ARTICLES

Effect of Substitution on the Photoinduced Intramolecular Proton Transfer in Salicylic Acid

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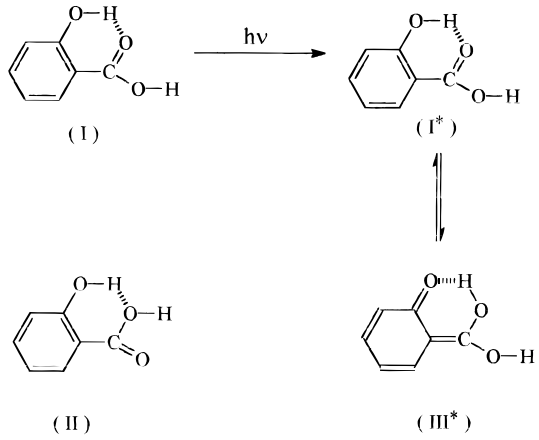
The influence of methyl and methoxy substitution in the *para* position of the phenolic OH functional group on the intramolecular proton-transfer properties of electronically excited salicylic acid (ESIPT) has been investigated both in solution and in the isolated gas-phase conditions provided by supersonic cooling. The dual fluorescence observed for 5-methylsalicylic acid (5-MeSA) in alkane solutions has been attributed for its blue part to the excited tautomer resulting from the intramolecular proton-transfer process and for its UV component to the dimer. A single fluorescence emission peaking at 400 nm is observed in alkane solutions of 5-methoxysalicylic acid (5-MeOSA). In the presence of proton acceptors such as diethyl ether, the 5-MeSA solution emits only in the blue region while 5-MeOSA exhibits two fluorescence bands at 400 and 475 nm. This behavior shows that the ESIPT process is promoted by complexation with proton-accepting molecules. In the supersonic expansion, the excitation and dispersed emission spectra of 5-MeSA are very similar to those previously observed for unsubstituted salicylic acid and show that the ESIPT mechanism takes place without barrier, in agreement with the model of a distorted potential surface in the excited state. In contrast, the 5-MeOSA excitation and dispersed fluorescence spectra present a mirror-image relationship that indicates that the molecule keeps a similar geometry in the ground and excited state. In this case the ESIPT reaction is prevented. Complexation with diethyl ether and acetone does not give rise to a dual fluorescence as in solutions but results in a broad emission extending toward the visible. This result may be explained by a modification of the excited potential energy surface along the tautomerization coordinate without introducing an energy barrier in the proton-transfer reaction.

Introduction

Since the pioneering work of Weller,[1] salicylic acid (SA, **I**) and its derivatives such as methylsalicylate (MS) represent prototypical molecular systems for the widely studied class of photochemical reactions usually referred to as excited-state intramolecular proton transfer (ESIPT).[2] These molecules have a strong intramolecular hydrogen bond between the phenolic hydroxy group and the nearby carbonyl proton-accepting group and become respectively more acidic and more basic in the excited state and as a consequence give rise in solution to a dual emission due to an excited-state intramolecular proton transfer (ESIPT) according to the following scheme:



Although the anomalous large Stokes shifted fluorescence (blue fluorescence) is assigned to the formation of tautomer **III*** resulting from ESIPT, the UV component of the fluorescence was first attributed by Weller to the fluorescence of the initially excited phenol form **I*** in equilibrium during its lifetime with the proton-transferred form **III***. Further work on methylsalicylate[3,4] has shown that the blue and UV emission components do not have the same excitation spectrum and thus arise from different ground-state species that have been assigned to the two rotameric forms of MS (**I** and **II**). Hence, the Weller hypothesis on keto−enol equilibrium in the excited state has been abandoned, although it might be valid for other molecules. Rotamer **II** cannot undergo excited-state tautomerization, since it involves a weak H−O···H−O bond between the oxygen atom of the carboxylic OH and the acidic phenolic OH and is responsible for the UV band. In nonpolar medium it is usually present to a minor extent relative to the main rotamer **I**, which is stabilized by the intramolecular H bond. However, for methylsalicylate in alcoholic solvents, it has been recently shown[5] that the relative population of rotamer **II**/rotamer **I** is expected to be increased because of the loss in intramolecular hydrogen bonding strength in rotamer **I** due to intermolecular H bonding with solvents molecules. These findings have been confirmed in the spectroscopic study of MS[6] and SA[7] in a supersonic jet where the two rotamers of SA have been discriminated by their absorption in different spectral regions. The most abundant rotamer (**I**) was shown to emit both in the UV and blue range depending on the excitation energy, and this behavior has been explained in terms of a single minimum distorted potential energy surface along the tautomerization coordinate similar to that proposed for methylsalicylate.[8] This

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interpretation is confirmed by the real time measurements for the proton-transfer reaction in the case of methylsalicylate, which has been shown to take place within 60 fs.[9]

In contrast to the salicylic acid and methylsalicylate behavior, the possibility of modulating the tautomerization reaction and of observing an excited-state equilibrium between enol and keto forms may be obtained by modifying the excited-state acidity of the phenolic OH. The introduction of a CH_3 or an alkoxy electron-donating group in the *para* position of the phenolic OH is known to reduce its proton-donating ability. The effect of an ethoxy substituent in the 5 position of methylsalicylate has been first investigated by Weller[1] 30 years ago and studied further in the case of methoxy by Acuña et al.[10] both in the gas phase and in solution. The fluorescence of this methoxy compound exhibits a strong maximum at 400 nm and a shoulder at 490 nm. Both emissions at 400 and 490 nm have the same excitation spectrum, indicating that they originate from the same ground-state species. Thus, the 400 nm emission observed in 5-methoxysalicylate deviates appreciably from the usual UV emission of other salicylic derivatives and may be attributed to the emission from the initially excited rotamer **I** in its enol form, while the 500 nm shoulder is indicative of the ESIPT process. This behavior may be thus explained by a mechanism involving a keto−enol equilibrium in the excited state. The present work is aimed at investigating the photophysical properties of 5-methyl- and 5-methoxysalicylic acids in solution and in the isolated conditions provided in a supersonic expansion.

Experimental Section

The 5-methyl- and 5-methoxysalicylic acids (5-MeSA, 5-MeOSA) from Aldrich were used as supplied. The solvents were of spectrograde quality and used without further purification.

Solution absorption and steady-state fluorescence spectra have been recorded on a Cary 210 and a Perkin-Elmer spectrofluorometer, respectively.

Gas-phase experiments have been performed in a conventional supersonic continuous expansion using a 200 μm nozzle. The samples of 5-MeSA and 5-MeOSA contained in a reservoir before the nozzle were heated at about 80 °C to provide enough vapor pressure and seeded in a helium flow at a pressure of 2 atm. The compounds were excited perpendicularly to the beam axis by means of frequency-doubled dye laser pumped by the second harmonic of a Nd:YAG laser. The excitation spectra were obtained by collecting the emitted fluorescence at a right angle from both the excitation and jet directions through a low-resolution 25 cm monochromator acting as a broad band-pass detection system. The dispersed emission spectra were determined by using either the same 25 cm monochromator or a 60 cm monochromator (Jobin et Yvon) with a spectral resolution varying between 10 and 100 cm^{-1}. The output signal was measured with a Hamamatsu (R2059) photomultiplier and processed through a gated integrator to a personal computer.

Results

(I) Absorption and Fluorescence of 5-MeSA and 5-MeOSA in Solution. Figure 1 shows the absorption spectra and emission of 5-MeSA and 5-MeOSA in cyclohexane at a concentration of $\sim(2-3) \times 10^{-5}$ M. It can be observed that substitution with CH_3 and OCH_3 in the 5 position induces a bathochromic shift of the absorption with respect to the nonsubstituted molecule ($\lambda_{max} = 340$ nm for 5-MeOSA, 318 nm for 5-MeSA, 310 nm for SA). The fluorescence of 5-MeSA is weak and consists of two bands with two distinct maxima in the UV at 380 and in the blue at 450 nm, respectively. The fluorescence from

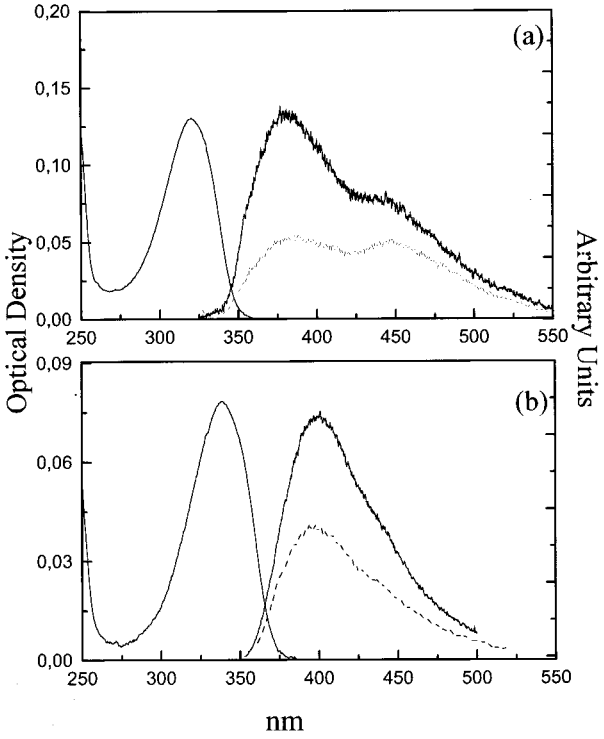

Figure 1. Absorption and emission spectra of 5-MeSA and 5-MeOSA in cyclohexane solutions: (a) 5-MeSA, $c = 3 \times 10^{-5}$ M (continuous line), $c = 0.9 \times 10^{-5}$ M (dotted line); (b) 5-MeOSA, $c = 2.13 \times 10^{-5}$ M (continuous line), $c = 0.5 \times 10^{-5}$ M (dotted line).

5-MeOSA exhibits a strong band peaking at 400 nm and a shoulder in the blue range at about 430 nm. The quantum yield of fluorescence of 5-MeOSA is higher by a factor of ∼10 than that of 5-MeSA. Although the relative intensity of the UV/blue emission increases with concentration in 5-MeSA (Figure 1a), the shape of the fluorescence spectrum from 5-MeOSA is independent of the concentration. Furthermore, this ratio depends also on the excitation wavelength in the case of 5-MeSA, as seen in Figure 2a. The excitation spectrum of the visible fluorescence is shifted by ∼10 nm to the blue of the UV excitation maximum. The excitation spectrum of 5-MeOSA fluorescence observed at 400 and 450 nm is identical (Figure 2b). These results indicate that MeSA and MeOSA behave differently. By analogy with salicylic acid and its derivatives, the blue fluorescence peaking at 450 nm in 5-MeSA exhibits a large Stokes shift (9000 cm^{-1}) and can be associated with the rotamer form **I**, which undergoes proton transfer in the excited state. The increase of UV emission as a function of concentration as well as the slight red shift of the excitation spectrum can be related to the equilibrium between the monomer and the dimer. Thus, the photophysical properties of 5-MeSA are very similar to that reported for SA.[11,12] In contrast, the fluorescence of 5-MeOSA deviates strongly from that of SA. First, since the Stokes shift of the fluorescence is only about 4500 cm^{-1}, no ESIPT process can be clearly deduced from the emission spectra and the shoulder obtained 1700 cm^{-1} to the red of the maximum may be due to a vibrational structure. No evidence for a dimeric form has be found in the case of 5-MeOSA, but this can be due to the fact that the strong fluorescence observed at 400 nm may hide a weaker one in this spectral region.

To get more information on the excited-state properties of salicylic acid derivatives, the addition of hydrogen bond acceptors has been examined. The addition of excess amounts of diethyl ether DEE (1 M) in hydrocarbon solution modifies strongly the fluorescence of both 5-MeSA and 5-MeOSA (parts

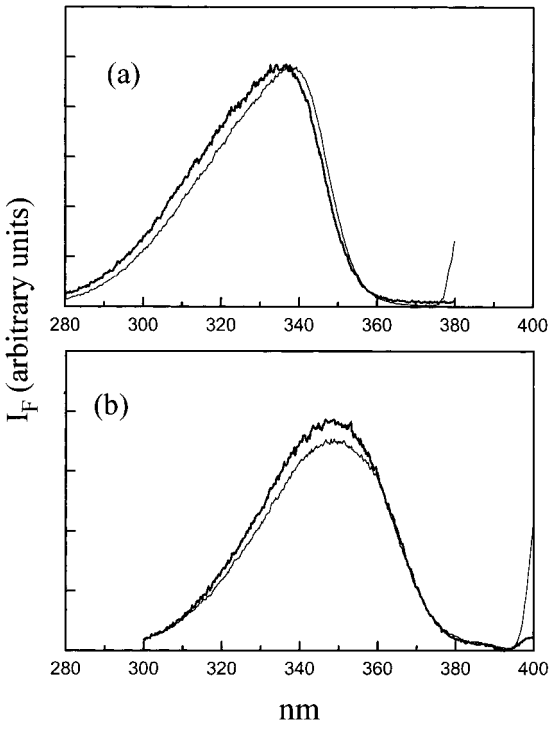

Figure 2. Excitation spectra of 5-MeSA and 5-MeOSA in cyclohexane solutions: (a) 5-MeSA, ─ bold line $\lambda_{obs} = 450$ nm, − light line $\lambda_{obs} = 380$ nm; (b) 5-MeOSA, ─ bold line $\lambda_{obs} = 450$ nm; − light line $\lambda_{obs} = 400$ nm.

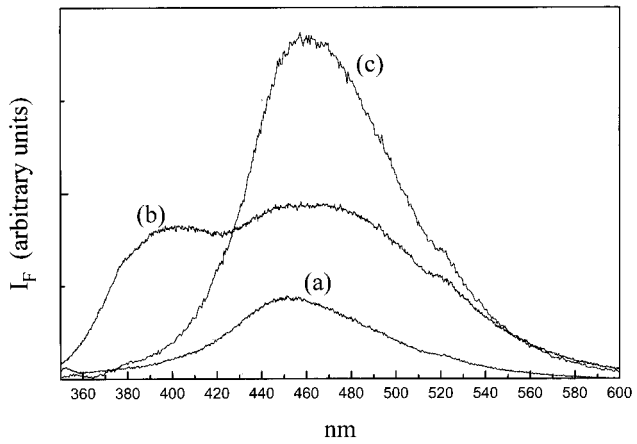

Figure 3. Fluorescence spectra of 5-MeSA and 5-MeOSA in cyclohexane solution in the presence of proton acceptor molecules: (a) 5-MeSA ($c = 1.1 \times 10^{-5}$ M) and diethyl ether (1 M); (b) 5-MeOSA ($c = 2.06 \times 10^{-5}$ M) and diethyl ether (1 M); (c) 5-MeOSA ($c = 4.5 \times 10^{-5}$ M + triethylamine).

a and b, respectively, of Figure 3). In the case of 5-MeSA, the UV band is completely suppressed, leaving only the blue fluorescence enhanced by a factor of ∼5. Meanwhile the absorption spectrum is shifted slightly toward higher energy. This behavior can be explained in terms of a specific complex between 5-MeSA and DEE involving an hydrogen bond linking the OH carboxylic group to the oxygen of DEE without breaking the intramolecular hydrogen bond responsible for the tautomerization. At low concentration of MeSA the dimerization process responsible for the fluorescent UV band is no longer competitive with complexation with DEE. A similar effect has already been reported in the case of SA.[13] For 5-MeOSA solutions in the presence of a large excess of diethyl ether (1 M), the emission spectrum presents two relatively well-separated components with maxima at 400 and 460 nm (Figure 3b). The same dual fluorescence is observed in pure ether. No sizable difference

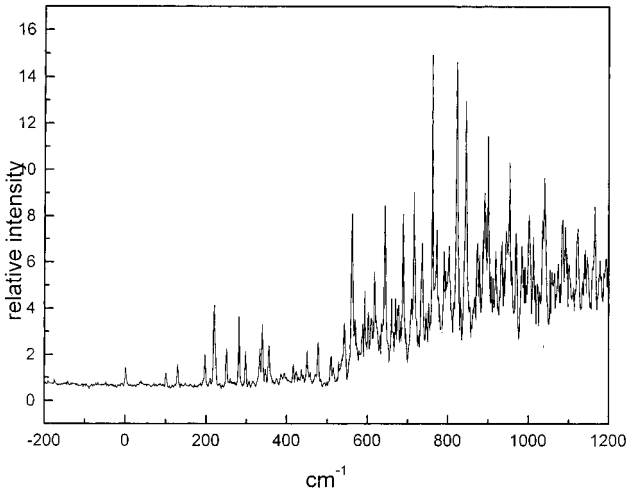

Figure 4. Fluorescence excitation spectrum of jet-cooled 5-MeSA ($T = 80$ °C, WG 420 Schott filter). The 0−0 transition is at 29 040 cm^{-1}.

is observed in the excitation spectrum of both components, indicating that they arise probably from the same species. Addition of a stronger base such as triethylamine to a cyclohexane solution of 5-MeOSA results in a single fluorescence band peaking in the visible at 460 nm (Figure 3c). The formation of complexes between 5-MeOSA and the additives is corroborated in both cases by the hypsochromic shift of the absorption, the λ_{max} being shifted from 340 nm in pure cyclohexane to 332 nm in the presence of ether and 325 nm in the presence of triethylamine. The large Stokes shifted fluorescence peaking at 460 nm indicates that the ESIPT process is favored by complexation of the 5-MeOSA with proton acceptor molecules. The dual fluorescence observed in the presence of the weak proton acceptors such as DEE may reveal an equilibrium in the excited state between enol form **I** and tautomer **III**.

Finally, one should stress the difficulty of characterizing unambiguously the excited-state properties of salicylic acid derivatives in solution, since several species, namely, the monomers in different conformations (rotamers **I** and **II**), the anionic form, and the dimer, may coexist depending on the solvent and on the concentration. These species have overlapping absorptions and emit sometimes in the same energy range, although with different quantum yields, and this makes it difficult to distinguish between them just on the basis of spectroscopic data in solution and to study selectively their behavior. For example, rotamer **II**, which has been identified in the case of methyl salicylate in solution by a blue-shifted excitation spectrum, has neither been reported in the case of salicylic acid[11] nor evidenced in the present solution work. Experiments on isolated molecules in a supersonic jet may help to elucidate the photophysics of the major species under more selective conditions.

(II) Spectroscopy of 5-MeSA in a Supersonic Jet. Figure 4 shows the fluorescence excitation spectrum of jet-cooled 5-MeSA heated at 80 °C and obtained by monitoring the light emitted at $\lambda > 420$ nm. The first weak feature at 29 040 cm^{-1} is assigned to the 0−0 transition. The spectrum presents a lot of features and becomes quite congested and more intense at about 600 cm^{-1} above the origin. The frequencies of the main vibronic bands are listed in Table 1. Although the density of vibrational bands is significantly larger in MeSA than in SA, the general shape of the spectrum looks similar to that of SA with a weak origin and increasing intensity toward high energy. By analogy with SA, it can be assigned to the S_0-S_1 ($\pi-\pi^*$) transition of the rotamer involving the strong OH−O═C

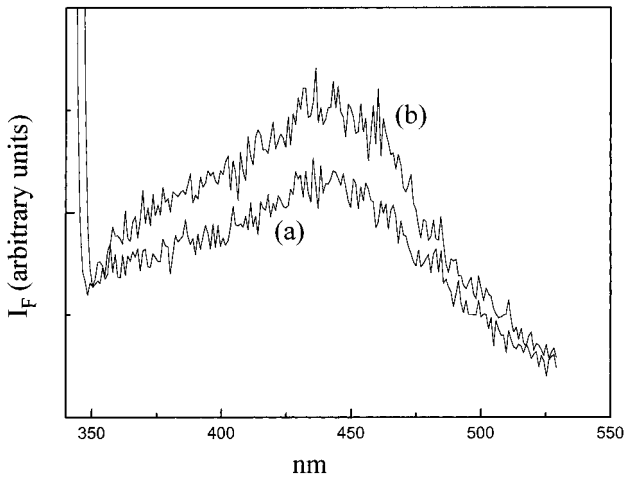

Figure 5. Low-resolution dispersed fluorescence spectra ($\Delta\lambda$ = 20 nm) of jet-cooled 5-MeSA: (a) $\nu_{exc} = 0-0 + 217$ cm^{-1}; (b) $\nu_{exc} = 0-0 + 556$ cm^{-1}.

TABLE 1: Observed Vibrational Frequencies for 5-MeSA and 5-MeOSA (cm^{-1})

5-MeSA 0−0 (29 040 cm^{-1}) S_1	5-MeOSA 0−0 (28 615 cm^{-1}) S_1	5-MeOSA 0−0 (28 615 cm^{-1}) S_0	SA[7] 0−0 (29 480 cm^{-1}) S_1	MS[6] 0−0 (30 052 cm^{-1}) S_1
100	171	170	88	176
127				
194				
217				
246				
279	272			
296	283	285		
335	330	332		347
353			364	
			370	
446	440	430	431	
		444		
475	482	480		
505	520	504	511	521
556	537			
	542	564		569
	601	599		
	645	657		
	694	717	704	694
	734	780	727	739
	798		734	770
			795	776
	847		811	
	863		835	
	890	936	849	

hydrogen bond. It is noted that methyl substitution shifts the origin of the absorption by 780 cm^{-1} toward lower energy relative to the unsubstituted molecule.

The low-resolution, dispersed emission following excitation of the intense vibrational levels at 217 and 556 cm^{-1} is shown in Figure 5. The weakness of the 0−0 feature prevents the acquisition of such a spectrum under similar conditions. These spectra do not depend of the excitation wavelength in this energy range, which extends from 350 nm toward the visible with a maximum at 440 nm. The large Stokes shift of the fluorescence at 440 nm confirms that ESIPT takes place in the isolated 5-MeSA molecule as well as in solution.

At higher temperature (T = 150 °C), the fluorescence excitation spectrum becomes very dense and exhibits close to the origin new features that can be attributed to the dimer. The relative intensity of the new bands with respect to that attributed to the monomer at lower temperature is larger when monitored in the UV (combination of UG and WG360 filters) than in the visible (WG 420 filter). This result indicates that the dimer emits mainly in the UV range as observed in solution. As in the case of SA, the first feature corresponding to the dimer origin is slightly shifted to the blue with respect to the monomer 0−0 transition ($\Delta\nu$ = 50 cm^{-1}).

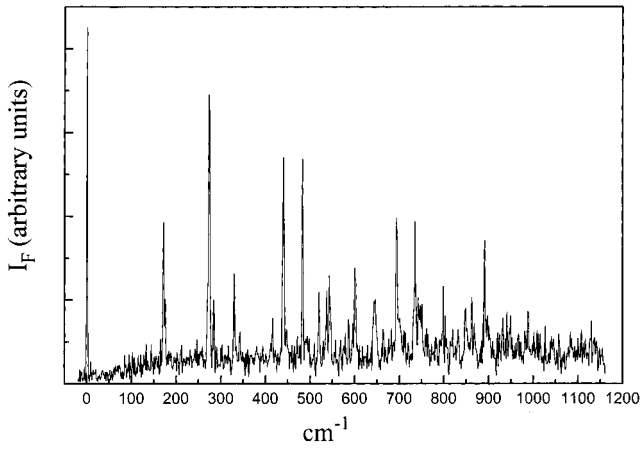

Figure 6. Fluorescence excitation spectrum of jet-cooled 5-MeOSA (T = 80 °C) observed at 400 nm through a low-resolution monochromator ($\Delta\lambda$ = 20 nm). The 0−0 transition is at 28 615 cm^{-1}.

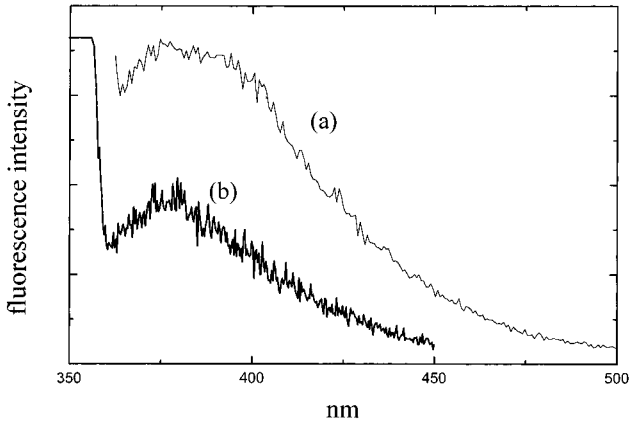

Figure 7. Low-resolution ($\Delta\lambda$ = 20 nm) dispersed fluorescence from jet-cooled 5-MeOSA excited (a) on the 0−0 transition at 28 615 cm^{-1} and (b) the first vibronic level at 170 cm^{-1}.

(III) Spectroscopy of 5-MeOSA in a Supersonic Jet. The fluorescence excitation spectrum of jet-cooled 5-methoxysalicylic acid is presented in Figure 6. The 0−0 transition located at 28 615 cm^{-1} is red-shifted by ∼1200 cm^{-1} relative to that of salicylic acid and is followed by a low-frequency mode of 170 cm^{-1}, which appears also in combination with other vibronic bands at 272, 458, and 736 cm^{-1}. The spectrum at the origin is strong, and the Franck−Condon distribution is very different from that observed in the case of SA and 5-MeSA. Although the 0−0 band appears as a single feature, many higher vibronic bands are composed of a doublet of unequal intensity and splitting. No change in the vibrational pattern or relative intensity distribution is observed by using selective detection wavelength at 370 and 400 nm. When monitored at 460 nm, the fluorescence signal is hardly detectable. The strongest vibrational bands in the spectrum of 5-MeOSA are listed in Table 1 together with those reported for SA and methylsalicylate.

Figure 7 shows the dispersed fluorescence resulting from the 0−0 level excitation obtained under low resolution ($\Delta\lambda$ = 20 nm). This spectrum exhibits a single broad band peaking at 380 nm. The higher energy part of the emission obtained under better resolution (Figure 8a) presents a resolved vibrational structure that exhibits a mirror-image relationship with the

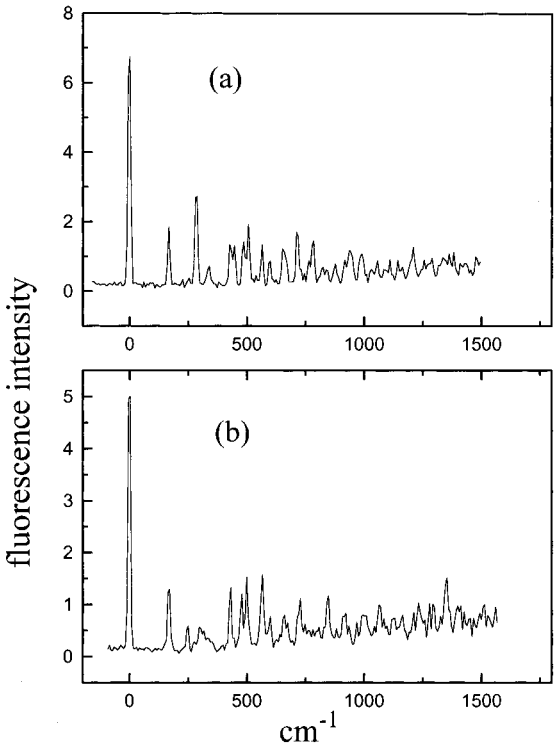

Figure 8. Higher resolution ($\Delta\nu = 20$ cm^{-1}) dispersed fluorescnce from jet-cooled 5-MeOSA: (a) 0−0 level excitation at 28 615 cm^{-1}; (b) 0−0 + 272 cm^{-1} excitation.

excitation spectrum. The main ground-state frequencies are reported in Table 1. The emission spectrum becomes gradually congested and structureless toward the low-energy side with its maximum shifted by about 2400 cm^{-1} from the origin. Resolved emissions from the higher vibronic level excitations have also been studied. For the excitation of the first vibronic level at 170 cm^{-1}, the $\Delta\nu = 0$ band appears at 170 cm^{-1}, indicating that this low-frequengy mode is not modified in the excited state with respect to the ground state. However, the excitation of the strong feature at 272 cm^{-1} gives rise to an anomalous emission (Figure 8b). The $\Delta\nu = 0$ band expected at 282 cm^{-1} is absent in the dispersed fluorescence when the excitation wavelength is set at the maximum of the 272 cm^{-1} band but appears clearly when excitation is set on the red side of this feature. This may be understood if one considers that the 272 cm^{-1} feature is composed of a doublet corresponding to two overlapping transitions. The red component of the doublet corresponds to a 270 cm^{-1} frequency mode in the excited state and is the counterpart of the 282 cm^{-1} mode observed in the dispersed emission from the 0−0 level excitation. The dispersed emission from the most intense blue component is typical of a 0^0 level fluorescence. Therefore, we assign the 272 cm^{-1} feature in the excitation spectrum to a different rotational isomer of the 5-MeOSA.

The fluorescence decays measured for excitation of the most intense bands, 0−0 (24 ns), 0−0 + 170 cm^{-1} (23 ns), 0−0 + 272 cm^{-1} (23 ns), and 0−0 + 930 cm^{-1} (22 ns), are quite constant and do not show the decrease usually observed at high excess energy. They are much longer than that measured in salicylic acid (9 ns).[7]

The addition of diethyl ether, acetone, and methanol gives rise to new bands in the excitation spectrum that can be assigned to the presence of complexes. In the case of ether and acetone the first band of the complex is blue-shifted with respect to the bare molecule by 130 and 205 cm^{-1}, respectively. In the case of methanol a small red shift is observed. The intensity of the features belonging to the complexes with ether and acetone

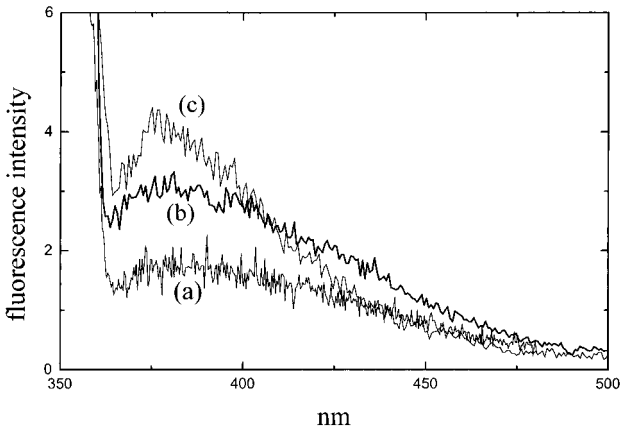

Figure 9. Low-resolution ($\Delta\lambda = 20$ nm) dispersed fluorescence from jet-cooled complexes of 5-MeOSA with (a) diethyl ether, (b) acetone, and (c) methanol.

relative to those of the isolated molecule is higher when the fluorescence is monitored at 430 nm than in the UV at 370 nm. This observation indicates that the complexes emit more toward the red than the isolated molecule and is confirmed in the dispersed spectra shown in Figure 9, which shows that the emission extends slightly more toward long wavelength. However, the emission spectra of parts a and b of Figure 9 do not display well-separated bands that can be assigned to the emission of different species as obtained in the presence of diethyl ether in cyclohexane solution. The dispersed fluorescence of the complex with methanol is similar to that of the bare molecule (Figure 9c).

Discussion

(I) Comparison of 5-MeSA and 5-MeOSA with SA and MS in Isolated Conditions. Both the excitation and fluorescence of jet-cooled 5MeSA bear strong resemblance to those of SA. The excitation presents a peculiar intensity distribution with low-intensity bands at the origin and stronger features at higher energy. The fluorescence of 5-MeSA displays clearly a visible part, showing that ESIPT takes place in the excited state, while a weaker part of the emission appears also in the UV. A similar trend has been observed in jet-cooled SA. This behavior has been interpreted in the case of SA[7] by distorted potential energy curves with different equilibrium geometry in the ground and excited state, and this description holds for the isolated 5-MeSA molecule.

In contrast to these results, the spectroscopic properties of 5-MeOSA appear very different. The excitation spectrum is sparse and displays a strong 0−0 transition. The fluorescence is resonant, and its vibrational structure exhibits a mirror-image relationship with the vibronic structure observed in excitation. At low resolution it appears as a single fluorescence band with its maximum shifted by ∼2400 cm^{-1} from the origin. There is no indication of the presence of a blue band characteristic of tautomer **III**. The lengthening of the fluorescence decay with respect to the SA molecule is also indicative of a different nature of the excited state. In the case of SA (and also of MS[15]) the lifetimes decrease monotonically from ∼10 to 4 ns and there is an abrupt decrease of the lifetimes at a threshold of ∼1100 cm^{-1}. This behavior has been interpreted as an efficient nonradiative process taking place in the excited proton-transferred form. In 5-MeOSA, the fluorescence decays (23 ns) are constant within 1000 cm^{-1} excess energy above the origin. From these results, it can be deduced that the S_0-S_1 transition observed in 5-MeOSA involves no significant displacement in the potential energy surfaces between ground and excited states, and this

behavior can be attributed to the "normal" enol form **I**. Thus, owing to the decrease of the intramolecular hydrogen bond strength induced by the methoxy substituent in the *para* position from the phenolic OH of salicylic acid, the excited-state potential energy surface has been deeply modified and the intramolecular proton transfer in the isolated molecule has been inhibited.

It is useful to stress some characteristics of 5-MeOSA. Two ground-state species have been identified from the dispersed fluorescence, and the question arises about the nature of these isomers. Two possibilities may be considered: (1) the presence of rotamer **II** in which the phenolic OH interacts with the oxygen atom of the carboxylic OH and (2) rotational isomers corresponding to different orientation of the OCH_3 group in the 5 position with respect to the chelate OH···O═C group. The first hypothesis can be excluded on the basis of the comparison with SA. In the case of SA, the S_0-S_1 transition of rotamer **II** has been shown to lie at $\sim$2000 cm^{-1} to the blue of that of the predominant rotamer (**I**) while the energy difference between the 0−0 transitions of the two isomers identified in 5-MeOSA is only 272 cm^{-1} . The vibronic pattern observed in the excitation spectrum may also help to distinguish between the two possibilities by comparison with SA and MS. In Table 1 are reported the frequencies of the main vibronic bands observed in the S_1 state of 5-MeOSA, SA, and methyl salicylate (MS) for comparison. The first low-frequency mode appears at 170 cm^{-1} for both isomers of 5-MeOSA, and a similar low frequency is observed in MS (rotamer **I**) but does not exist for the SA molecule. This vibration is also seen in the dispersed emission of both 5-MeOSA isomers and MS and has been assigned in the latter case to a distortion of the ring containing the intramolecular hydrogen bond. Although the absence of activity of this vibration in SA and 5-MeSA casts some doubt on its attribution, its observation in both MS and 5-MeOSA may be taken as an indication of a similar structure in both compounds exhibiting the chelate ring of the hydrogen-bonded rotamer **I**. We suggest therefore that the two isomers trapped in the jet correspond more likely to the two different orientations of the OCH_3 group in *cis* and *trans* positions relative to the chelate ring. The coexistence in the jet of isomers corresponding to the *cis* and *trans* conformations of the OH or OCH_3 in disubstituted aromatic molecules has been reported in numerous cases such as *p*-dimethoxybenzene.[14]

(II) Comparison with Solution Properties. In solution, the behavior of 5-MeSA parallels also that of SA. The two weak emissions in the UV and blue regions of the spectrum can be assigned to the dimer and the monomer, respectively. In the presence of diethyl ether only the blue tautomer fluorescence is seen. This result may be explained similarly as in the case for SA[14] in terms of a ground-state complex linking the carboxylic acid OH and $O(C_2H_5)_2$ acting as a hydrogen bond acceptor. Thus, the complexation with DEE inhibits the formation of the dimer and facilitates the ESIPT process.

The fluorescence of 5-MeOSA deviates appreciably from both SA and 5-MeSA, since an intense band with a maximum at 400 nm and a shoulder at 430 nm is obtained in alkane solution. This observation correlates with the 5-methoxysalicylate where a strong emission at 395 nm is observed. However, the fluorescence spectrum of 5-methoxysalicylate extends further to the red with a shoulder at 490 nm, which indicates the presence of a second component due to the ESIPT process. In the case of 5-MeOSA this process does not appear clearly, since a much less red-shifted shoulder is observed at 430 nm. Such a small Stokes shift is not representative of a proton-transfer process, and one can deduce that no ESIPT process takes place in 5-MeOSA in nonpolar solution, in agreement with the conclusions of isolated jet-cooled gas-phase results.

Nevertheless, it has been shown that the presence of diethyl ether or of a stronger proton acceptor such as triethylamine promotes the ESIPT reaction, since it induces the long wavelength fluorescence. These results show that intermolecular hydrogen bonding of the solvent to the carboxylic OH does not break the intramolecular H bond but rather reinforces it and thus allows the ESIPT reaction to occur by increasing the electron density on the C═O group. A similar effect has been reported in the case of 3-hydroxy-2-naphthoic acid[16] where the presence of a base such as pyridine is necessary to observe the long wavelength emission attributable to the ESIPT process. This effect can be interpreted in terms of a charge transfer within the intermolecular hydrogen bond from the electron-rich ligand to the carboxylic group, which in turn results in a strengthening of the intramolecular hydrogen bond. The behavior of salicylic acid derivatives with respect to the ESIPT process can be understood on the basis of this mechanism: when the acidity of the phenolic OH is attenuated by substitution of an electron-releasing group in the *para* position as it is the case in 5-MeOSA, the reaction normally forbidden becomes allowed by acting on the proton-accepting properties of the C═O. The enhancement of the electron density on the C═O group can be achieved by replacing the carboxylic acid by its methyl ester, which would explain why ESIPT is observed in 5-methoxysalicylate in alcane solutions and not in 5-MeOSA, by intermolecular complexation with proton acceptors, or even by formation of the carboxylate anion as is the case in the presence of a stronger base such as TEA. This last possibility is corroborated by a recent photophysical study of 3,5-ditertiobutylsalicylic acid (*t*BSA)[17] in different solvents. By comparison with the fluorescent properties of the Li salt of *t*BSA, it has been suggested that *t*BSA in solution undergoes very rapid deprotonation in the excited state and that the tautomerization of the excited anion is responsible for the long wavelength emission.

However, the behavior of the 5-MeOSA/DEE complexes in solution differs from that observed for the isolated complex in the gas phase, since in this latter case no dual emission is clearly in evidence. Although the double fluorescence obtained in solution may be interpreted by the existence of two minima in the excited-state potential energy surface, the broad emission from the isolated complex with DEE indicates more likely an evolution from a deep well in the bare chromophore toward a more flat barrierless curve along the tautomerization coordinate. The reasons for this discrepancy are not obvious at the present stage but may indicate that solvation plays a determining role in stabilizing the dipolar tautomer structure responsible for the long wavelength emission. The influence of complexation with a stronger hydrogen bond acceptor will be examined in the near future.

Conclusion

The present study has shown that although the fluorescent properties of salicylic acid are not very sensitive to methyl substitution, the presence of a OCH_3 substituent in the *para* position from the phenolic OH modifies drastically its photophysics. This molecule, both in the jet conditions and in a nonpolar medium, emits a "normal" fluorescence arising from the initially excited form **I***. The characteristic blue fluorescence has been quenched. The ESIPT reaction is thus suppressed, and this effect is to be related to the weakening of the intramolecular O−H···O═C bond due to the lower acidity of the phenolic OH.

Our results for 5-MeOSA in nonpolar solution are also different from those obtained for methyl-5-ethoxy-[1] or 5-methoxysalicylate,[10] since, in contrast to these latter examples, there is no indication of the low-energy fluorescence characteristic of the tautomer in the case of 5-MeOSA. Moreover, although complexation of 5-MeOSA with weak proton acceptors in solution gives rise to a dual fluorescence that may be explained by the existence of two minima in the excited-state potential surface, the results fail to demonstrate the existence of a barrier and an equilibrium between enol and keto forms in the excited state of jet-cooled isolated complexes.

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