Proton Transfer in 3-Hydroxyflavone Studied by High-Resolution 10 K Laser-Excited Shpol'skii Spectroscopy

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High-resolution 10 K Shpol'skii spectra of 3-hydroxyflavone (3HF) and its deuterated analogue (3DF) in *n*-octane and *n*-octane/octanol mixtures are presented for the first time. In pure *n*-octane for both 3HF and 3DF, well-resolved excitation and emission spectra were observed, showing fluorescence shifted from 380−460 to 513−550 nm because of excited-state intramolecular proton/deuteron transfer (ESIPT/ESIDT). Compared to those of 3DF, the 3HF excitation and emission bands are much wider because of lifetime-limited homogeneous broadening. Proton transfer is at least a factor of 4 faster than deuteron transfer. From the homogeneous contribution to the total bandwidth of 3HF, the rate constants of ESIPT and ground-state back proton transfer were estimated to be 39 ± 10 and 210 ± 30 fs, respectively. The effect of four octanol additives was investigated. Only for 2-octanol and—though less favorable—3-octanol, a new site in the emission spectrum was observed, blue-shifted over 7 and 10 nm, respectively, versus the 3HF spectrum in *n*-octane. The new site is attributed to a 1:1 3HF/octanol complex. Its ground-state vibrational pattern differs from that of free 3HF. For 3DF, no Shpol'skii spectrum of a complex could be obtained. It is suggested that in the complex the proton/deuteron transfer mechanisms differ from those of the free molecules; furthermore, a molecular structure for the tautomeric form of the complex is proposed.

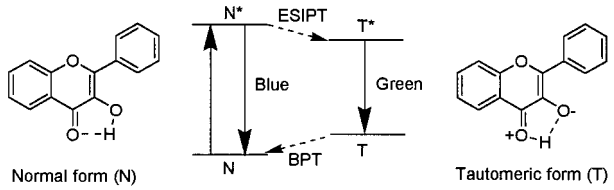
Introduction

Compounds that undergo excited-state intramolecular proton transfer (ESIPT) have been intensively studied throughout the last two decades, one of the most striking examples being 3-hydroxyflavone (3HF).[1−17] This compound is known to have fluorescence bands both in the blue (380−460 nm) and in the green (510−570 nm). As early as 1979, Sengupta and Kasha showed that this dual emission is due to ESIPT and that the two bands can be assigned to the normal and the tautomeric form of excited state 3HF, respectively[1] (see Scheme 1). Since then, a large number of investigations have been carried out to elucidate the mechanism and kinetics of this system.[1−17] Especially, the effects of hydrogen-bonding solvents or impurities in nonpolar solvents on the kinetics received wide attention.[7,9,11,15−17]

In highly purified and dried hydrocarbon solvents, the ESIPT mechanism is well established; the hydroxy proton is transferred intramolecularly to the oxygen of the ketone group on a subpicosecond time scale.[10,11,15−17] Exact lifetimes of N* and T, however, are not easily measured. Recently, ultrafast pump/probe experiments were reported by Ameer-Beg et al.;[16] they propose a value of 35 fs for the rise time of T* in methylcyclohexane (MCH) or acetonitrile at room temperature, though their measurements were instrument-limited. For a more accurate determination of the ESIPT rate in 3HF, faster instruments are needed or a different approach should be followed, that is, the measurement of homogeneous broadening of spectral transitions in excitation and emission.

The latter approach is followed in the present paper, utilizing Shpol'skii matrixes at 10 K. It is shown that for 3HF—and for its deuterated analogue (3DF)—in *n*-octane at 10 K highly resolved fluorescence spectra can be obtained. In the polycrystalline matrix, the remaining inhomogeneous broadening is low enough to make homogeneous broadening effects clearly visible. The homogeneous broadening of the excitation spectrum yields the lifetime of N*, that is, it reflects the rate of the ESIPT process. Because the lifetime of T* is relatively long (nanosecond scale), in emission, the homogeneous broadening is a measure for the lifetime of T, that is, the rate of back proton transfer (BPT).

SCHEME 1: ESIPT and BPT in 3HF



Earlier attempts to record high-resolution spectra have been reported in the literature.[8,10−12] McMorrow and Kasha were the first to report the Shpol'skii spectrum of 3HF in octane at 77 K, but unfortunately, their spectra were still far from highly resolved.[8] Matrix isolation experiments in argon under cryogenic conditions were mainly carried out to study the isolated 3HF and 3HF/monosolvate complexes.[10,11] Brucker and Kelley used their poorly resolved 30 K emission spectra in an argon matrix to estimate the back-transfer rates for 3HF and 3DF; they found a substantial difference in lifetimes, 60 and 260 fs, respectively.[11]

Apparently, in matrix isolation spectroscopy a significant amount of inhomogeneous broadening remains present, even under cryogenic conditions.[18] In Shpol'skii spectroscopy on the other hand, an impressive increase in resolution can be achieved

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at temperatures below 30 K,[19,20] provided that the solidification of the sample is sufficiently fast. For that reason, we present here laser-excited Shpol'skii spectra of 3HF and 3DF at 10 K; the excitation and emission spectra allow a fairly accurate determination of the time constants of the ESIPT and BPT processes.

Interestingly, our approach also enabled us to study proton transfer in the presence of a hydrogen-bonding solvent; in other words, a hydrogen-bonding solvent can be incorporated in the *n*-octane matrix without destroying the crystalline structure too much. The influence of such solvents received extensive attention in the literature. Already in the first reports about ESIPT in 3HF, it was shown that for methylbutane as a solvent there was exclusively green emission, whereas in methanol both the blue and the green emission were observed.[1] In a 77 K methylcyclohexane (MCH) glass containing substoichiometric amounts of water, an additional emission around 490 nm was detected, which was attributed to the 3HF/monosolvate complex.[4,8] In matrix-isolated spectra in argon, the same effect was observed.[11] Other reports showed that in the presence of a hydrogen-bonding compound the transfer rate decay curve becomes biexponential.[6,9,11,15−17] In the recent work of Ameer-Beg et al. dealing with pump/probe experiments, it was shown that the fast component of the excited-state proton-transfer rate in ethanol is 60 fs, whereas the slow component is 10 ps.[16] The slow component was attributed to an interaction with a hydrogen-bonding compound. Nonetheless, the detailed mechanism of proton transfer in the presence of a hydrogen-bonding compound remains unknown.[16] In our work, a hydroxy group was incorporated into the *n*-alkane matrix by adding various isomers of octanol; the highly resolved spectra obtained for 2-octanol and 3-octanol provide detailed information on the solute−solvent interaction, including vibrations characteristic for the complex.

Experimental Section

All measurements were done using a 10^{-5} M solution of 3-hydroxyflavone (Extrasynthèse, Genay, France) in *puriss* octane (Fluka). 1-, 2-, 3-, and 4-Octanol were obtained from Fluka, Sigma, Fluka, and Aldrich, respectively. Deuteration of 3HF was achieved by dissolving 3HF in deuterated methanol (Aldrich), followed by evaporation of the solvent. To the 3DF/2-octanol samples, D_2O was added to deuterate the octanol; the octane layer was measured. No additional purification steps were applied to any of the samples.

The samples were transferred to a homemade sample holder that contains four sample cells. The sample holder was cooled to 10 K by a Cryodyne model 21 closed-cycle helium refrigerator (CTI Cryogenics, Waltham, MA). The sample was illuminated at an angle of 30° with a XeCl excimer laser (Lambda Physik LPX 110i, Göttingen, Germany) pumping a dye laser (Lambda Physik, LPD 3002). The excimer laser was operated at 10 Hz, producing 10 ns 50 mJ pulses. With the use of DMQ as a dye, a tuneable output in the 360−377 nm range was obtained. The fluorescence emission was collected by a 3 cm F/l.2 quartz lens and focused on the entrance slit of a Spex 1877 0.6 m triple monochromator (Edison, NJ) by a 10 cm F/4 quartz lens. The spectral resolution of this monochromator was 0.1 nm. For detection, a Princeton Instrument (Trenton, NJ) intensified CCD camera type 576T was used in the gated mode. The gate was opened at the end of the (scattered) laser light pulse.

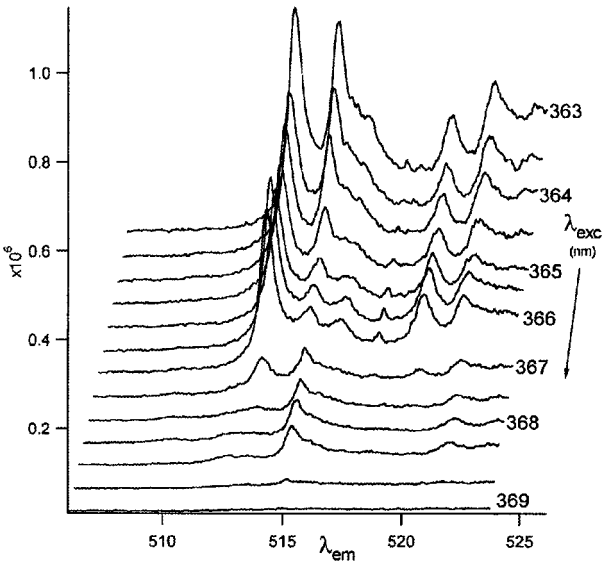


Figure 1. Emission spectra of 3-hydroxyflavone (3HF) in *n*-octane measured at 10 K. The excitation wavelength was varied from 363 to 369 nm with 0.5 nm steps. 3HF is present in two sites, one emitting at $\lambda_{em} = 513.1$ nm and one at $\lambda_{em} = 515.0$ nm. The emission bandwidth was estimated to be 0.7 nm; the excitation bandwidth was estimated to be 2 nm.

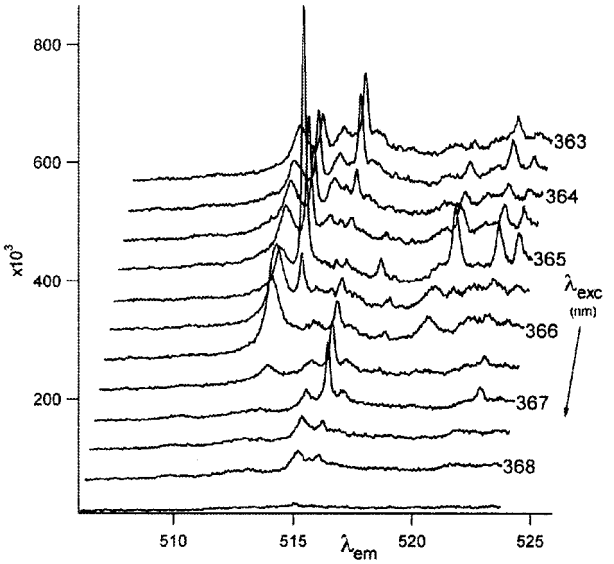


Figure 2. Emission spectra of 3-deuterioxyflavone (3DF) in *n*-octane measured at 10 K. The excitation wavelength was varied from 363 to 368.5 nm with 0.5 nm steps. 3DF is present in two sites, one emitting at $\lambda_{em} = 514.1$ nm and one at $\lambda_{em} = 515.8$ nm. In the sample, there was still 3HF present because the sites at 513.1 and 515.0 nm can still be seen. The emission bandwidth was determined to be 0.2 nm. The excitation bandwidth was estimated to be 0.5 nm.

Results and Discussion

3HF and 3DF in *n*-Octane. High-resolution fluorescence spectra of the tautomeric form of 3HF were obtained using the Shpol'skii approach with *n*-octane as a solvent. In Figure 1, an excitation−emission plot of 3HF in an *n*-octane matrix at 10 K is shown. In this figure, it can be seen that 3HF is present in two different sites in the matrix, with 0,0 absorption transitions at approximately 365.5 and 367.5 nm. The corresponding 0,0 transitions of the tautomeric form are found at 513.1 and 515.0 nm, respectively. Figure 2 shows the same plot for a 3DF sample (which also contained some remaining nondeuterated 3HF). The corresponding spectra can be readily distinguished. Obviously,

for 3DF, there are also two sites in absorption, but compared to those of 3HF, these are blue shifted to 365.1 and 366.7 nm. The 0,0 transitions of the tautomeric form are shifted in the opposite direction, that is, to 514.1 and 515.8 nm, respectively.

The selectively excited Shpol'skii emission spectra of 3HF and 3DF are given in Figure 3A−D; the ground-state vibration wavenumbers are included in the figure; weak sites are left out of consideration. The spectra shown in Figure 3 have some interesting features. First of all, the bands for 3DF are much sharper than those for 3HF—a result that applies to the excitation spectra as well, see Figures 1 and 2. Second, the low-frequency vibrations of 3HF and 3DF in the ground-state tautomer indicated in the spectra are not significantly different.

There are good reasons to assume that the inhomogeneous broadening in 3HF and 3DF are the same, that is, for both molecules the variation in interaction with and the positioning in the crystalline *n*-octane matrix are equal. So, the line width differences observed reflect differences in homogeneous line broadening. In line with the literature, proton-transfer reactions are much faster than deuteron-transfer reactions.[14] This holds for both ESIPT and BPT. Apparently, for 3HF, the lifetimes of N* and T are much shorter than for 3DF.

A quantitative analysis of these results can be performed as follows. For convenience, it is assumed that the experimental line width is composed of three Gaussian-shaped, independent contributions, the instrumental resolution (4 cm^{-1}), the inhomogeneous line width, and the homogeneous line width. Furthermore, for 3HF and 3DF, the inhomogeneous broadenings are set equal. Though its exact value cannot be inferred from the available data, its maximum value and its minimum value can be readily estimated from the 3DF spectra. Obviously, its minimum is zero. Its maximum is equal to the line width of the 3DF spectra, which applies if homogeneous broadening plays no role at all.

The results are collected in Table 1. In excitation, the inhomogeneous band broadening ranges from 0 to 45 cm^{-1}, which implies that the homogeneous broadening in the excitation spectrum of 3HF ranges from 110 to 180 cm^{-1}. From this homogeneous broadening, the lifetime of N* can be calculated using $\tau = 1/(2\pi\Delta\nu c)$ (wherein $\Delta\nu$ is the homogeneous broadening); it is found to be 39 ± 10 fs. Analogously, the lifetime of T (determined by the BPT) can be calculated. In this case, the inhomogeneous broadening ranges from 0 to 7.3 cm^{-1} so that the homogeneous broadening in the emission lines of 3HF ranges from 22 to 29 cm^{-1}. As a result, the lifetime of T is found to be 210 ± 30 fs. Thus, the rate constant of ESIPT is five times higher than that of BPT. Considering the lifetimes of 3DF, only the lower limiting values can be estimated. Excited-state intramolecular deuteron transfer is slower than 180 fs, while back deuteron transfer is slower than 730 fs.

Of course, the three line width components considered above do not all have a Gaussian shape. Nevertheless, the results of Table 1 give a good, though rough, estimate of the lifetimes of the N* and T forms of 3HF in a *n*-octane crystalline matrix at 10 K. The reported BPT rate derived from the bandwidth in the emission spectrum of 3HF in an argon matrix at 30 K is three to four times faster (60 fs[11]) than the value shown in Table 1. It should, however, be realized that the spectra reported in that publication were relatively broad, so the homogeneous component of the bandwidth could only be very roughly estimated. Interestingly, the N* lifetime is in line with the most recent literature data, being obtained by transient absorption measurements in MCH at room temperature.[16] Apparently, there is no strong difference between N* lifetimes at room temperature and under cryogenic conditions. This points to a tunneling model for ESIPT, a model that is also in correspondence with the fact that for 3DF ESIPT is much slower. In this study, we have

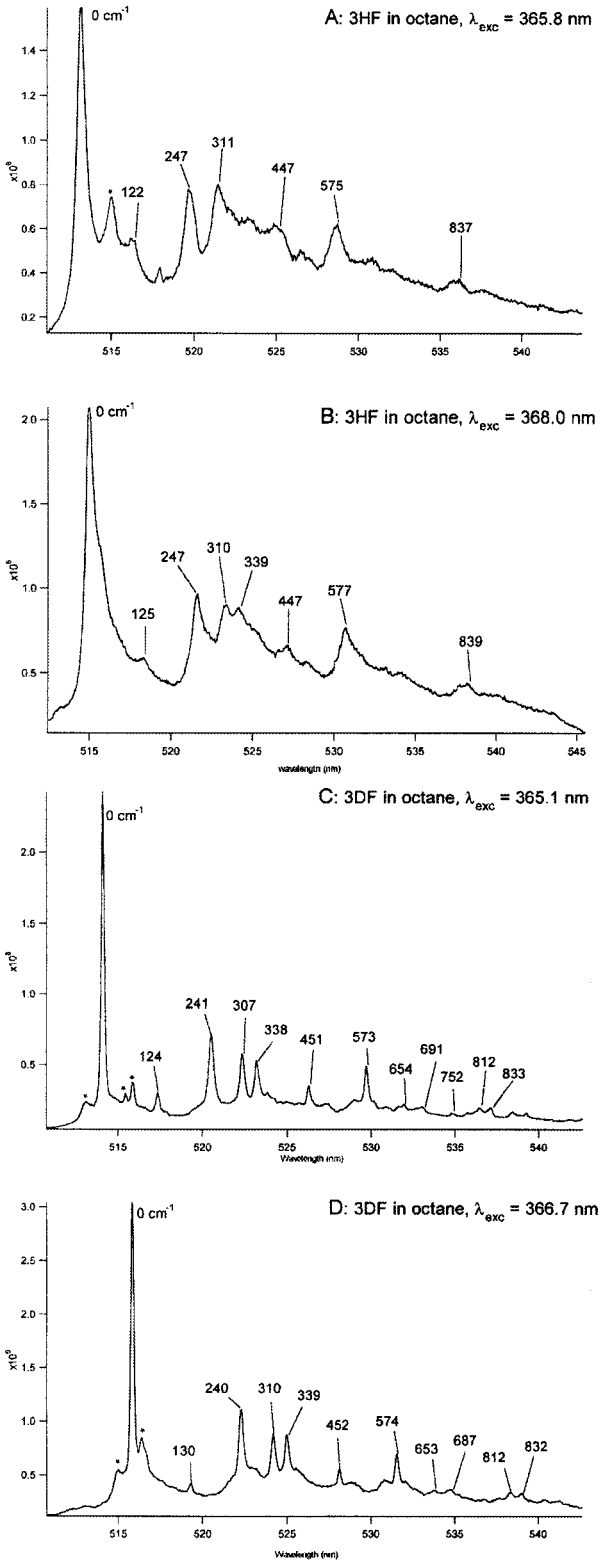


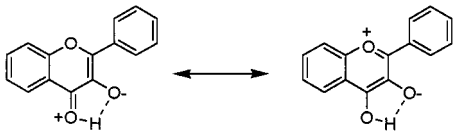
Figure 3. 10 K Shpol'skii spectra of 3HF/3DF. In each spectrum, one site is selectively excited. Panels A and B show the emission spectra of 3HF in *n*-octane excited at 365.8 and 368 nm, respectively. Panels C and D show the emission spectra of 3DF in *n*-octane, excited at 365.1 and 366.7 nm, respectively. Peak labels indicate ground-state vibrational frequencies in wavenumbers. The starred peaks are other sites due to nonselective excitation. The 339 cm^{-1} band in spectrum A is not readily visible because of an overlap of a vibration band of the 368 nm site.

TABLE 1: Rates of Excited State Intramolecular Proton Transfer (ESIPT) and Back Proton Transfer (BPT) in 3HF and 3DF[a]

	Γ_{tot} (cm^{-1})		Γ_{instr}	Γ_{inh} (cm^{-1})		Γ_{hom} (cm^{-1})		
	min	max	(cm^{-1})	min	max	min	max	τ_{pt} (fs)
				ESIPT				
3DF	30	45	4	0	45	0	45	>180
3HF	120	180	4	0	45	110	180	39 ± 10
				BPT				
3DF	6.8	8.3	4	0	7.3	0	7.3	>730
3HF	24	29	4	0	7.3	22	29	210 ± 30

[a] The rate of ESIPT is obtained from the total bandwidth, which was determined to be 2 and 0.5 nm for 3HF and 3DF, respectively (an uncertainty of 20% was included). The rate of BPT was obtained from the total bandwidth of 0.7 and 0.2 nm for 3HF and 3DF, respectively (an uncertainty of 10% was included). The homogeneous broadening (Γ_{hom}) was calculated from the total broadening (Γ_{tot}), the instrumental broadening (Γ_{instr}), and the inhomogeneous broadening (Γ_{inh}) via $\Gamma_{tot}^2 = \Gamma_{instr}^2 + \Gamma_{inh}^2 + \Gamma_{hom}^2$.

SCHEME 2: Mesomeric Structures of 3HF in the T Form



shown deuteron transfer to be slower by a factor of at least 4.5 and 3.5 for ESIPT and BPT, respectively. These values are in agreement with the isotope effect found by Brucker and Kelley[11] for the same component in frozen argon at 30 K. The same group[14] did not find a significant isotope effect in acetonitrile at room temperature, indicating a different mechanism under these conditions.

The observation that the low-frequency vibrations of the T form in 3HF and 3DF are not different (see Figure 3) points to a structure of T in which the hydrogen/deuterium atom is indirectly coupled to the π-electronic structure involved in the electronic transition. This might indicate that the mesomeric structure of T, shown in Scheme 2, plays a significant role.

Addition of Octanol. As mentioned in the Introduction, the effect of hydrogen bonding caused by impurities has been discussed extensively in the literature. We observed that in a 10 K *n*-octane Shpol'skii matrix, addition of a hydrogen bonding impurity like water, methanol, or diethyl ether to the sample does not affect the high-resolution spectra of 3HF. The reason for this is that 3HF fits tightly into the matrix so there is no space available for an additional hydrogen-bonding molecule; upon cooling, the added polar solvent is simply frozen out and a phase separation is obtained. If, on the contrary, a hydrogen bonding impurity is added that can replace a particular octane molecule of the crystalline surrounding of a 3HF molecule, an effect can be expected. This was observed for 2-octanol and 3-octanol. Addition of a minor amount of 2-octanol results in the appearance of a new site at 507.2 nm. Addition (of a much larger amount) of 3-octanol results in a new site further shifted to the blue, that is, at 504.7 nm. On the contrary, addition of 1-octanol or 4-octanol has no effect.

The new site in the emission spectrum at 507.2 nm is already observed at very low concentrations of 2-octanol (see Figure 4), down to 0.001%. At increasing concentrations of 2-octanol, the intensities of the 513.1 and 515.0 nm sites decrease, while simultaneously the 507.2 nm band is growing in intensity. Therefore, it is likely that in the ground state (N) a 3HF/2-octanol complex is formed, in fact, a chemical entity distinguishable from the free 3HF (that is characterized by two emission sites in *n*-octane). Because the additional site is already present at a low concentration of 2-octanol, it can be concluded that the 3HF/octanol complexes are formed in the liquid phase, in advance of sample solidification. Apparently, the exact position of the hydroxy group in the octanol molecule determines whether the complex fits in the *n*-octane matrix. Both the 3HF/2-octanol complex and the 3HF/3-octanol complex fit into the matrix in a well-defined way (only weak additional sites are observed), whereas the 3HF/1-octanol and 3HF/4-octanol complexes do not give rise to the Shpol'skii effect.

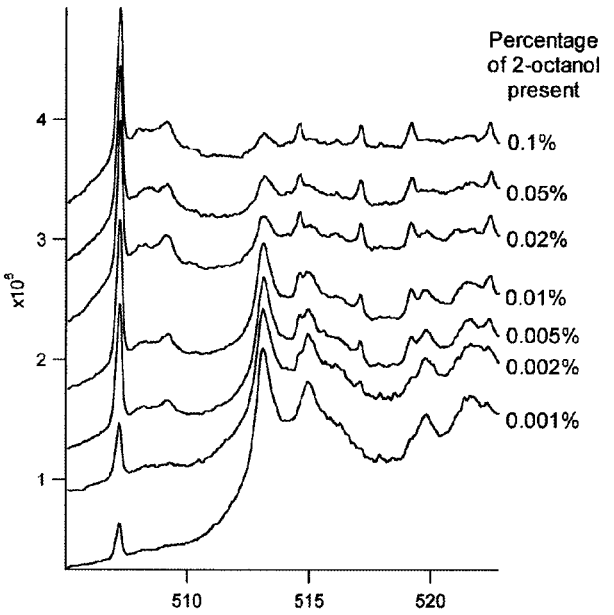


Figure 4. 10 K Shpol'skii spectra of 3HF in *n*-octane with increasing concentration of 2-octanol added. The sample was excited at 365 nm. A 2-octanol concentration of 0.001% corresponds to 70 μM. The concentration of 3HF was 10 μM.

Excitation−emission spectra for 3HF in *n*-octane containing a minor amount (0.005%) of 2-octanol are depicted in Figure 5. The three sites considered above can be readily observed, that is, the sites of pure 3HF at 513.1 and 515.0 nm (as also observed in Figure 1) and furthermore the 507.2 nm site showing the 3HF/2-octanol complex. It should be noted that upon excitation at wavelengths higher than 370 nm only the latter site is observed. Figure 6 shows the detailed emission spectra of 3HF/2-octanol and 3HF/3-octanol; the low-frequency vibrations—quite similar but not fully identical for the two complexes—are indicated in the spectra.

Two features emerge from Figures 5 and 6. First of all, a large Stokes' shift is observed for the complexes (507−372 nm for 3HF/2-octanol). It strongly suggests that, also in the complex, excited-state proton transfer is operative. Second, the vibrational pattern in Figure 6 is different from that in Figure 3. In other words, the tautomeric species generated upon excited-state proton transfer in 3HF/2-octanol is structurally different from T in Scheme 1. Some vibrations are equal, for instance, 451, 572, and 653 cm^{-1}, while some are distinctly different, for instance, 279 and 375 cm^{-1} in the complex but 247, 310, and 339 cm^{-1} in 3HF.

Of course, we also tried to record Shpol'skii spectra of 3DF/2-deuterioxyoctane, the deutero analogue of the 3HF/2-octanol complex. It could not be observed, that is, there was no additional site in the emission spectrum of 3DF in octane/2-deuterioxyoctane mixtures when excitation wavelengths in the 365−375 nm range were used. This suggests that in the 3DF/

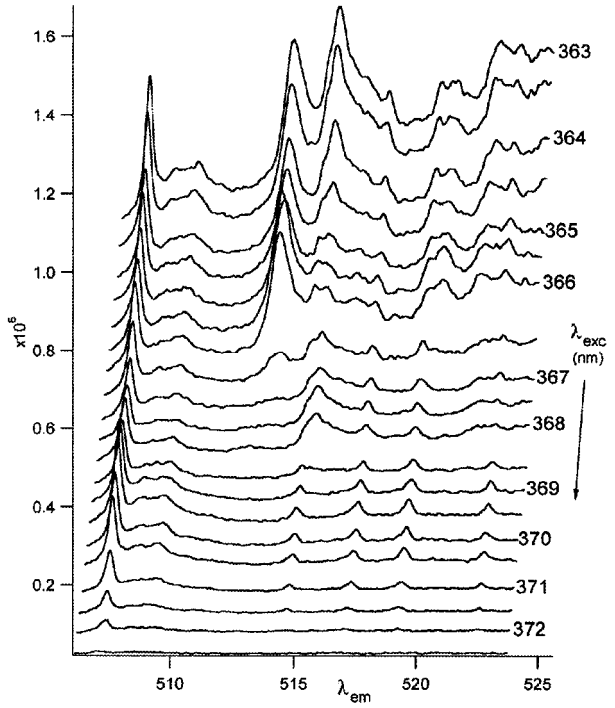


Figure 5. Emission spectra of 3-hydroxyflavone (3HF) in *n*-octane with 0.005% 2-octanol measured at 10 K. The excitation wavelength was varied from 363 to 372.5 nm with 0.5 nm steps. The normal 3HF sites emit at $\lambda_{em} = 513.1$ nm and at $\lambda_{em} = 515.0$ nm. The site due to the presence of 2-octanol can be found at $\lambda_{em} = 507.2$ nm.

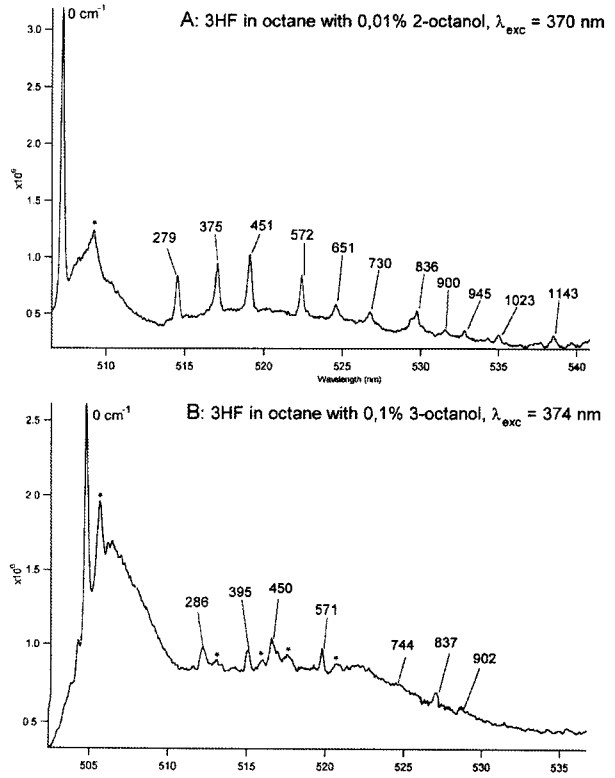
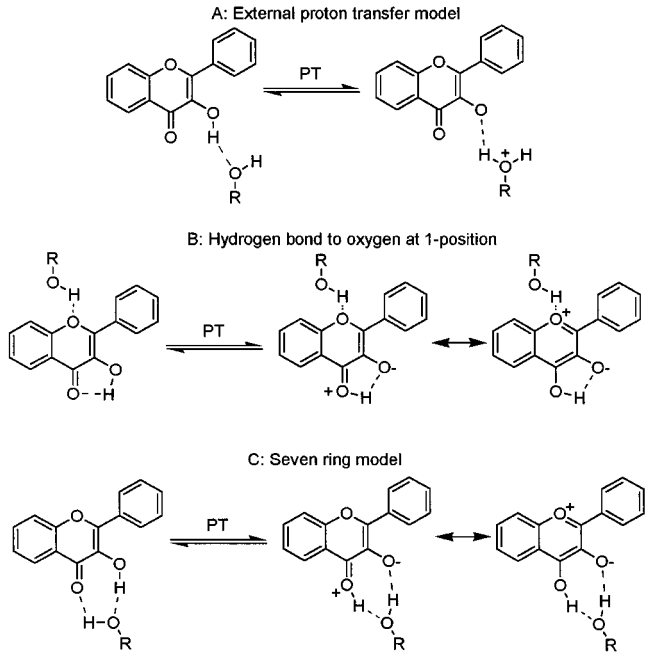


Figure 6. Emission spectra of 3HF in the presence of octanol measured at 10 K: (A) 3HF in *n*-octane with 0.01% 2-octanol present excited at 370 nm; (B) 3HF in *n*-octane with 0.1% 3-octanol present excited at 374 nm. Peak labels indicate ground-state vibrational frequencies in wavenumbers. The starred peaks originate from an additional site.

octane complex excited-state deuteron transfer is very slow, that is, not able to successfully compete with the normal decay of the complex (broad-banded emission in the blue). Apparently,

SCHEME 3: Possible Structures for External Proton Transfer (R = octyl)



there is an extremely large difference in proton and deuteron transfer rates, a phenomenon that is well-known from the literature.[14] A large rate difference generally indicates a large difference in tunneling distance.

To summarize the above results, the excited-state proton transfer in 3HF/2-octanol is not the same as in 3HF. The tunneling distances or the barrier profiles are different, and furthermore, the structure of the tautomeric ground-state species generated after emission differs from that of T (see Scheme 1).

It is likely that upon addition of 2-octanol or 3-octanol one octane molecule in the crystalline environment of 3HF is replaced by one octanol molecule. However, the relative orientation of the OH group of octanol with respect to the 3HF molecule is not easily predicted. Possible structures of the 3HF/2-octanol complex are depicted in Scheme 3 (there are only few possibilities for a 1:1 complex that would fit in the octane matrix). Their appropriateness to explain the above results is discussed successively.

Scheme 3A shows external proton transfer. After excitation, the 3-OH group in the 3HF molecule becomes acidic and the proton is transferred to the OH group of octanol. This results in the formation of octyl-OH_2^+ and the anionic form of 3HF. Differences in vibrational frequencies for this species compared to T can be readily conceived. Whereas in T the positive charge on the proton-accepting group can be delocalized (see Scheme 2), giving 3HFs six ring an aromatic character, such a delocalization is impossible for the anion formed upon external proton transfer. Thus, Scheme 3A would account for differences in vibration energies. However, it is not very likely that the tautomeric form and the anionic form of 3HF show such similar emission wavelengths, the difference being as small as a few nanometers.

Scheme 3B shows a complex structure with the hydrogen bound to the oxygen at the 1-position of 3HF. For this complex, the positive charge can be more efficiently delocalized than in T so that a change in vibrational frequencies might be expected. However, the proton transfer as such will hardly be affected so that the absence of excited-state deuteron transfer in the 3DF/octanol complex cannot be rationalized.

Scheme 3C shows a seven-ring model, in which two hydrogen bonds are involved. In such a structure, the proton-transfer mechanism will differ from that in Scheme 1: two protons are involved and different tunneling distances are dealt with. The first proton is transferred from the OH group in 3HF to the octanol molecule, while the second one goes from octanol to the carbonyl oxygen in 3HF. As such, the tautomer in Scheme 3C is structurally rather similar to T in Scheme 2. The major structural difference presumably is that because of the nonflat seven ring, the hydroxy group and the carbonyl group in the complex will be located out-of-plane of the six ring of 3HF, thereby changing the low-energy, out-of-plane vibrational energies of 3HF.

To conclude this section, the following two features should be noted. First, the difference in behavior observed for the octanol isomers can be conceived as follows: for 1-octanol and 4-octanol, the formed 3HF complexes do not fit adequately in the *n*-octane matrix; the 3-octanol complex fits to some extent, while the 2-octanol complex fits appropriately. However, the detailed structures of 3HF/2-octanol and 3HF/3-octanol will not be fully identical, especially as regards the hydrogen-bond distances.

Second, for the 3HF/2-octanol and 3HF/3-octanol complexes, it is not possible to derive the rate constants from the line widths because the inhomogeneous broadening contributions are fully unknown and a comparison with the 3DF complexes cannot be made. Nonetheless, a marked difference in line width in excitation and emission is worth noting; the line width in excitation is approximately 3 nm but in emission only 0.4 nm, a larger difference than that observed for the free 3HF molecule. This supports the abovementioned assumption that the proton-transfer mechanisms in 3HF and in the 3HF/octanol complexes are not the same. Furthermore, it indicates that also in the complex the excited-state proton-transfer rate is much faster than the rate of the proton back transfer.

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