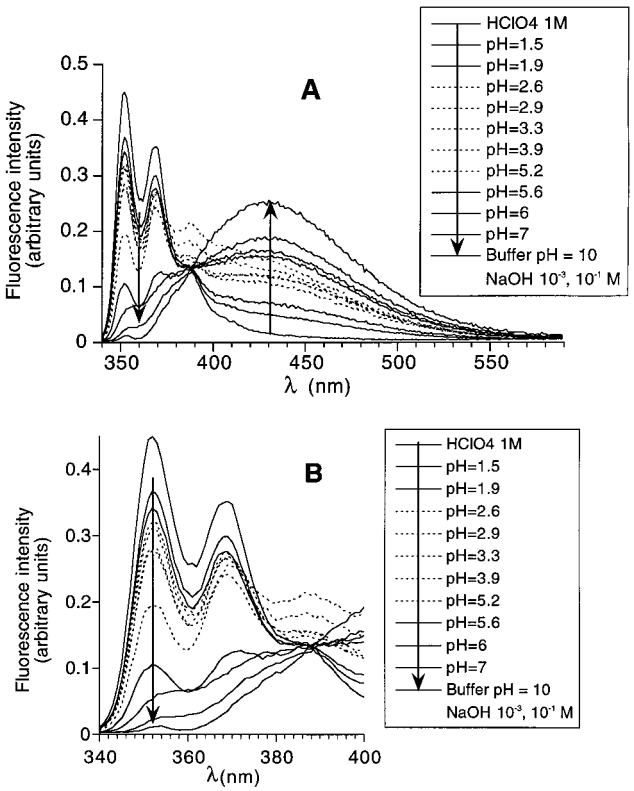


Figure 4. (A) Corrected fluorescence spectra of chromotropic acid, when going from pH $\approx$ 0 ([$HClO_4$] = 1 M) to 10^{-1} M NaOH. (B) Zoom on the blue edge of these spectra (λ_{exc} = 316 nm).

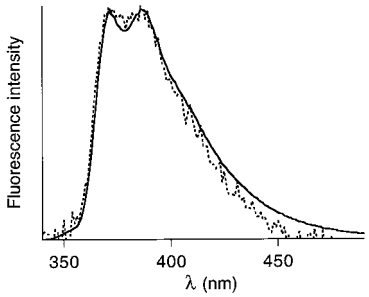


Figure 5. Dotted line: Corrected fluorescence spectrum obtained by subtracting the spectra recorded in 4 M $HClO_4$ and in pH = 10 buffer, respectively, from the emission spectrum of chromotropic acid at pH = 3.9 (or 5.2), after appropriate normalizations at 352 and 500 nm, respectively. Solid line: Corrected fluorescence spectrum the 1:1 aluminum chelate of chromotropic acid recorded in aqueous solution at pH = 4, and for a ratio [aluminum]/[ligand] = 10 (λ_{exc} = 316 nm). Both spectra were normalized at 386 nm for comparison.

In basic media (buffer pH = 10, 10^{-3}, and 10^{-1} M NaOH), the sole ground-state form undergoing excitation was HCA^{3-}. The fluorescence spectra turned out to be identical (Figure 4A). They mainly consisted of the broad band whose maximum is at 430 nm.

The whole evolution of the emission spectra did not show a single isoemissive point, but an intermediate rise of the vibronic band at 386 nm coupled with the band at 369 nm, particularly from pH = 2.6 to 5.2. It was possible to extract this intermediate contribution by subtracting the spectrum of H_2CA^{2-}* (recorded in strongly acidic media, for example, in 4 M $HClO_4$), plus the spectrum obtained in basic media (for example, at pH = 10), from the spectra obtained at either pH = 3.9 or 5.2. Similar results were obtained (Figure 5, dotted line).

The analogy between this difference spectrum and the emission spectrum of the 1:1 aluminum chelate of chromotropic acid (Figure 5, solid line) is striking.[21] Because the emission of other metal chelates is similar to that of the aluminum chelate,[2−4] one may wonder whether some metallic contamination could have been the reason of the intermediate fluorescence emission. However, this hypothesis can be ruled out when considering the results of the time-resolved experiments. The fluorescence decays could be analyzed in a sum of three exponentials from pH $\approx$ 0 to 5.2 (see below, and Table 3). If one of these components was a chelate decay, this would signify that a metal chelate could be formed already at pH $\approx$ 0, which was never observed at so low pH value.[1−5,21] The chelate lifetime would rather be an additional constant decay time only between pH $\approx$ 2.6 and 5.2. However, τ_1 occurs from [$HClO_4$] = 1 M (pH $\approx$ 0) to [NaOH] = 0.1 M, τ_3 is always a rise time, and τ_2 appears in some analysis as a rise time. Moreover, no time evolution of the chromotropic acid spectra was observed as soon as the samples were made, whereas complexation of $\approx 10^{-5}$ M chromotropic acid with an undesirable metal ion, expected to be at a concentration lower than 10^{-5} M, should occur over more than 10 min at pH $\approx$ 4.[21] The last argument in disfavor of the presence of a chelate is that the evolution of the emission spectra from pH = 2.6 to 5.2 was unchanged in solutions buffered with $\approx$0.1 M citric acid/sodium citrate. In such solutions, a citric buffer behaves as a masking agent for most metal ions that are preferentially complexed by citrate ions than by a ligand whose typical concentration is $\approx 10^{-5}$ mol L^{-1}.

Therefore, the intermediate band can rather be ascribed to an intermediate species arising between two successive excited-state processes following excitation of H_2CA^{2-}*. The first mechanism to be considered is composed of two successive excited-state deprotonations from H_2CA^{2-}* to CA^{4-}*. The first step would lead to HCA^{3-}*, which is consistent with an enhancement of acidity of the first −OH group upon excitation, as often observed for hydroxyaromatic compounds (see the Introduction). However, the fluorescence spectrum of CA^{4-}* obtained by direct excitation of CA^{4-} in 10 M NaOH (see below, and in Figure 6) is different from the spectrum recorded in diluted 10^{-3} and 10^{-1} M NaOH (Figure 4A), which rules out the hypothesis of two successive excited-state deprotonations from H_2CA^{2-}*. Thus, in pH = 10 buffer or in either 10^{-3} or 10^{-1} M NaOH, the ground-state species is HCA^{3-} and the emission spectrum is therefore that of the HCA^{3-}* form.

TABLE 3: Decay Times of Chromotropic Acid in Moderately Acidic, Neutral, and Moderately Basic Solutions ([$HClO_4$] = 1 M to [NaOH] = 0.1 M), Obtained by Global Analysis of the Fluorescence Decays Recorded at 350, 369, 386, 420, and 500 nm, Respectively, for Each Solution (0.9 $\leq \chi^2 \leq$ 1.2)

solution	pH	τ_1 (ns)	τ_2 (ps)	τ_3 (ps)[a]
[$HClO_4$] = 1 M	$\approx$0	0.8−1.7	460 ± 40	50 ± 10
[$HClO_4$] = $3.5_5 \times 10^{-2}$ M	1.4_5	0.9 ± 0.2	460 ± 50	200 ± 15
[$HClO_4$] = 1.0×10^{-2} M (or buffer pH = 2)[b]	2.0	1.2 ± 0.1	400 ± 50[a]	200 ± 50
[$HClO_4$] = 3.2×10^{-3} M	2.5	1.6 ± 0.1	450 ± 30[a]	220 ± 10
[$HClO_4$] = 1.0×10^{-3} M (or buffer pH = 3)[b]	3.0	2.0 ± 0.1	440 ± 20[a]	215 ± 15
[$HClO_4$] = 1.3×10^{-4} M	3.9	2.10 ± 0.05	500 ± 50	250 ± 25
[$HClO_4$] = 6.3×10^{-6} M	5.2	2.15 ± 0.05	520 ± 20	230 ± 10
buffer	6.0	2.10 ± 0.1		230 ± 30
buffer	7.0	2.15 ± 0.05		270 ± 40
[NaOH] = 1.0×10^{-3} M[c]		2.10 ± 0.05		
[NaOH] = 1.0×10^{-1} M[c]		2.10 ± 0.05		

[a] Rise time at 420 and 500 nm. [b] The reproducibility of the measurements carried out in the perchloric acid solution was checked in a buffer solution. [c] Decays only recorded at 369, 386, 420, and 500 nm.

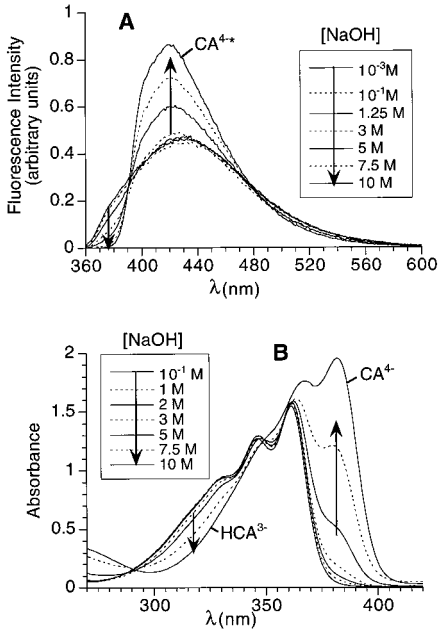


Figure 6. Corrected fluorescence spectra (A) and absorption spectra (B) of chromotropic acid in concentrated NaOH solutions (A, λ_{exc} = 350 nm; B, concentration of chromotropic acid = 1.1×10^{-4} mol L^{-1}).

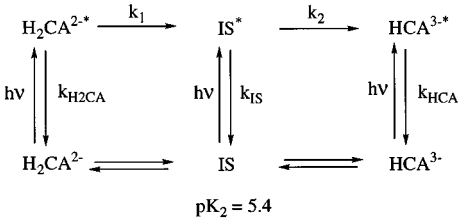
HCA^{3-}* must then be the ultimate excited-state species obtained by photoinduced deprotonation of H_2CA^{2-}* at lower pH values. Consequently, the excited-state conversion of H_2CA^{2-}* into HCA^{3-}* turns out to be a two-step process.

Before considering in detail a possible mechanism, let us examine the structure of the monoprotonated form HCA^{3-}* in the excited state. The shape of its emission spectrum is noteworthy. The spectrum mainly consists of a broad and structureless band whose λ_{max} is 430 nm, which looks like a charge transfer band. A charge reorganization is then expected, leading the molecule to possibly adopt ketonic forms. HCA^{3-}* is greatly stabilized by resonance (Chart 4). The internal H bond can be maintained between the hydroxyl group and the carbonyl group.

Concerning the intermediate species, further denoted IS*, its possible structure will be discussed below.

Let us see now the time-resolved measurements carried out in the same pH range as the steady-state study. Thus, the experiments were performed in seven perchloric acid solutions, whose pH's were ≈0, 1.4_5, 2.0, 2.5, 3.0, 3.9, and 5.2, in two solutions buffered at pH = 6.0 and 7.0 and in two sodium hydroxide solutions (10^{-3} and 10^{-1} M). For each solution, the fluorescence decays were recorded at five emission wavelengths: 350, 369, 386, 420, and 500 nm (excitation at 330 nm). They could be analyzed in (i) a sum of three exponentials from pH ≈ 0 to 5.2, (ii) a sum of two exponentials at pH = 6 and 7, and (iii) one exponential in 10^{-3} and 10^{-1} NaOH solutions (Table 3).

SCHEME 1



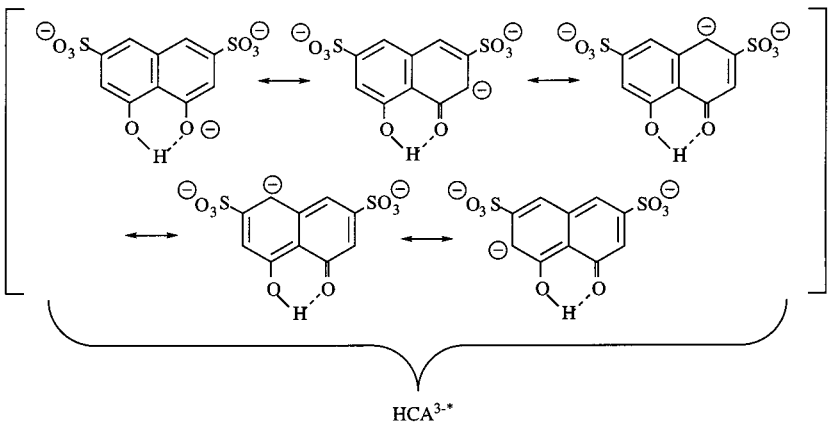
From pH ≈ 0 to 5.2, H_2CA^{2-} was either the only form present in the ground state (pH = 0, 1.4_5, 2.0, 2.5, and 3.0) or the main one (at pH = 3.9 and 5.2). Two cases can be distinguished when considering the decay times: (i) At pH ≤ 3.0, the values of the decay times were pH dependent. (ii) At pH > 3.0, the three decay times (τ_1 = 2.1 ns, τ_2 ≈ 500 ps, and τ_3 ≈ 230 ps) became independent of pH, within experimental error.

Moreover, at the longest wavelengths 420 and 500 nm, τ_3 was always a rise time (negative preexponential factor). The existence of three decay times, one of them being a rise time at the longest emission wavelengths, is consistent with the occurrence of two successive photoinduced processes from H_2CA^{2-}*. The corresponding kinetic equations and complementary comments will be given below.

Above pH = pK_2 = 5.4, the predominant ground-state form is HCA^{3-}. However, still at pH = 6 and 7, a biexponential decay (τ_1 = 2.1 ns and τ_3 ≈ 230−270 ps) was observed, τ_3 being a rise time at the longest wavelengths, 420 and 500 nm. However, the contribution of the τ_3 component became weak (consistently with the decreasing contribution of H_2CA^{2-} in the ground state), and the accuracy on the τ_3 value was getting worse. The 2.1 ns component was dominant, and extraction of a third component out of the decay was not reliable. These results show consequently that the lifetime of HCA^{3-}* is 2.1 ± 0.1 ns, consistently with the single decay time in 10^{-3} and 10^{-1} NaOH solutions (Table 3).

At pH > 3, when the decay times appear to be independent of pH, the following mechanism of the photoinduced processes triggered by excitation of H_2CA^{2-} and/or HCA^{3-} (according to pH) can be proposed (Scheme 1): k_{H2CA}, k_{IS}, and k_{HCA} represent the reciprocal of H_2CA^{2-}*, IS*, and HCA^{3-}* intrinsic

CHART 4



lifetimes. k_1 and k_2 are the first-order rate constants of the two successive steps in the excited state.

Actually, in the excited state, the back reprotonation of HCA^{3-}* may be observed in sufficiently acidic solutions for allowing the diffusional recombination to occur. If k_D denotes the second-order diffusional rate constant, recombination is then expected when k_D [H^+] is competitive with the deexcitation rate constant of HCA^{3-}*. Because of the three negative charges of HCA^{3-}*, k_D is expected to be larger than the value of $\approx 4 \times 10^{10}$ mol^{-1} L s^{-1} assumed at infinite dilution for recombination of a proton with a neutral molecule and can reach 10^{11} mol^{-1} L s^{-1}.[22] With the lifetime of HCA^{3-}* being 2.1 ns, the excited-state proton recombination may be observed in acidic media until pH $\approx$ 2.5−3.

After a δ-pulse excitation of the sole H_2CA^{2-} species, the following rate equations may be written from the kinetic scheme:

$$\frac{d[H_2CA^{2-}*]}{dt} = -(k_1 + k_{H2CA})[H_2CA^{2-}*]$$

$$\frac{d[IS*]}{dt} = -(k_{IS} + k_2)[IS*] + k_1[H_2CA^{2-}*]$$

$$\frac{d[HCA^{3-}*]}{dt} = -k_{HCA}[HCA^{3-}*] + k_2[IS*]$$

and the decays obey the following equations:

$$[H_2CA^{2-}*] = [H_2CA^{2-}*]_0 e^{-(k_1+k_{H2CA})t}$$

$$[IS*] = \frac{[H_2CA^{2-}*]_0 k_1}{X - Y}[-e^{-(k_1+k_{H2CA})t} + e^{-(k_2+k_{IS})t}]$$

$$[HCA^{3-}*] = \frac{[H_2CA^{2-}*]_0 k_1 k_2}{[Y - X][k_{HCA} - X][Y - k_{HCA}]}[(X - Y)e^{-k_{HCA}t} + (k_{HCA} - X)e^{-(k_2+k_{IS})t} + (Y - k_{HCA})e^{-(k_1+k_{H2CA})t}]$$

where

$$X = k_1 + k_{H2CA} \qquad Y = k_2 + k_{IS}$$

In the decay of [HCA^{3-}*], the sum of the preexponential factors is equal to 0.

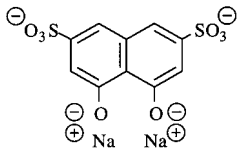
None of the decay times are, in fact, pH-dependent. On the contrary, for pH $\leq$ 3, a more sophisticated model must be proposed, including two back reactions in the excited state. One of them may be the diffusional reprotonation, and the corresponding pseudo first-order rate constant, k_D [H^+], depends of course on pH. The expressions of the decay constants are then more complex and pH dependent.

The results of the steady-state experiments carried out for 0 $\leq$ pH $\leq$ 5.2, and given above (Figure 4), are also consistent with those equations. The evolution of the emission spectra obtained by excitation of H_2CA^{2-} went on between pH = 0 and 2.9 (Figure 4A), but at pH = 2.9 and 3.3 (H_2CA^{2-} still being the only excited species), identical spectra were recorded (see above).

For the pH values where HCA^{3-} is the main ground-state species, i.e., at pH 6 and 7 in the present study, the decays contained the overwhelming 2.1 ns component (τ_{HCA}). The only observed component characterizing the H_2CA^{2-}* conversion was the rise time of 230 ps.

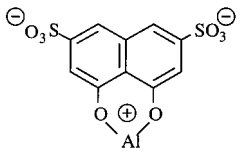
The results of the time-resolved measurements (Table 3) allow us to conclude that $1/(k_1 + k_{H2CA}) \approx 500$ ps and $1/(k_2 + k_{IS}) \approx$ 230 ps, given that $\tau_{HCA} = 1/k_{HCA} = 2.1 \pm 0.1$ ns. None of the two successive excited-state reactions is then rate-determining, which explains that it could be possible to observe the emission of the intermediate species IS* in the suitable pH range.

CHART 5



CA^{4-} and CA^{4-*}

CHART 6



1:1 Aluminum chelate of chromotropic acid

[NaOH] ≥ 0.1 M. The emission spectra obtained when increasing the concentration of sodium hydroxide showed the progressive appearance of the emission of the CA^{4-}* form (Figure 6A). The fluorescence spectrum of this form was obtained in 10 M NaOH, where the most predominant form in the ground state was the fully deprotonated CA^{4-} form. The wavelength of the maximum emission is then 420 nm. The emission spectrum does not include any charge-transfer band, contrary to the emission spectrum of HCA^{3-}*. The hydroxylate groups may then be fully stabilized by the sodium ions, in such a concentrated NaOH solution, as shown in Chart 5.

The evolution of the fluorescence spectra exactly matched the evolution of the absorption spectra around the value of pK_1 = 15.6 (Figure 6B). This implies that no excited-state deprotonation of HCA^{3-}* ever occurred despite the strong basicity of the medium. This important result has already been taken into account when the mechanism of the excited-state processes occurring in dilute aqueous solutions was built up. It means that the species HCA^{3-}* has no photoacid character.

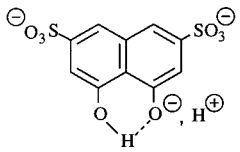
Lifetime determination of the CA^{4-}* form could be carried out either in 10 mol L^{-1} NaOH or, upon selective excitation at 390 nm, in solutions of sodium hydroxide of concentrations larger than 5 mol L^{-1}. The result was $\tau_{CA} = 1.76 \pm 0.01$ ns. No quenching effect due to the large concentrations of NaOH was observed.

IS Species.* Considering the results as a whole, a tentative structure of IS* can now be proposed. The analogy between IS* fluorescence spectrum (λ_{max} = 369 and 386 nm) and the emission spectrum of the 1:1 aluminum chelate of chromotropic acid[21] reported above (Figure 5) must be reminded. The aluminum complex, that bears one positive charge on the aluminum atom bound to the oxygen atoms (Chart 6), cannot undergo the charge transfer from the chelating oxygen atoms to the naphthalene ring, and in fact, its spectrum exhibits no charge-transfer band.

If a similar situation exists for the intermediate species, it would mean that the negative charge on the hydroxylate group generated by the deprotonation is not free to move. It could be balanced by the positive charge of H^+, with the proton remaining in the Coulomb cage of the anion bearing three negative charges. IS* might then be an ion pair (Chart 7).

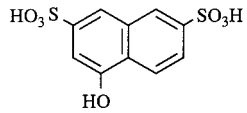
The kinetic scheme should then include a geminate recombination process[23,24] as the first reverse step in the excited state and, at pH $\leq$ 3.0, a diffusional reprotonation as the second

CHART 7



Tentative structure for IS*

CHART 8



1-Naphthol-3,6-disulfonate

reverse step. It is noteworthy that geminate recombination was shown to occur after deprotonation of the parent compound 1-naphthol-3,6-disulfonate[25] (Chart 8). The kinetic analysis should then require us to take into account the time-dependent diffusion equation.[25] This aspect will be the subject of a further investigation.

Finally, an evaluation of the excited-state pK_2* for chromotropic acid can be done from the rate constants. In a first approach (which is to be refined if geminate recombination is confirmed to occur), K_2* can be considered as the ratio k_1/k_D. Given that $1/(k_1 + k_{H2CA}) \approx 500$ ps and that $1/k_{H2CA}$ is expected to be at least 1.8 ns (even if it was not possible to determine its value precisely, see experiments in concentrated $HClO_4$ solutions and Table 2), k_1 may range around 1.5×10^9 s^{-1}. Assuming, as explained above, that $k_{-1} = 10^{11}$ mol^{-1} L s^{-1}, one obtains pK_2* ≈ 1.8. Such a result is fully consistent with the observation of proton ejection for $[HClO_4] \leq 1$ mol L^{-1}. Moreover, comparison with the previously reported value, pK_2* $= 2.82-2.86$ for 1,8-dihydroxynaphthalene,[26] shows the same pK difference of ca. -1 pK unit between the two excited-state pK_2* values and the two ground-state pK_2 values of the two compounds (see above).

Conclusion

The present work, which deals with the excited-state behavior of chromotropic acid in aqueous solutions, relies on a close investigation of its prototropic behavior and fluorescence emission from strongly acidic media to strongly basic media ($[HClO_4] = 8$ mol L^{-1} to $[NaOH] = 10$ mol L^{-1}).

In concentrated perchloric acid solutions ($[HClO_4] \geq 1$ mol L^{-1}), two fluorescence quenching phenomena of the fully protonated H_4CA form, due to $HClO_4$, on one hand, and to water, on the other hand, occur competitively. Below $[HClO_4] = 1$ mol L^{-1}, the sulfonic acid groups of chromotropic acid are deprotonated. Excitation of the H_2CA^{2-} form triggers the photoinduced deprotonation of one $-$OH group within $\approx$500 ps, and two successive steps lead to the monoprotonated form which rises within $\approx$230 ps. The characteristic times of the two steps are of the same order of magnitude; thus, none of them is rate determining, and the emission spectrum of the intermediate species IS* could be isolated. The lack of any charge-transfer band in this spectrum, contrary to the spectrum of HCA^{3-}*, allowed us to tentatively propose that IS* be an ion pair. Thus, between $[HClO_4] = 1$ mol L^{-1} and pH $= 7$, the fluorescence spectrum consists of the three contributions of H_2CA^{2-}*, IS*, and HCA^{3-}*. The result is a broadening of the emission spectrum over 250 nm, and in particular, between pH $= 3$ and 7 (i.e., under the usual pH conditions for metal ion complexation), the lack of any prominent emission band. The so-called "fluorogenic" character of the ligand chromotropic acid is, consequently, based on the fact that the free ligand displays an apparently "flat" spectrum, compared to the emission spectrum of fluorescent chelates.

In concentrated basic media, fluorescence from the fully deprotonated CA^{4-}* form is only observed after direct excitation of this form present in the ground state. With the corresponding ground-state pK being 15.6, one can see that the species HCA^{3-}* does not exhibit any photoacid character at all.

The excited-state stability of the monoprotonated form HCA^{3-}* must thus be pointed out, together with the completely asymmetric excited-state behavior of the two $-$OH groups of chromotropic acid, despite the symmetry of the molecule. The first proton is photoejected for $[HClO_4]$ lower than 1 mol L^{-1}, and the corresponding pK_2* value was evaluated to be 1.8. With the ground-state pK_2 being 5.4, the pK change upon excitation is $\Delta pK \approx -3.6$ pK units. The displayed photoacidity is then moderate compared to the well-known photoacids 1- and 2-naphthols whose ΔpK's are ≈ -9 and ≈ -7 pK units, respectively.[7] As for the second proton, it cannot be photoejected, even in concentrated sodium hydroxide solutions.

Acknowledgment. The authors wish to thank Professor Bernard Valeur for fruitful discussions, and acknowledge ICCTI and the French Embassy in Portugal for financial support.

References and Notes

(1) (a) Duda, J. *Wiad. Chem.* **1994**, *48*, 181. (b) Duda, J. *Chem. Soc. Rev.* **1994**, 425.
(2) (a) Lapid, J.; Farhi, S.; Koresh, Y. *Anal. Lett.* **1976**, *9*, 355. (b) Capitán, F.; Navalón, A.; Manzano, E.; Capitán-Vallvey, L. F.; Vilchez, J. L. *Fresenius J. Anal. Chem.* **1991**, *34*, 6.
(3) Pal, B. K.; Baksi, K. *Mikrochim. Acta* **1992**, *108*, 275.
(4) Baksi, K.; Pal, B. K. *Talanta* **1994**, *41*, 81.
(5) Park, C.-I.; Cha, K.-W. *Talanta* **2000**, *51*, 769.
(6) Krishnan, R.; Lee, J.; Robinson, G. W. *J. Phys. Chem.* **1990**, *94*, 6365.
(7) Förster, T. *Z. Elektrochem.* **1950**, *54*, 531.
(8) Bardez, E.; Goguillon, B. T.; Keh, E.; Valeur, B. *J. Phys. Chem.* **1984**, *88*, 1909.
(9) Pines, E.; Huppert, D. *Chem. Phys. Lett.* **1986**, *126*, 88.
(10) Heller, J.; Schwarzenbach, G. *Helv. Chim. Acta* **1951**, *34*, 1876.
(11) Zollinger, H.; Büchler, W. *Helv. Chim. Acta* **1951**, *34*, 591.
(12) Sakaguchi, M.; Mizote, A.; Miyata, H.; Tôei, K. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 885.
(13) L'Heureux, G. A.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1966**, *28*, 481.
(14) Athavale, V. Y.; Mahadevan, N.; Mathur, P. K.; Sathe, R. M. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1947.
(15) Banerjee, A.; Dey, A. K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 995.
(16) Budesinsky, B. *Talanta* **1969**, *16*, 1277.
(17) Kas, T. S.; Egorov, A. M. *Zh. Fiz., Khim.* **1972**, *46*, 2151.
(18) Letkeman, P.; Martell, A. E.; Motekaitis, R. J. *J. Coord. Chem.* **1980**, *10*, 47.
(19) Charlet, P.; Deloume, J. P.; Duc, G.; Thomas-David, G. *Bull. Soc. Chim. Fr.* **1985**, *5*, 683.
(20) Yagil, G. *J. Phys. Chem.* **1967**, *71*, 1034.
(21) Destandau, E.; Alain, V.; Bardez, E. Submitted.
(22) *Comprehensive Chemical Kinetics*; Bamford, C. H., Ed.; Elsevier: New York, 1985; Vol. 25, Chapter 2.
(23) Pines, E.; Huppert, D. *Chem. Phys. Lett.* **1986**, *126*, 88.
(24) Agmon N. In *Theoretical and Computational Models for Organic Chemistry*; Formosinho, S. J., et al., Eds.; Kluwer Academic Publishers: Norwell, MA,K 1991; pp 315−334.
(25) Masad, A.; Huppert, D. *Chem. Phys. Lett.* **1991**, *180*, 409.
(26) Dergacheva, L. D. *Opt. Spektrosk.* **1960**, *9*, 209.