Laser-Induced Fluorescence Study of the S_0-S_1 Transition of 1- and 2-Perfluoronaphthol in a Supersonic Jet

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The S_0-S_1 transition of 1- and 2-perfluoronaphthol (1-FN and 2-FN) has been studied by fluorescence excitation and dispersed emission in a continuous supersonic expansion. Each compound gives rise at the origin to two dissimilar excitation systems which can be distinguished by their emission region. While the higher energy systems exhibit both in absorption and in emission the characteristic features of unsubstituted perfluoronaphthalene, the low-energy systems present a different complex pattern typical of a strongly distorted excited state. The dispersed fluorescence from 1-FN shows a resolved resonant structure for both systems, but the emission extends largely toward the red for the excitation of the low-energy system excitation. The dispersed emission from 2-FN low-energy system is totally diffuse and red shifted, with a maximum at about 4500 cm^{-1} from the excitation. The two absorption spectra have been tentatively attributed to the presence of the ground state *cis* and *trans* rotamers corresponding to a different orientation of the OH group with respect to the naphthalene frame and involving different weak hydrogen bonding of OH with the neighboring fluorine atom. The spectroscopic properties of each rotamer have been shown to be strongly sensitive to the position of the weak internal hydrogen bond.

Introduction

The fluorescence excitation spectroscopy of the first electronic transition of 1- and 2-naphthol in a supersonic expansion has recently been the subject of detailed studies.[1−3] These investigations were motivated by the well-known property of OH-substituted aromatic derivatives which exhibit a strongly enhanced acidity in the excited state and can undergo acid−base reactions resulting in an intermolecular proton transfer in microclusters containing molecules with large proton affinity.[4−8] The effect of the position of the acidic OH substituent has also been recognized and the larger photoacidity of 1-naphthol over 2-naphthol in solution has been explained by the inversion of the relative position of the L_a and L_b states of naphthalene derivatives in protic solvents.[9]

A further interest in the spectroscopy of naphthols stems from the observation that both compounds exist in the ground state under two conformers usually referenced as the *cis* and *trans* rotamers and corresponding to different orientations of the OH substituent with respect to the naphthalene nucleus.[1−3,10]

Our objective in this work was to examine the effect of substitution of the ring H atoms by fluorine on the S_0-S_1 transition of jet-cooled naphthols. Perfluorination of naphthols is expected to have two consequences.

The first is the out of plane deformation of the C−F bonds in the excited state, which should manifest itself by the appearance of low-frequency vibrational modes. This effect has already been reported for 1,2,4,5-tetrafluorobenzene,[11] where a tunneling inversion involving an out of plane butterfly motion of the F atoms has been evidenced. More recently, a similar low-frequency anharmonic progression has been observed in perfluoronaphthalene.[12]

The second consequence is the presence of weak intramolecular hydrogen bonds between the OH group and the ortho fluorine atoms. The formation of such internal bridges resulting in the existence of *cis* and *trans* isomeric forms has been established long ago in the case of ortho halophenols by IR measurements[13−15] and more recently by fluorescence excitation spectroscopy in a supersonic expansion.[16]

Experimental Section

The compounds 1- and 2-perfluoronaphthol (1-FN and 2-FN) have been synthesized as described in ref 17a,b.

Experiments were performed in a continuous supersonic jet produced by expanding the perfluoronaphthol sample seeded in He carrier gas at a total pressure of 2 atm through a 200 μm nozzle. The 1-FN was heated at ∼40 °C and the 2-FN at about 70 °C in order to provide enough vapor pressure. The spectra were obtained with laser excitation of the cooled sample approximately 5 mm downstream of the nozzle using a frequency-doubled DCM dye laser pumped by a Nd:YAG pulsed source (B.M. Industrie). In fluorescence excitation spectra the fluorescence was monitored at selected wavelengths through a 25 cm monochromator acting as broad band-pass filters. The dispersed fluorescence spectra were obtained either with the same 25 cm monochromator to get the general shape of the emission at low resolution or with a 60 cm monochromator (Jobin et Yvon) with a spectral resolution varying between 10 and 100 cm^{-1}.

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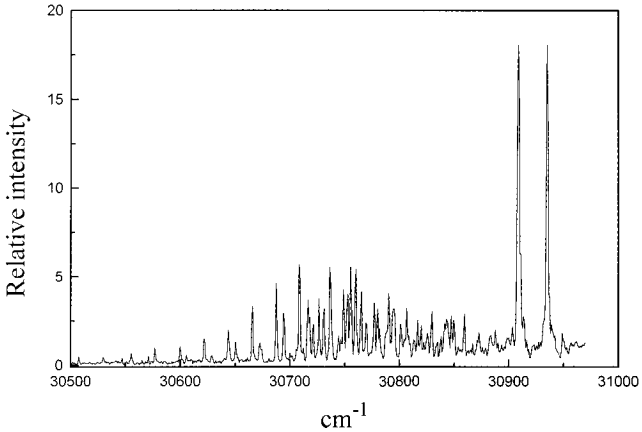

Figure 1. Extended view of the red part of the global fluorescence excitation spectrum of 2-FN (T = 67 °C, filter WG 335).

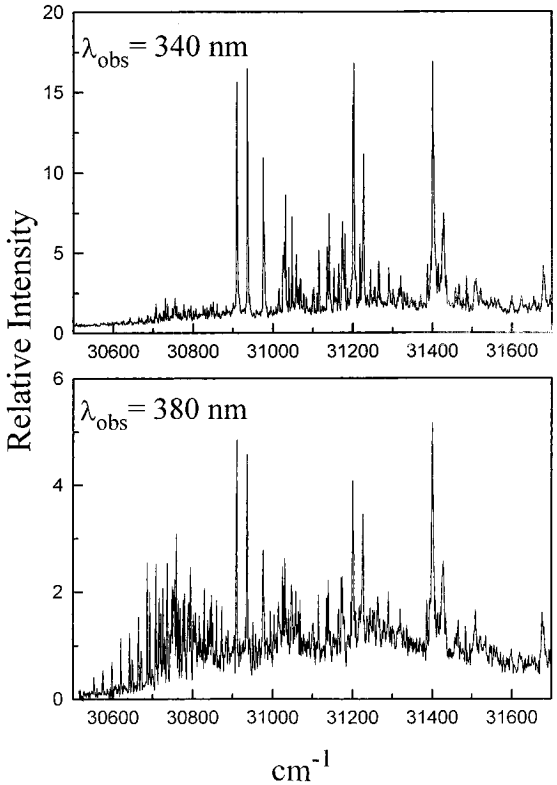

Figure 2. Fluorescence excitation spectrum between 30 500 and 31 500 cm^{-1} of 2-FN (T = 95 °C) obtained by monitoring the emission: (a) at λ = 340 nm; (b) at λ = 380 nm.

Results

(I) 2-Perfluoronaphthol (2-FN). The fluorescence excitation spectrum was recorded by monitoring either the total fluorescence (Figure 1) or at selected wavelengths of 340 and 380 nm, as shown in Figure 2. The most intense feature appears at 30 911 cm^{-1} and is shifted by only 8 cm^{-1} to the blue of the *cis*-2-naphthol located at 30 903 cm^{-1}. This main band is followed by relatively intense low-frequency vibronic bands at 25 and 65 cm^{-1}. The same pattern appears in connection with the two prominent vibronic features at 291 and 489 cm^{-1}. Higher vibronic levels are also observed at 761, 1182, 1411, 1499, and 1697 cm^{-1} above the 30 911 cm^{-1} origin. This system will be referred to hereafter as the B bands.

At about 300 cm^{-1} to the red of the main band, there is a weaker series of features (called in the following the R system) developing over more than 400 cm^{-1} which appears only weakly for the 340 nm observation (Figure 2a) and becomes more apparent with respect to the B bands when the fluorescence is detected at 380 nm (Figure 2b). This system clearly exhibits two overlapping long progressions over a low-frequency mode of 21 cm^{-1}. Because of the observed pattern, the origin of the progression cannot be easily identified. The first very weak feature appears at 30 518 cm^{-1}, while the intensity distribution peaks at about 30 761 cm^{-1}. Because of their low intensity and their extended structure, higher vibronic levels of this system are difficult to observe among the numerous and congested features at higher energy.

It can be shown that this bunch of lines is not due to either an impurity absorbing close to the 2-FN molecule or to a complex of 2-FN with an impurity contained in the sample since its relative intensity remained unchanged after purification of the 2-FN sample by HPLC. Another assumption was to assign the R system to clusters with water which could have been present in the apparatus or in the carrier gas. However, the addition of water in the helium flux does not enhance the intensity of the R bands but rather reduces it without the appearance of new features attributable to complexes with water. A third possibility could be the formation of a dimer, but by increasing the temperature of the sample the relative intensity of the R system with respect to the B bands remains constant. In addition, it is remarkable that no complexes can be evidenced in the fluorescence excitation spectra following addition of water, methanol, dioxane, diethyl ether, NH_3, and triethylamine, while all these ligands lead to a very efficient quenching of the R and B systems. It should be concluded that, in the condition of the supersonic expansion, complexation of 2-FN does not give rise to fluorescent complexes which absorb in the studied spectral range. It is therefore very unlikely that van der Waals complexes with some impurities can be responsible for the R bands.

Thus, the R system must be assigned to the bare 2-FN molecule, and the observed Franck−Condon distribution of this absorption indicates a large modification of the geometry of the excited state with respect to that of the ground state. In agreement with the excitation spectrum of the fluorescence monitored at 380 nm, the dispersed fluorescence obtained with broad band resolution by pumping the most intense feature of the R system at 30 716 cm^{-1} displays a broad red-shifted spectrum peaking at 375 nm (26 600 cm^{-1}), corresponding to a red shift of the Franck−Condon maximum of about 4500 cm^{-1}, which is larger than the expected OH stretching frequency (Figure 3b). In contrast to this spectrum, the emission resulting from the excitation of the B bands has a normal Franck−Condon distribution, with a maximum at 340 nm (Figure 3a).

The dispersed emission resulting from the excitation of the strong 30 911 cm^{-1} band exhibits under better resolution a structured resonant fluorescence spectrum typical of a naphthalene derivative (Figure 4). This dispersed emission is very similar to that reported for perfluoronaphthalene.[12] The main ground state frequencies are observed in 130, 295, 400, 504, 798, 1240, 1378, and 1512 cm^{-1} and, with the exception of the 130 cm^{-1} band, are characteristic of a naphthalene derivative skeletal deformation (Table 1). The 295 and 505 cm^{-1} frequencies can be correlated with the 291 and 491 cm^{-1} vibronic modes observed in the excitation spectrum. The 130 cm^{-1} frequency can be related to the 135 cm^{-1} observed for perfluoronaphthalene and by analogy with this molecule can be assigned to two quanta of the out of plane deformation of the C−F bonds (I_2^0). Following the similarity with perfluoronaphthalene, this ground state frequency can be correlated with the low-frequency features at 26 and 65 cm^{-1} observed in the excitation spectrum (I_0^2 and I_0^4). A similar negative anhar-

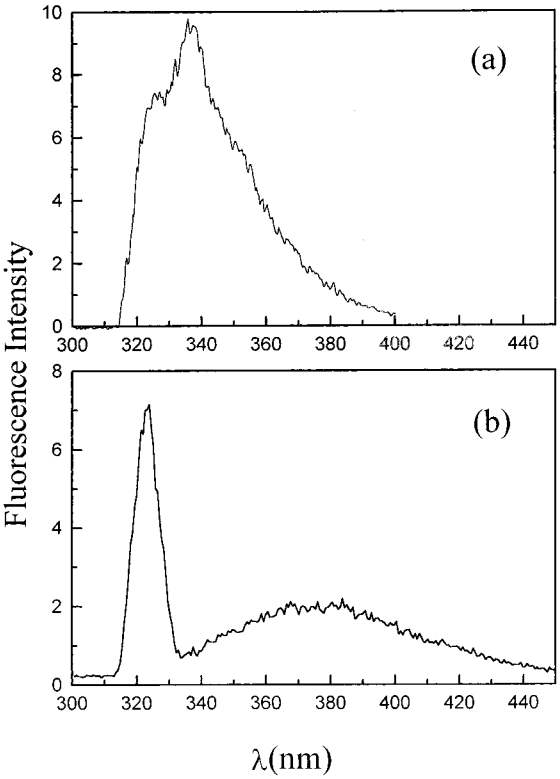

Figure 3. Comparison of the fluorescence spectra of 2-FN under broad band resolution for the excitation of (a) the strongest B band at 30 911 cm^{-1} ($\Delta\lambda = 2$ nm) and (b) the strongest R band at 30 716 cm^{-1} of 2-FN ($\Delta\lambda = 10$ nm). The peak at 325 nm is the scattered light from the excitation laser.

monicity of the excited state progression and a large decrease of the frequency upon excitation are observed in perfluoronaphthalene and 2-perfluoronaphthol.

Over the entire excitation spectrum the fluorescence decay times are within the excitation laser pulse (10 ns), indicating a very low fluorescence yield.

(II) 1-Perfluoronaphthol (1-FN). The first part of the fluorescence excitation spectrum of 1-FN is shown in Figure 5. In this case also, at the onset of the spectrum, there is a compact group of overlapping bands extending between 30 450 and 30 650 cm^{-1} (referred to hereafter as the R system), followed by a more intense series of four bands, with the first prominent one at 30 727 cm^{-1} (B system). Similarly to the 2-FN the relative intensity of the R to B features strongly depends on the observation wavelength, the R bands being

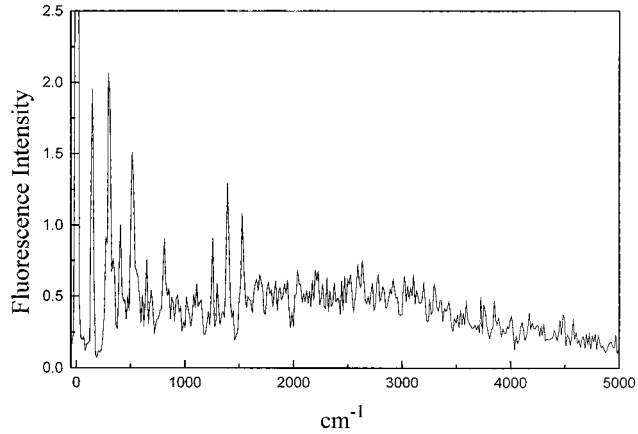

Figure 4. Dispersed fluorescence of 2-FN obtained with 20 cm^{-1} spectral resolution for the excitation of the strongest B band at 30 911 cm^{-1}.

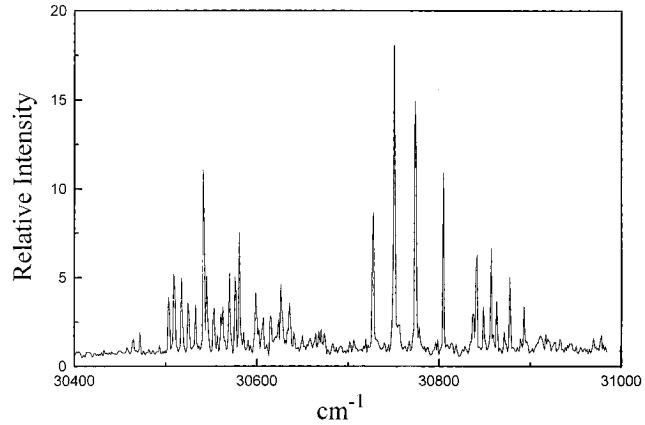

Figure 5. Extended view of the red part of the total fluorescence excitation spectrum of 1-FN ($T = 35$ °C, filter WG 335).

relatively more intense for the 380 nm detection range than for the 340 nm (Figure 6). The low-energy bands (R system) exhibit a much more irregular pattern than that observed for 2-FN, and this system is dominated by an intense feature shifted by 185 cm^{-1} to the red of the first blue (B) transition at 30 727 cm^{-1}. These observations indicate that, as for 2-FN, both systems emit in a different spectral region, which is corroborated by the dispersed emission spectrum recorded at low resolution, as shown in Figure 7a,b. While for the B system excitation, the dispersed emission peaks at about 340 nm, the fluorescence resulting from the main R band excitation extends toward the low-energy side with a maximum around 370 nm. In the 1000−

TABLE 1: Origin Positions and Main Observed Vibrational Frequencies in the S_0-S_1 Spectra of 1- and 2-Perfluoronaphthols, Perfluoronaphthalene, and 1- and 2-Naphthols (Values in cm^{-1})

1-FN 30 475 (R) 30 727 (B)		2-FN 30 518 (R) 30 911 (B)		PFN[12] 31 255		1-HN[1] 31 181 (*c*) 31 455 (*t*)		2-HN[11] 30 586 (*t*) 30 903 (*c*)	
ν'' [a]	ν' [a]	ν'' [a]	ν' [a]	ν''	ν'	ν''	ν'	ν''	ν'
125	23	130	26	135	26				
	47								
	78		65		65				
300	295	295	291	290	282	281	276	286	287
394		400		385	368	425	412	422	397
						465	454	461	451
515	493	504	491	515	483	524	493	523	490
652		638							
798		798	761	805	769	715	665	773	720
1289	1268	1240	1182	1250	1196	1280	1282		
1397	1403	1378	1411	1380	1411	1390	1380	1389	
1536	1467	1512		1521	1493				

[a] These frequencies correspond to the B system.

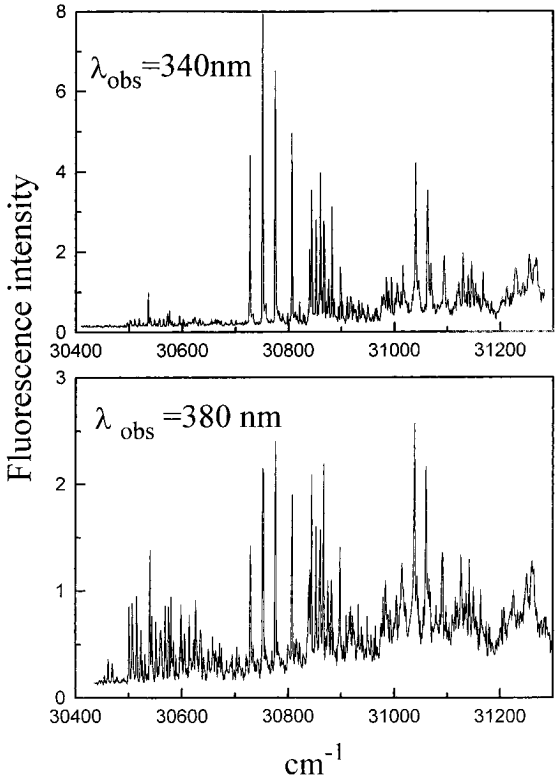

Figure 6. Partial view of the fluorescence excitation spectrum of 1-FN ($T = 50$ °C) obtained by monitoring the emission: (a) at $\lambda = 340$ nm; (b) at $\lambda = 380$ nm.

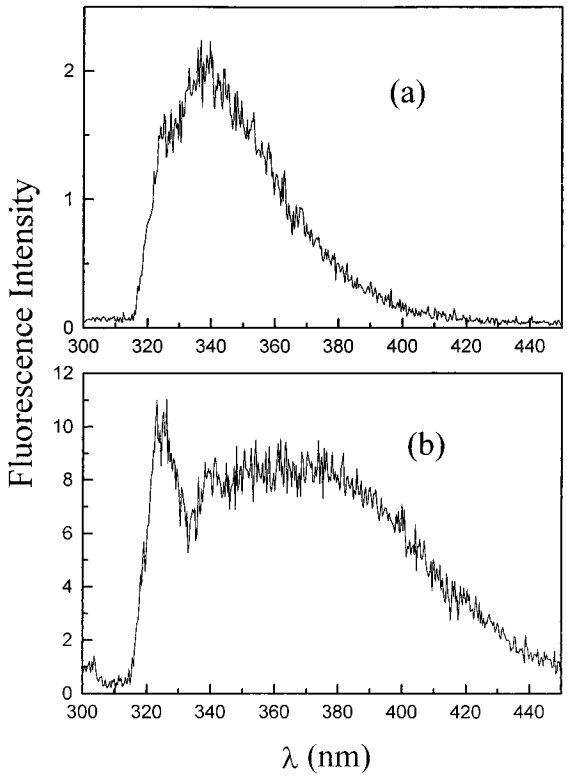

Figure 7. Comparison of the fluorescence spectra of 1-FN under broad band resolution for the excitation of (a) the strongest B feature at 30 751 cm^{-1} ($\Delta\lambda = 2$ nm) and (b) the strongest R feature at 30 542 cm^{-1} ($\Delta\lambda = 10$ nm). The peak at 327 nm is the scattered light from the excitation laser.

2000 cm^{-1} energy range above the origin of the B bands the excitation spectrum displays discernible vibronic features at 1172, 1268, 1403, and 1460 cm^{-1} superimposed on a broad continuum of increasing intensity. The relative intensity distribution of the bands with respect to the continuum is not modified when observed at 340 or 380 nm.

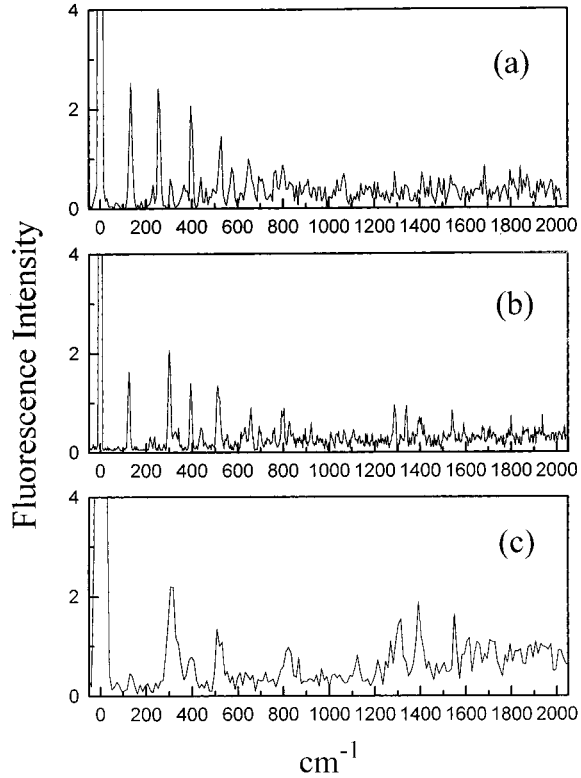

Figure 8. High-energy part of the emission spectrum of 1-FN for the excitation of (a) the B band at 30 727 cm^{-1} (spectral resolution 20 cm^{-1}), (b) the strongest B band at 30 751 cm^{-1} (spectral resolution 12 cm^{-1}), and (c) the R band at 30 542 cm^{-1} (spectral resolution 50 cm^{-1}).

The dispersed fluorescence spectra obtained with better resolution by pumping the main bands of the excitation spectrum at 30 542 cm^{-1} (R system) and 30 727, 30 751 cm^{-1} (B system) present a vibrational structure in the first part of the spectrum which is followed by a congested and continuous part peaking at about 2000 cm^{-1} from the pumped transition for the B band excitation. This broad red tail extends more toward the low-energy side for the excitation of the R line at 30 542 cm^{-1} than for the B lines, as already mentioned. The vibrational structures of the high-energy part of the emission spectra are shown in Figure 8, and the frequencies of the main ground state vibrational modes are given in Table 1. As can be seen in Figure 8 the vibrational structure and its intensity distribution are strongly dependent on the initially excited level. Excitation of the first B band at 30 727 cm^{-1} give rise to a progression over the 125 cm^{-1} mode, while only one vibrational feature is observed for this mode following excitation of the second most intense band at 30 751 cm^{-1}. The other features at 300, 394, 515, 798, and 1397 cm^{-1} are characteristic of skeletal naphthalene deformations as observed in PFN, 1-NOH, and 2-NOH (Table 1).

Solution Spectra

It is interesting to compare the absorption and emission spectra of 2-FN and 1-FN (Figure 9) in a nonpolar solvent at room temperature with those of the hydrogenated naphthols in order to have information on the position of the L_b and L_a naphthalene type electronic states.[18] Both the S_0-S_1 and S_0-S_2 transitions appear strong and well separated in 2- and 1-FN, with the 0−0 transition of the first absorption respectively at 326 and 328 nm and the maximum of the second absorption at 280 and 290 nm. For comparison the S_0-S_1 origins are respectively at 328 and 322 nm in 2-HN and 1-HN. The

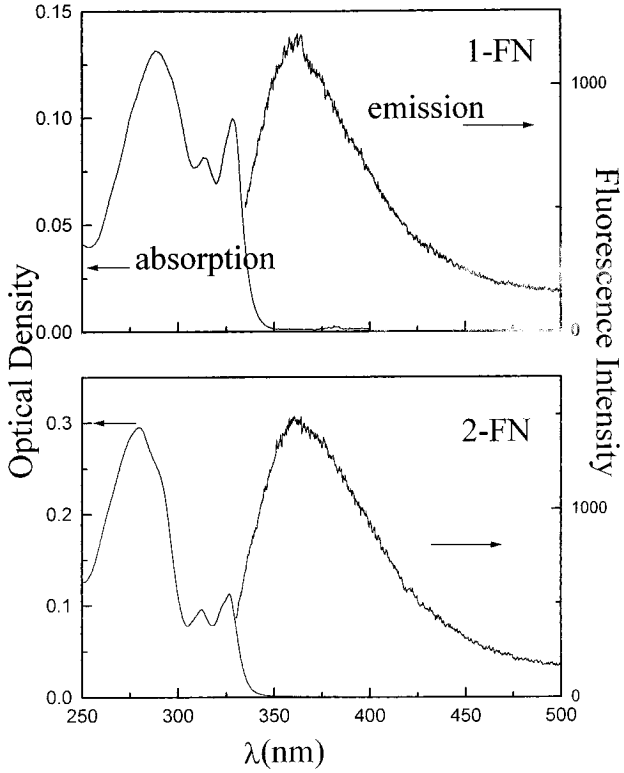

Figure 9. Absorption and emission spectra of 1-FN and 2-FN in cyclohexane.

fluorescence spectra are structureless and peak at about 360 nm for both compounds, being somewhat red shifted with respect to the hydrogenated naphthols. The fluorescence quantum yields have been estimated relative to 2-naphthol to be 0.07 for 2-FN and 0.05 for 1-FN.

While the absorption spectra of perfluoronaphthols are not modified in polar acetonitrile, the fluorescence spectra are broader, with their maxima shifted at 390 nm for 2-FN and 385 nm for 1-FN. In water or methanol the absorption is strongly modified, with the emergence of a new band peaking at about 343 nm which can be assigned to the perfluoronaphtholate (FNO^-). The anions are very weakly fluorescent at room temperature ($\lambda_{max} = 450$ nm for 2-FNO^-). Thus, ground state deprotonation occurs readily in perfluoronaphthols in protic solvents. The ground state pK_a have been determined from spectrophotometric titration to be 5.1 and 5.7 for 2-FN and 1-FN, respectively. This result shows that fluorine substitution leads to a strong enhancement of the acidity of naphthols.

Discussion

The spectroscopy of jet-cooled 2- and 1-FN in the region of the onset of the first electronic transition appears to be surprisingly complex, and both compounds exhibit two series of bands which can be distinguished by their emission regions.

(1) Origin of the Two Excitation Spectra. As a first approach to understanding the unusual spectroscopic properties of perfluoronaphthols, it is interesting to compare their behavior with that of hydrogenated naphthols (2-HN and 1-HN). As previously mentioned, jet-cooled 1-HN and 2-HN give rise to two electronic origins of the S_0-S_1 transition which are separated respectively by 274 and 317 cm^{-1} and have been related to the presence of the *cis* and *trans* rotamers.[1−3,10] High-resolution rotational contours of each 0_0^0 transition have allowed the determination of inertial constants and the direction of the transition moments with respect to the main inertial axis for each species.[3] According to these data, the lower energy origin of 1-HN was shown to correspond to the *cis* rotamer, while the lower energy origin in the spectrum of 2-HN was that of the *trans* rotamer. Similarly to their hydrogenated analogs (1- and 2-HN), one can expect the perfluoronaphthols to be present under two conformations due to a different orientation of the OH substituent with respect to the naphthalene frame, and one can postulate that these two ground state rotamers are responsible for the R and B systems (see Figure 10).

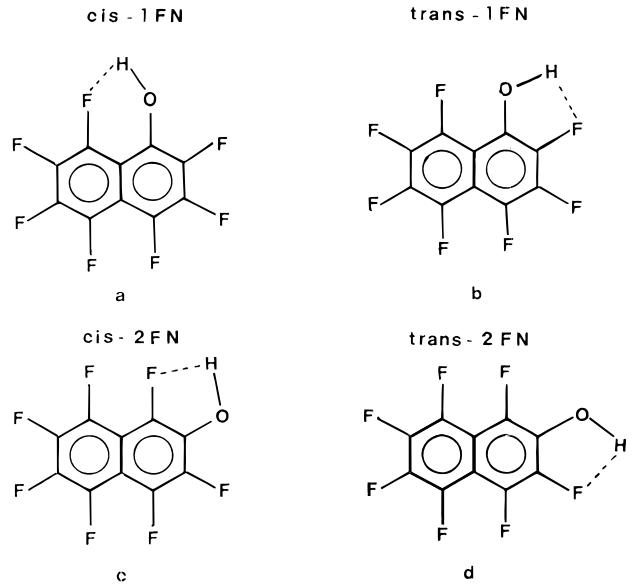

Figure 10. *Cis* and *trans* conformations of 1- and 2-FN.

Under the assumption that the R and B spectra of 2- and 1-FN correspond also to the two rotameric forms of each compound, one can evaluate respectively the energy gap between the two systems to be about 390 cm^{-1} by taking into account the first observed weak band at 30 518 cm^{-1} of 2-FN and 252 cm^{-1} estimated for 1-FN (Table 1). These values are comparable with those obtained in the case of hydrogenated naphthols.

To confirm the existence of two rotational isomers in 1-FN and 2-FN, AM1 calculations[19] have been performed to get optimized geometries of ground state perfluoronaphthols. Both the *cis* and *trans* conformations shown in Figure 6 are found to have very close heats of formation. In the case of 2-FN the two rotamers are calculated to be planar, with the *cis* form being stabilized by only 100 cm^{-1} relative to the *trans* configuration. The distance between H and the neighboring F atom is slightly shorter in the *trans* rotamer (2.30 Å versus 2.32 Å). For 1-FN, the geometry of the two rotamers differs from each other: While the *trans* conformer is planar with a heat of formation similar to the *cis* 2-FN, in the *cis* 1-FN form the OH bond lies out of the naphthalene plane by 30°. This out of plane geometry is the result of the balance between steric repulsion and the attractive hydrogen bond of the acidic H with the F atom in the 8 position. The interatomic distance OH···F is much shorter than for the other three rotamers (1.99 Å), showing significant interaction between the OH group and the F atom at the 8 position. This finding is corroborated by the observation of two different absorption bands in the region of the OH stretch in the IR spectra.[17] However, this structure is calculated to be destabilized with respect to the planar *trans* rotamer by 420 cm^{-1} probably because of its nonplanar geometry. From these data, it can be tentatively deduced that the R system, which has a lower intensity, originates from the less stable *cis* conformation. Consequently, the higher energy transition should be assigned to the *trans* conformation. The case of 2-FN is

more difficult to rationalize on the basis of ground state configurations, and the strong difference between the two R and B spectra should be related to the excited state properties of the two conformers.

(2) B System Excitation. The higher energy system (B) of 1-FN and 2-FN bears obvious resemblance to that of perfluoronaphthalene and can thus be similarly assigned to the L_b type state of naphthalene. In both cases there is little influence of the presence of the OH group, the main vibrational modes appearing in excitation and emission being close to those involved in perfluoronaphthalene (Table 1). As mentioned above, the low-frequency vibronic features appearing close to the origin are also similar to those observed in the case of perfluoronaphthalene and deserves the same assignment.[12] They can be attributed to an out of plane inversion motion of the C−F bonds with respect to the aromatic ring ("butterfly motion") which is allowed from the ground state by $\Delta v = 2n$ transitions according to symmetry selection rules. The corresponding ground state frequency is 62 cm^{-1}, as deduced from the first vibronic transition at 125 cm^{-1} in the dispersed fluorescence spectrum. This antisymmetrical mode exhibits a negative anharmonicity in the excited state which reveals a large change in the S_1 potential with respect to S_0 and can be understood in terms of double-minimum potential involving a low-energy barrier.[11,12] Tunneling between levels below the energy barrier should result in a splitting of the degenerate levels with only one of the components being allowed by symmetry in the one-photon excitation as observed. The energy levels and the Franck−Condon distribution observed in the fluorescence excitation spectra have been reproduced by assuming a ground state harmonic potential and an excited state Gaussian type double-minima potential[20] given by

$$V(Q) = (1/2)\lambda Q^2 + A\exp(-a^2Q^2)$$

where λ is related to the harmonic frequency ν_0 by $\lambda = (2c\pi\nu_0)^2$. The potential parameters A and a are related to the harmonic frequency ν_0, to the barrier height b, and to the ρ parameter which defines the slope of the outer wells of the potential relative to the barrier by the following relations:

$$a^2 = e^{\rho}\lambda/2A$$

$$b = B\nu_0 = A(e^{\rho} - \rho^{-1})/e^{\rho}$$

Defining λ, ρ, and B defines the shape of the potential and thus the Franck−Condon distribution. In a qualitative way, one can see that if B increases, the Franck−Condon (FC) distribution peaks at higher vibronic levels and the negative anharmonicity increases. For a given B value, increasing ρ, that is, increasing the slope of the potential outer walls, favors a doublet structure for the energy levels. For the 2-FN B bands which bear strong resemblance to perfluoronaphthalene, the FC factor distribution has been reproduced with $B = 0.6$ and $\rho = 0.9$. For 1-FN, the FC factor distribution is maximum for $\Delta v = 2$ and can be qualitatively fitted with $B = 1.7$ and $\rho = 0.9$ (Figure 11). In both cases the harmonic frequency is 23 cm^{-1}, the same value as in perfluoronaphthalene. The intensity distribution over the inversion mode has also been calculated for the dispersed fluorescence. The FC factors from 2-FN $\nu' = 0$ and 1-FN $\nu' = 2$ decrease rapidly for increasing ν'', in good agreement with the experimental results. In the case of 1-FN $\nu' = 0$ the calculated distribution shows an extended progression over five levels, as observed in Figure 2a.

The B system of 1-FN was tentatively assigned on the basis of AM1 calculations to the *trans* rotamer. At higher excitation energy, one may consider the possibility of interconversion between B and R forms. As seen in Figure 6, the group of bands between 30 850 and 30 950 cm^{-1} exhibit a relative increase in intensity with respect to the B origin when detected with $\lambda_{obs} = 380$ nm, and this observation may be taken as an indication of excited state isomerization.

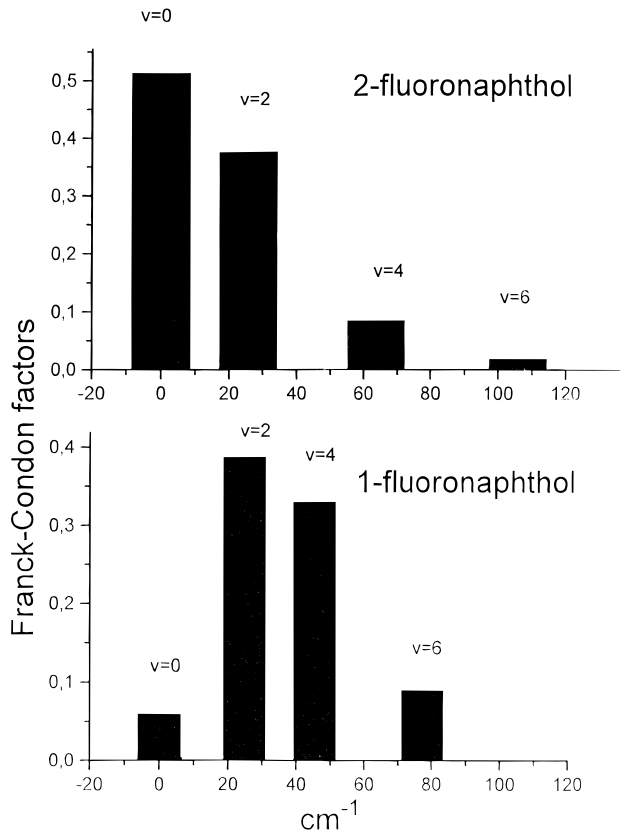

Figure 11. Calculated intensity distribution over the inversion progression for 2-FN and 1-FN.

Taking into account the strong intensity and the similarity to perfluoronaphthalene of the two systems in 1-FN and 2-FN in both absorption and emission, we propose to assign the B system of 2-FN to the *cis* conformer. It is to be noted that these two rotamers are related to each other by exchanging the relative position of the OH and F substituent involved in the weak intramolecular hydrogen bond and are thus expected to have similar behavior.

(3) R System Excitation. The low-energy spectra (R) of 1- and 2-FN are markedly congested and lead to a broad emission, with the maximum of the Franck−Condon distribution distinctly red shifted with respect to excitation. In both cases this indicates a strong asymmetry of the excited state with respect to the ground state. Under the assumption that these R absorptions are due to the other rotameric forms of perfluoronaphthols, namely, *cis* 1-FN and *trans* 2-FN, this distortion should involve not only the out of plane inversion of the fluorine atoms as previously but also a perturbation due to a stronger OH···F interaction. The presence of an OH···F interaction has been shown to strongly perturb the spectroscopy of *o*-fluorobenzyl alcohol near the origin of the S_0-S_1 transition.[21] In this case, the low-frequency vibronic structure appearing at the onset of the spectrum has been interpreted by bending motion of the OH group coupled with H atom motion in the OH···F hydrogen bond.

In the case of *cis* 1-FN AM1 calculations predict an out of plane geometry of the OH group and a shorter distance between

the H atom and the interacting F atom, and one can thus expect a stronger distortion in the excited state. The onset of the excitation spectrum in 1-FN appears as an intense line surrounded by a bunch of features of lower intensity. This pattern is difficult to understand if we consider that the observed transitions correspond to the 0−0 transition region and may rather indicate that because of substantial geometry changes in the excited state, higher energy vibronic levels are reached by Franck−Condon excitation from the ground state. The dispersed fluorescence which exhibits the same resonance fluorescence in its blue part as that originating from the B features and extends to the red is also indicative of a strong distortion of the excited geometry relative to that of the ground state. A more regular pattern is observed in the R excitation spectrum of 2-FN. The low-frequency mode of 21 cm^{-1} making a long progression of increasing intensity is on the same order of magnitude as the inversion frequency calculated previously. However, this out of plane mode is expected to be allowed for $\Delta v = 2n$ if the planar geometry of the naphthalene ring is retained in the ground state of 2-FN. Thus, under the assumption that transitions lead to the harmonic upper part of the double potential as indicated by the intensity distribution, the observed progression should in that case involve a 42 cm^{-1} interval. The observed pattern may rather be associated with a large amplitude motion localized on the OH···F bond and suggests in this case also an important change of the excited state geometry. The strongly displaced Franck−Condon distribution along this mode shows that high-energy levels are reached by electronic excitation from the ground state. The shift of about 4500 cm^{-1} of the fluorescence may be the result of Franck−Condon-allowed transitions between a displaced and shallow potential well in the excited state and the steep part of the deeper ground state potential curve.

In both cases, the peculiar properties of the excitation and emission spectra may be the result of the increased charge transfer contribution in the excited state. Because of the donor character of the OH substituent and of the presence of fluorine substituents which introduce low-energy σ^* orbitals, one can expect a larger coupling of the locally excited states with internal charge transfer configurations than in the hydrogenated naphthols. Such an effect can be evidenced from the red shift of the fluorescence spectrum obtained in polar acetonitrile solution with respect to nonpolar cyclohexane.

However, the unusual spectroscopic behavior of perfluoronaphthols seems to be strongly dependent on the orientation of the hydroxyl group and on the location of the weak intramolecular OH···F bond since it is observed for one rotamer and not for the other. The *cis* 1-FN conformation involves interaction between substituents in position 1 and 8 of the naphthalene ring, while in the *trans* 2-FN rotamer the substituents in position 2 (OH) and 3 (F) interact through a weak hydrogen bond. The specific structure of these conformers thus seems to play a role in reinforcing the strength of the local OH···F interactions and to modify the geometry of the excited state. These effects may be related to charge redistribution in the excited state. Qualitative inspection of the AO coefficients for the molecular orbitals involved in the electronic transition to the L_b state of naphthols shows a significant increase in the electronic density in the C(8) upon electronic excitation, while the C(2) is less affected for 1-substituted naphthalene.[8] In the case of 2-substituted naphthalene a similar increase is shown for the C(3). This effect may strengthen the local charge transfer character of the OH···F bond and be responsible for the geometry change specifically observed for the *cis* 1-FN and *trans* 2-FN.

Conclusion

The spectroscopy of the first S_0-S_1 transition of 1- and 2-perfluoronaphthols in the conditions of supersonic expansion has been studied in detail and has been shown to exhibit very unusual trends. Both compounds give rise to two dissimilar absorption systems at the origin. The lower energy system appears as a series of congested and overlapping features and results in a broad and red-shifted fluorescence. The higher energy system bears a close resemblance both in absorption and in emission to that of unsubstituted perfluoronaphthalene and presents a low-frequency progression which is attributed to an out of plane mode of the fluorine atoms with respect to the skeletal molecular plane. The two absorption spectra have been attributed to the presence of two ground state conformers corresponding to a different orientation of the OH group with respect to the naphthalene nucleus and involving different weak hydrogen bonding of the OH group with the neighboring fluorine atoms. The complex structure of the lower energy absorption system and its fluorescent characteristics have been tentatively interpreted in terms of a strongly distorted excited state whose equilibrium geometry is strongly sensitive to the position of the internal hydrogen bond. Further experiments with selected monofluoronaphthols as well as time-resolved data should be useful to confirm the present findings.

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