

Fluorescence studies of the excited-state proton transfer in substituted 3-hydroxychromones in supersonic jet

Michiya Itoh

Department of Physical and Chemical Biodynamics,
Graduate School of Kanazawa University, and Faculty of
Pharmaceutical Sciences, Kanazawa University, Kanazawa 920,
Japan

Abstract

Intramolecular excited state proton transfer (ESPT) of 3-hydroxychromone (3-HC), 3-hydroxyflavone (3-HF) and 2-(2-naphthyl)-3-hydroxychromone (2-NHC), and of their water clusters were investigated in a supersonic expansion. The visible tautomer fluorescence excitation spectra of these compounds exhibit considerably well resolved vibrational structures, while no significant uv fluorescence excitation spectrum due to the normal form was observed. Upper limit of rate constant of the tautomer formation was estimated to be $1.77 \times 10^{12} \text{ s}^{-1}$ for 3-HC, $6.5 \times 10^{11} \text{ s}^{-1}$ for 3-HF and $1.54 \times 10^{11} \text{ s}^{-1}$ for 2-NHC in supersonic expansion by simulation of line width of the respective origin bands in the visible fluorescence excitation spectra. The fluorescence excitation and dispersed fluorescence spectra demonstrate 1;1 and 1;2 water complex formations of 3-HF and 2-NHC and no ESPT in these water clusters. However, no evidence of water complex formation was obtained in jet-cooled 3-HC.

INTRODUCTION

Usual intramolecular hydrogen bonding systems such as methyl salicylate and o-hydroxyacetophenone in hydrocarbon solution are believed to undergo a barrierless proton transfer in their singlet excited state. Since Sengupta and Kasha (ref. 1) reported an energy barrier in the excited state proton transfer (ESPT) of 3-hydroxyflavone at the first time, some research groups including us concerned in intramolecular excited state proton transfer of this compound. In 1982 (ref. 2) and 1986 (ref. 3), we reported rather slow rise of tautomer fluorescence in carefully purified hydrocarbon solution of 3-HF, while no slow rise was detected in 3-hydroxychromone (3-HC) which lacks the 2-phenyl group of 3-HF.

We suggested that the different feature of the intramolecular ESPT between 3-HF and 3-HC was ascribed to the torsional effect of the phenyl group of 3-HF. However, McMorro and Kasha (ref. 4), and some other research groups that the different feature between these compounds is the results of varying traces of H-bonding impurities in the hydrocarbon solvents. Further, Kelley and his coworkers (ref. 5) reported picosecond fluorescence studies of 3-HF in low temperature Ar matrix, and they suggested fast ESPT in a monosolvate of 3-HF with water in a 10K Ar matrix.

In spite of numerous investigations including recent picosecond and femtosecond fluorescence studies, there are still several and serious controversies among them. These controversies are concerned with potential barrier of the excited state proton transfer and also

of the ground state reverse proton transfer. These controversies are attributable to a limitation of the experimental condition in the condensed phase. Recent supersonic jet spectroscopy provides us with environment of obtaining a sample of the molecules in the cooled and isolated molecular condition to investigate weak inter- and intra-molecular interactions. In 1989, Ernsting and Dick (ref. 6) reported the tautomer fluorescence and excitation spectra of 3-HF in Ar matrix and in supersonic jet. At the almost same time, we have reported a preliminary result of supersonic jet spectroscopy of 3-HF in comparison with 3-HC. This paper presents the comparative studies of ESPT of several substituted 3-HC, and their water clusters in supersonic jet.

EXPERIMENTAL

Fluorescence excitation and dispersed fluorescence spectra of the supersonic free jet were measured with the same method and procedures as those described in previous papers (ref. 7). Two atm He gas was introduced into a stainless steel sample reservoir leading to a pulsed nozzle (0.4 mm diameter). The complex formation with H_2O/D_2O in the free jet was performed by mixing H_2O/D_2O vapor (1–12 Torr) with He carrier gas.

RESULTS AND DISCUSSION

Figure 1(a) shows a visible fluorescence (> 510 nm) excitation spectrum of 3-hydroxyflavone in supersonic expansion. The visible fluorescence spectra is due to the tautomer generated by the intramolecular excited state proton transfer. A main vibrational progression of 45 cm^{-1} may be attributable to the phenyl torsional motion, since similar progressions are reported in phenylanthracene. However, no significant uv fluorescence excitation spectrum was observed. Figure 2a shows a dispersed fluorescence spectrum in the excitation of the origin band at 28080.7 cm^{-1} . The spectra are almost identical with the tautomer fluorescence in static vapor and in nonpolar solution. The decay times of the tautomer fluorescence were 14–15 ns, which are almost independent of excitation wavelength in the excess vibrational energy region less than 500 cm^{-1} . Unfortunately, picosecond fluorescence rise of the tautomer was not obtained because of very weak fluorescence in the jet cooled condition. The fluorescence excitation and dispersed fluorescence spectra were observed in the similar supersonic expansion of several 3-HF derivatives with F, Cl, Br, and methyl substituents at the para position of 2-phenyl group. The vibrational progressions and decay times of these compounds are almost similar to those of 3-HF.

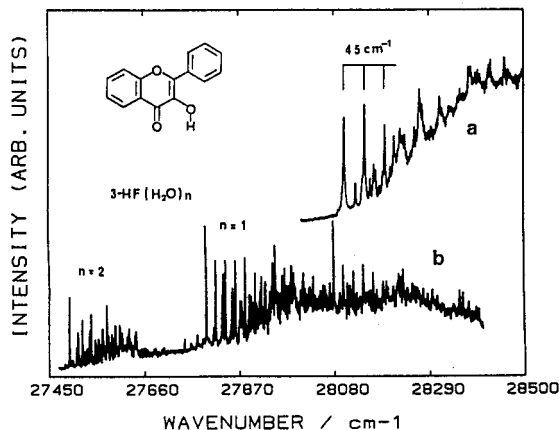


Fig. 1. (a) Fluorescence (> 510 nm) excitation spectra of jet-cooled 3-HF, (b) uv fluorescence (360–480 nm) excitation spectra of 3-HF water clusters.

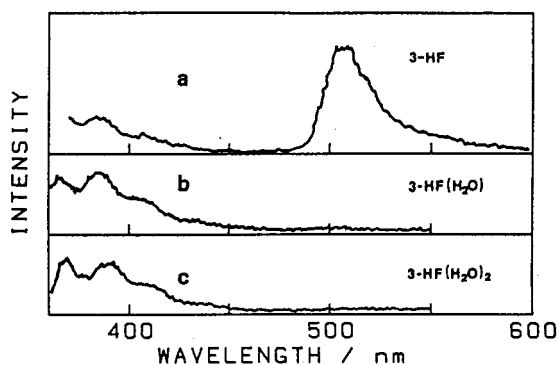


Fig. 2. Dispersed fluorescence spectra of (a) 3-HF excited at 28080.7 cm^{-1} , a uv fluorescence is attributable to a vdW complex with a trace amount of water contaminated. (b) and (c) are spectra of water clusters of 3-HF.

The 3-methyl pentane solution of 2-naphthyl-3-hydroxychromone (2-NHC) exhibits the ESPT tautomer fluorescence at λ_{\max} 538 nm. The tautomer fluorescence excitation spectrum in supersonic expansion exhibits a dominant low frequency vibrational mode of 36 cm^{-1} which is ascribed to naphthyl torsional motion. Similar to 3-HF, no significant uv fluorescence excitation spectrum was detected. In the origin and vibronic band excitation, the dispersed tautomer fluorescence spectra were observed. The decay of this tautomer fluorescence exhibits a single exponential decay with decay times of 11-12 ns.

Figure 3 shows a visible fluorescence excitation spectrum of jet cooled 3-HC monitored at $>480\text{ nm}$. The spectrum exhibits very diffused bands without the low frequency vibrational progression of 45 cm^{-1} . However, a broad low-frequency band with a spacing of 182 cm^{-1} was observed. In jet-cooled methyl salicylate, a low frequency mode of 176 cm^{-1} was reported in the blue tautomer fluorescence excitation spectra. Further, 180 cm^{-1} vibrational progression was reported in the dispersed blue fluorescence of this jet-cooled compound. These low frequency modes in methyl salicylate were ascribed to an out-of-plane bending motion containing an intramolecular hydrogen bonding in the ground and excited states. Therefore, it is likely that broad low frequency mode of 182 cm^{-1} in this 3-HC is attributable to the out-of-plane bending motion in this compound. In the excitations of the origin and main vibronic bands, the large Stokes-shifted tautomer fluorescence was observed (see Fig. 4). The decay time of the tautomer fluorescence was obtained to be 2-11 ns depending on the excitation wavelength (313-329nm). The decay time decreases with increasing excess vibrational energy of excitation. These fluorescence excitation spectra lack low frequency vibrations with 45 and 36 cm^{-1} spacings observed in those of 3-HF and 2-NHC. Therefore, 45 and 36 cm^{-1} spacing are ascribed to the phenyl and naphthyl torsional motions. The important role of the phenyl and naphthyl torsional motion in the ESPT will be mentioned later.

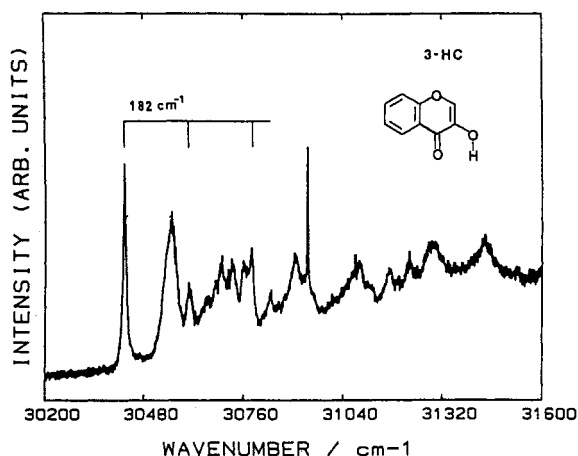


Fig. 3. Fluorescence ($>480\text{ nm}$) excitation spectrum of jet-cooled 3-HC.

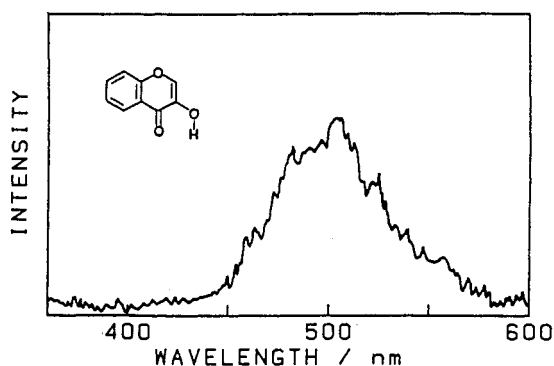


Fig. 4. Dispersed fluorescence spectrum of jet-cooled 3-HC excited at 30390.2 cm^{-1} .

In the excitation spectrum of 3-HC, we can look at a remarkable broad line width of the origin band, compared with those of other related compounds. The observed band widths of the origin bands of tautomer fluorescence excitation spectra of 3-HC, 3-HF, and 2-NHC were compared with each other, as shown in Figure 5. The spectral line shape of the origin band were simulated by deconvolution method taking account of Lorentzian line shapes. In 1989, Ernsting and Dick have

reported the estimation of electronic decay time of isolated 3-HF (1.8 ps) in its first singlet excited state from a line width of the $S_1 - S_0$ transition. These line widths indicate significant dependence on substituents at 2-position of pyrone ring. Since it is not likely that rotational contour of origin bands of these three compounds is very much different from each other within this experimental condition, the remarkable difference of line widths between these compounds may be attributable to the reflection of the respective decay rate constant of the S_1 state of these compounds. Further, the decay rate constant may reflect the upper limit of proton transfer rate constant. In this discussion on the ESPT, however, rate constant of the ESPT only means rate of the tautomer formation from the normal form in the excited state.

The rate constant obtained $0.69 \times 10^{12} \text{ s}^{-1}$ for 3-HF is consistent with that estimated by Ernsting and Dick¹¹ within experimental error. In our previous papers, the intramolecular ESPT in the 3-HC solution was reported to take place much faster than those of 3-HF and related compounds in hydrocarbon solutions. The estimated rate constant $1.8 \times 10^{12} \text{ s}^{-1}$ for 3-HC provides us with the concrete confirmation of faster ESPT than 3-HF. Further, the rate constant for 2-NHC indicates considerably slow proton transfer compared with the other related compounds. The slow rate constants in the related compounds may reflect the naphthyl and phenyl torsional motion as well as electronic effect at 2-position of r-pyrone ring. The substituted 3-HF shows almost same torsional vibration ($44-46 \text{ cm}^{-1}$) of para-substituted phenyl group at 2-position and decay time (1.5 - 2.0 ps) of the normal S_1 state, though substituted phenyl groups seem to make some electronic effect on the excited state proton transfer. Therefore, it seems that the torsional motion of 2-phenyl and naphthyl groups is responsible not only to the nonradiative process of the normal S_1 state but also to the excited state proton transfer.

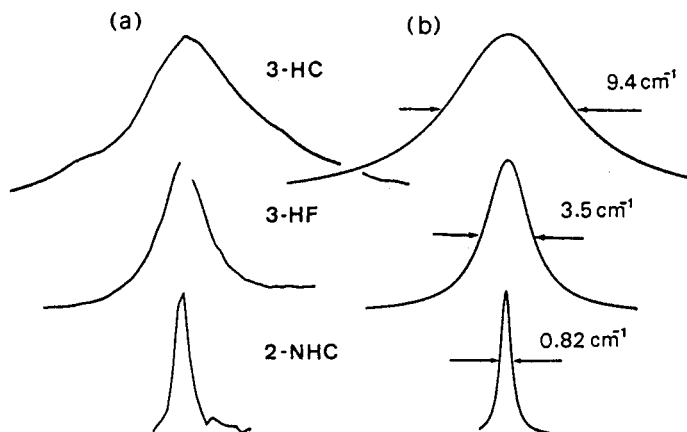


Fig. 5. (a) Band shapes of origin bands of fluorescence excitation spectra and (b) simulation of linewidths by Lorentzian line shapes.

In jet-cooled methyl salicylate, the vibrationally well resolved origin band was reported in the blue tautomer fluorescence excitation spectra, and the large Stokes shifted tautomer fluorescence exhibiting excess vibrational energy dependence was detected. The facts demonstrated an existence of a potential barrier in the ESPT of this jet-cooled compound. In jet-cooled 3-HC, 3-HF, and 2-NHC reported here, appreciably resolved vibrational structures starting from their respective strong origin bands in the excitation spectra seem to

suggest a small potential minimum in the Franck Condon excited state of the normal form. If there is no appreciable potential minimum in the S_1 state of the normal form, the origin band of the tautomer fluorescence excitation spectrum can not be practically observed because of very small Franck Condon factor. The initially excited state may be optically active intramolecular mode, and initial excitation energy redistributes into the reactive mode. The reactive states may strongly mix with the vibronic manifold of the tautomer leading to the tautomer formation. The mixing of the reactive states of normal form with the vibronic levels of the tautomer may be sufficiently strong, probably because of high level density of vibronic levels of the tautomer. Consequently, it seems that the tautomer formation takes place within picosecond time domain.

In the intramolecular hydrogen bonding system exhibiting ESPT, H-bonding impurities in hydrocarbon solution used sometimes induce a matter of controversy. Further, in the H-bonding solution of intramolecular ESPT system, it is considerably difficult to distinguish whether an observed ESPT is attributable to intermolecular interaction with the solvent molecules or intramolecular one. As mentioned above, Brucker and Kelley suggested that a monosolvate of 3-HF with methanol exhibits fast ESPT in 10 K Ar matrix while a disolvate does not proton transfer by a small spectral change of vibrationally unresolved fluorescence/excitation spectra in the absence and presence of methanol in the Ar matrix. However, there is a limit to determine number of solvent molecule concerned in the condensed phase spectroscopy.

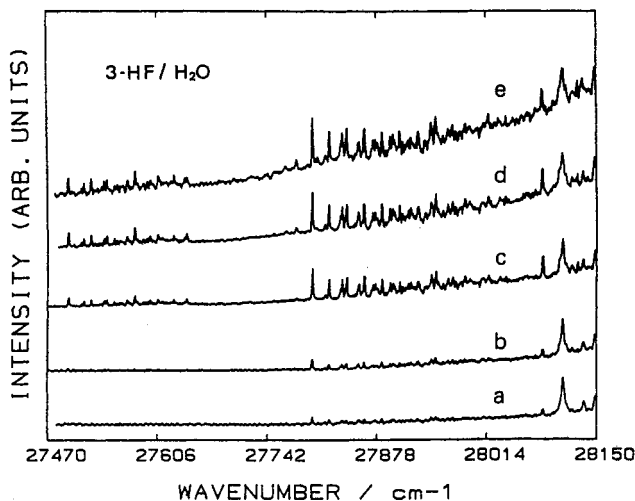


Fig. 6. Fluorescence excitation spectra of jet-cooled 3-HF in the absence and presence of water vapor in He carrier gas: (a) H_2O , $p = 2$ Torr, (b) $p = 4$ Torr, (c) $p = 6$ Torr, (d) $p = 8$ Torr, (e) $p = 10$ Torr.

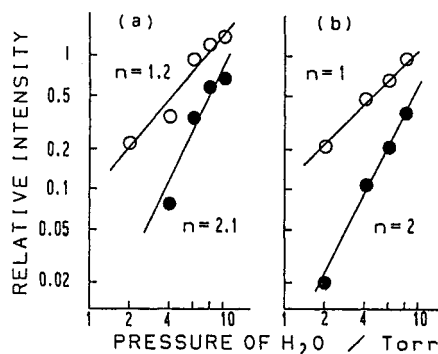


Fig. 7. Log plots of relative intensities of uv fluorescence excitation spectra of (a) 3-HF and (b) 2-NHC vs. H_2O pressure. \circ and \bullet are corresponding to mono- and dihydrates.

All of 3-HF and related compounds exhibit no significant uv fluorescence attributable to the normal form, which means the fast ESPT and predominant nonradiative relaxation of the S_1 state. Figure 6 shows uv-visible total fluorescence excitation spectra in the presence of water vapor of 3-HF. In the absence of H_2O vapor in seeded He gas, no significant excitation spectrum was observed in the lower energy region than 28080.7 cm^{-1} . In the presence of water vapor, the longer wavelength bands appeared and remarkably increased in intensity with increasing water vapor pressure. However, no

significant difference of tautomer fluorescence excitation spectra was observed in the absence and presence of water vapor. Similar water cluster formation was observed in jet-cooled 2-NHC in the almost identical experimental condition with that of 3-HF. Figure 7 shows logarithmic plots of these band intensities versus vapor pressure of H₂O in the He carrier gas. Slopes of both plots suggest that vibrational envelopes are attributable to 1;1 complexes with water. In jet-cooled 3-HC, however, no uv fluorescence excitation spectrum was detected even by seeding water vapor (2-6 Torr) in the He carrier gas. Increasing vapor pressure of H₂O to 6-12 Torr, further red shifted vibrational structures gradually appeared and increased in intensity of both 3-HF and 2-NHC. Slope of these log plots of further red-shifted band intensities indicates approximately 2. The fact implies that the further red-shifted bands are attributable to clusters of two water molecules complexed of these compounds. The mono- and dihydrate formations of 3-HF and 2-NHC, and their spectral features are very similar each other. Figure 1b shows the uv fluorescence excitation spectra attributable to these water clusters of 3-HF, $n = 1$ and 2 for 3-HF(H₂O)_n in comparison with the vis fluorescence excitation spectrum of bare 3-HF. Figure 2b and 2c show dispersed fluorescence spectra of mono- and dihydrates of 3-HF in the excitation of the origin bands of clusters. The dispersed fluorescence spectra of water clusters of 2-NHC are almost identical with those of 3-HF. These spectra exhibits no tautomer fluorescence but only uv normal form fluorescence. The fact indicates that the ESPT in these compounds does not take place in intermolecularly H-bonded clusters, but does occur only in the isolated molecular condition. That means that the ESPT of 3-HF and related compounds takes place only in the isolated molecular condition.

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