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Spectroscopy of Amplified Spontaneous Emission Laser Spikes in Polyhydroxyflavones[†,‡]

David Gormin, Alexander Sytnik, and Michael Kasha*

Institute of Molecular Biophysics and Department of Chemistry, Florida State University,
Tallahassee, Florida 32306-3015

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Research spectroscopy on some polyhydroxyflavones has revealed extraordinary wavelength red-shifts for the *amplified spontaneous emission* (ASE) laser spikes, displaced from the corresponding proton-transfer fluorescence maxima. The shifts observed are 150 cm^{-1} for 3-hydroxyflavone, 740 cm^{-1} for 3,4′,7-trihydroxyflavone, and 1070 cm^{-1} for 3,3′,4′,7-tetrahydroxyflavone in dioxane at 298 K (excited by the third harmonic of Nd:YAG laser, 15.5 mJ). The unorthodox shifts are interpreted as arising from intermolecular dipolar field perturbation effects associated with the high population of the proton-transfer tautomer lowest excited state. The *zwitterion* structure of the proton-transfer tautomer is treated as the origin of the extraordinarily large dipole moments, modulated by extra hydroxy group substitution. Variations of solvent dielectric constant, solute concentration, and the pumping Nd:YAG laser energy support the mechanism given for the ASE laser spike shift.

Research on *amplified spontaneous emission* (ASE)[1] laser spikes derived from the proton-transfer fluorescence spectra of polyhydroxyflavones has revealed 8-shifts of as much as 1000 cm^{-1} or more to the red of the corresponding Franck−Condon maximum of the proton transfer (PT) fluorescence band. This highly unorthodox behavior constitutes such a contrast to what seemed to be normal λ-shifts on the order of 100 cm^{-1} or less that an exploratory study of the origin was undertaken. This paper presents a full account of our previous brief communication.[2]

The amplified spontaneous emission technique, using a mirrorless laser cell,[1,3] is a necessary procedure for the evaluation of the authentic gain intensity versus wavelength.[1] The gain coefficient $\alpha(\lambda)_L = (2/L)\ \ln(I_L/(I_{L/2} - 1))$ evaluates the exponentiality of the induced emission by comparing the intensity for full cell length vs half cell length. In the present paper we shall be occupied with the unorthodox displacement of the principle ASE laser spike from the Franck−Condon (FC) fluorescence maximum. In a companion paper[4] on ASE spectra of some phenyloxazoles a fuller discussion is given of the ASE spectroscopy theory and technique.

The aim of the present research is not to explore molecular cases for new laser materials but to demonstrate the powerful insight that ASE spectroscopy can give to the chemical physics of excitation dynamics of complex molecular electronic systems and the electronic characteristics of transient excited electronic states. In three current studies in this laboratory, new phenomena have been exposed that are completely hidden in normal steady-state fluorescence and absorption experiments. These include the unorthodox ASE laser spike shifts for PT fluorescence bands, the anomalous ASE laser spike for nondominant FC vibronic bands in phenyloxazoles,[4] and the anomaly of solvent-invariance of PT fluorescence FC maxima in cases of very high excited-state dipole moment magnitudes (to be presented in a forthcoming paper).

Experimental Note

The experimental arrangement used was that previously described[3] except for the substitution of the Nd:YAG laser using the third harmonic at 355 nm with a laser pulse repetition rate of 10 Hz. A critical feature of efficient ASE laser spike observation is the use of a pinhole aperture before the detector. In this work, an aperture of 0.05 cm at a distance of 50 cm from the special laser cell was used. This optimizes the gain coefficient by carefully selecting a position for maximum multiplication. The special cell was a Molectron DL251, having an optical path length of 0.80 cm and oblique exit windows as an antiresonance feature. The stability of the flavonols under extended pulsed laser driving is high for a stirred cell, the solution having been degassed by bubbling with Ar or N_2 gas.

Proton-Transfer Excitation in Hydroxyflavones

The excited-state intramolecular proton-transfer (ESIPT) fluorescence (Figure 1) of many molecules has now been studied widely[5,6] with many excitation dynamics aspects explored. The characteristic feature of this excitation process is the very large frequency displacement between the normal tautomer lowest $S_0 \rightarrow S_1$ absorption (or $S_1 \rightarrow S_0$ fluorescence) and the proton-transfer (PT) tautomer $S_1' \rightarrow S_0'$ fluorescence.[7] For example, the PT fluorescence for 3-hydroxyflavone (**I**, Scheme 1) exhibits[7−9] a shift of 9100 cm^{-1} (not a "Stokes" shift, since the PT fluorescence is from a different molecular species than the initially excited one). Analogous spectra for fisetin (**III**, Scheme 1) are given in Figure 2 for which $\Delta\bar{\nu} = 10\,050$ cm^{-1} (first absorption FC peak to PT fluorescence peak).

The schematic proton-transfer potential (Figure 1) results in an $S_1 \rightarrow S_1'$ conversion on a subpicosecond or a femtosecond time scale[10] and an $S_0' \rightarrow S_0$ reverse PT process certainly in the picosecond range. These circumstances suggested[11] that a unique four-level laser could be developed in which the S_1' state could be strongly populated by laser pumping, the $S_1' \rightarrow S_0'$ subsequent PT tautomer fluorescence behaving like a normal (nanosecond) emission, although strongly wavelength shifted.

[†] This paper is dedicated to Dr. Saburo Nagakura whose extraordinary career in science spans 5 decades, with a profound influence on the development of sciences in Japan and with much influence on international science development.

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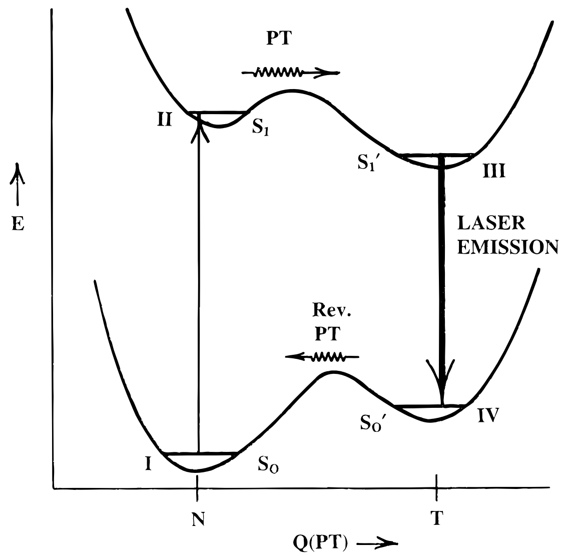


Figure 1. Schematic potential energy curves for a four-level molecular laser based on excited-state intramolecular proton transfer (ESIPT).

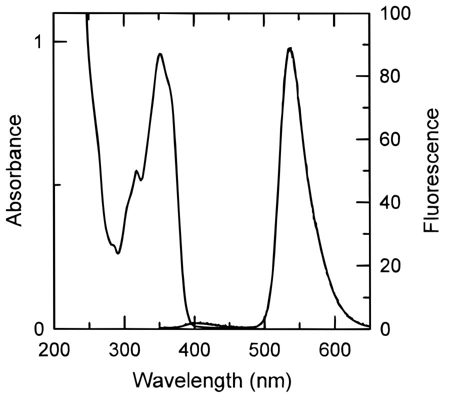
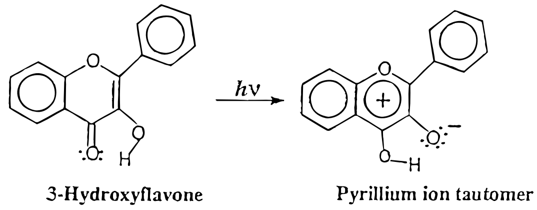


Figure 2. Fisetin (**III**, Scheme 1) ultraviolet absorption (onset 390 nm, first band at $\lambda_{max} = 340$ nm) and proton-transfer tautomer green fluorescence band (onset 500 nm, first band at $\lambda_{max} = 535$ nm), both in dioxane at 298 K. The $\Delta\bar{\nu}$ peak-to-peak (first absorption to fluorescence) is 10 050 cm^{-1}. Also observed is a weak violet fluorescence of the normal tautomer with $\lambda_{max} = 410$ nm.

The rapid depopulation of the S_0' ground-state results in an unusual population inversion for the S_1'/S_0' states. This expectation proved to be the case[3] for 3-HF (**I**, Scheme 1), and in addition, the optical window provided by the large wavelength shift of the PT fluorescence permitted the development of a dual-frequency laser[12] upon the introduction of a second ordinary proprietary laser dye.

For the 3-HF ASE laser spike it was observed that a small λ-shift to the red (150 cm^{-1}) (dioxane, 298 K) occurred, which was then attributed[3] to a physical optics effect (a λ^4 dependence of the gain coefficient α). However, subsequent studies indicate that the λ-shift is a variable, changing dramatically for PT-capable systems from molecule to molecule and solvent to solvent. For example, Figure 3 presents the PT fluorescence and the corresponding ASE laser spike (dioxane solution, 298 K) for 3-HF, 3,4′,7-trihydroxyflavone, and fisetin (structures **I**−**III**, Scheme 1), indicating the strong variation of the λ-shift of the ASE laser spike with molecular electronic structure variations. The respective shifts are for **I**, 150 cm^{-1}, for **II**, 740 cm^{-1}, and for **III**, 1070 cm^{-1}.

SCHEME 2

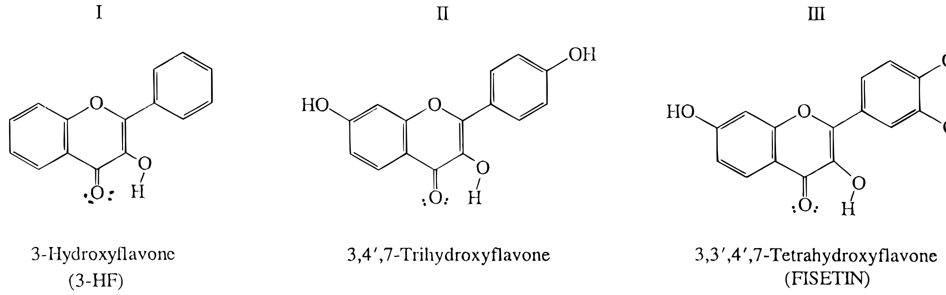


The very large λ-shifts in the ASE laser spike position obviously require a molecule-specific interpretation. We recognized in the first study[7] of *o*-hydroxyflavone fluorescence spectroscopy that an internal proton transfer would be favored by an increase of basicity (electron density) of the carbonyl group, and also an increasing acidity[13] (reduced electron density on the heteroatom) of the hydroxy group, upon excitation. It was also apparent[7] that the intramolecular proton-transfer would lead to a benzpyrillium structure featuring aromatization of the ring oxygen (Scheme 2). Such a structure is analogous to the benzpyrillium structures of the anthocyanine flower pigments. This could account for the shift to the *visible region* of the proton-transfer fluorescence of the *o*-hydroxyflavones.

The proton-transfer tautomer would be expected to develop a strong, permanent dipole moment as suggested by the inevitable *zwitterion* character of the PT tautomer (Scheme 2). Thus, the electronic states S_0', S_1', etc. should exhibit rather large *permanent* dipole moments, which could be an order of magnitude greater than those of the normal tautomer states S_0, S_1, etc. Trial calculations of the electronic distribution for the S_0, S_1, S_0', and S_1' were attempted for several cases of structures related to the hydroxyflavones and indicated some large magnitude dipole moment changes upon PT tautomerization.[14,15] The calculations as carried out offer only a hint of the zwitterion dipole moment induction.

The progressive λ-shift of the ASE laser spike with successive hydroxy-group substitution might be attributable to a substitution-sensitive shift in a *transient absorption* during the PT tautomer excitation process. Such an absorption, if it had underlain the PT fluorescence, could shift the apparent λ_{max} of the fluorescence and its corresponding ASE laser spike. However, if this effect did apply to fisetin, the lasing action could be promptly quenched owing to the parasitic action of the competing transient absorption. This type of competition proved to be the case for 2-methyl-3-hydroxychromone,[16] a benzpyrillium analogue of 3-HF, which exhibits no lasing action

SCHEME 1



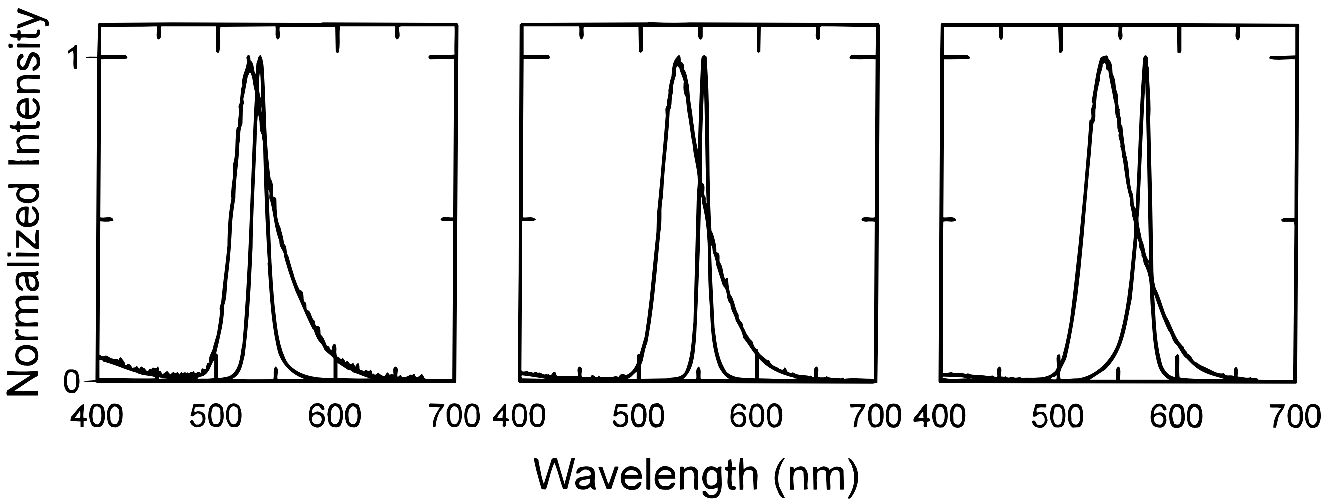


Figure 3. Proton-transfer fluorescence and corresponding ASE laser spike for hydroxyflavones (dioxane solution, 298 K): (left) 3-hydroxyflavone (**I**); (center) 3,4′,7-trihydroxyflavone (**II**); (right) 3,3′,4′,7-tetrahydroxyflavone (**III**, Scheme 1). The corresponding values for the laser spike shifts are for **I**, 150 cm^{-1}, for **II**, 740 cm^{-1}, and for **III**, 1070 cm^{-1}.

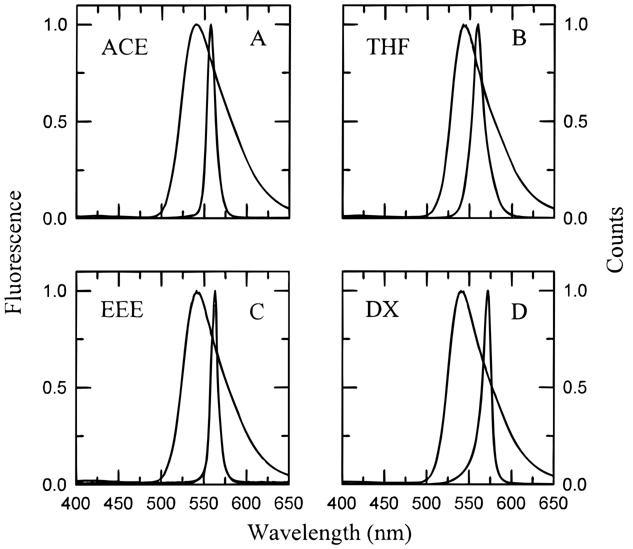


Figure 4. Solvent effect on ASE laser spike for fisetin (**III**, Scheme 1), all at 298 K. The solvents are ACE (acetone), THF (tetrahydrofuran), EEE (ethoxyethyl ether), and DX (dioxane) with respective shifts of 575, 610, 720, and 1070 cm^{-1}.

in contrast to 3-HF, both nevertheless exhibiting strong PT fluorescence bands. This will be discussed further in the interpretation section at the end of this paper.

We shall explore in the remainder of the paper the idea of dipolar field perturbation effects in the population inversion case as the origin of the ASE laser spike λ-shift for the PT fluorescence of polyhydroxyflavones.

Solvent Dielectric Effects on ASE Laser Spike λ-Shift

As a first test of an intermolecular dipolar field effect on the ASE laser spike wavelength, a solvent variation for the dielectric constant effect on the λ-shift was studied. The usable dielectric constant range was restricted by molecular parameters. The polyhydroxyflavones are not soluble in hydrocarbon solvents, so the lowest dielectric solvent used was dioxane, which offers good solubility for the most polar polyhydroxyflavone. At the high dielectric constant end, protonic solvents (alcohol, water) were excluded by the interference,[8] in the *o*-hydroxyflavone cases, with the internal hydrogen bonding required for ESIPT. Figure 4 presents the comparison for fisetin PT fluorescence and ASE laser spikes for the solvents dioxane, ethoxyethyl ether, tetrahydrofuran, and acetone all at 298 K (Nd:YAG laser pulse energy at 15.5 mJ, the maximum value used; cf. Figure 7). A very strong influence of the dielectric constant of the solvent is evident. We interpret these results as showing that in the lowest dielectric constant solvent (dioxane, Figure 4, curve D), the maximum shift is seen corresponding to the maximum intermolecular dipolar field. Here, we consider the large population inversion achieved at the maximum driving laser energy used. In the dipolar field of neighboring excited molecules in the highest population inversion environment, the reference S_1' molecule initiating the induced emission in the ASE laser train would be exposed to a maximum perturbation, and hence, the emission *transition dipole* is expected to have a λ-shift to lower frequency. As the dielectric constant of the intervening medium is increased (acetone, Figure 4, curve A), the λ-shift would minimize as the intermolecular dipolar field perturbation is reduced. A graph of the variations of $\Delta\bar{\nu}$ for the red-shift of the ASE laser spike for fisetin (**III**, Scheme 1) is given in Figure 5. The dielectric constant for ethoxyethyl ether was not available, so the molecular dipole moment of the solvents was used as a qualitative index of the dielectric property. These

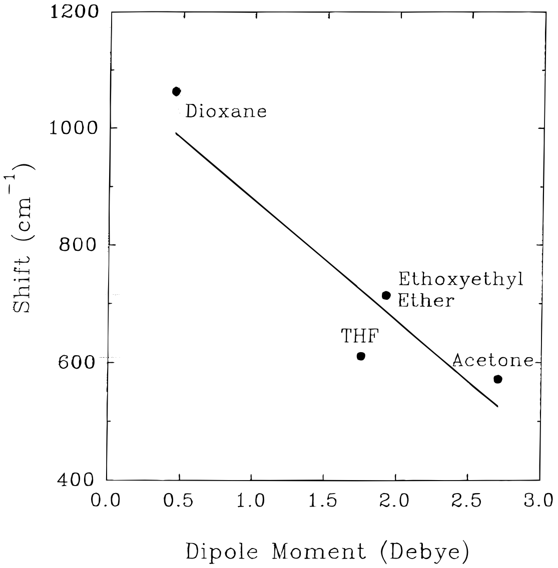


Figure 5. Frequency shift for the ASE laser spike for fisetin (**III**, Scheme 1) from PT fluorescence in plot of $\lambda_{\max}$ vs solvent dipole moment. The solution is at 298 K, and the Nd:YAG laser pulse energy is at 15.5 mJ (cf. Figure 7).

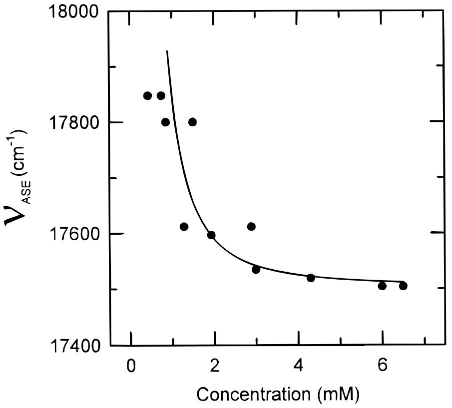


Figure 6. Frequency of ASE laser spike for fisetin (**III**, Scheme 1) vs concentration of fisetin. The dioxane solution is at 298 K, and the Nd:YAG laser pulse energy is at 15.5 mJ (cf. Figure 7).

results conform to the expected reduction of an intermolecular dipolar perturbation for the excited PT molecule system.

Influence of Molecular Concentration on the ASE λ-Shift

The intermolecular dipolar perturbation should vary with the total solute molecule concentration. Here, we assume that the highest population inversion would come at the highest molecular concentration. A test of this variation is presented for fisetin (in dioxane, 298 K) in Figure 6 in which the absolute frequency in cm^{-1} of the ASE laser spike is plotted against a function of concentration. The spectral position of the ASE laser spike is a measure of the λ-shift from the PT fluorescence of the molecule, here, in a single solvent (dioxane). The limiting intercept would occur at 18 620 cm^{-1}, the position of the PT fluorescence peak. The large errors in the data arise mainly from difficulty in reading the progressively weaker ASE laser spike with decreasing concentration. There is evidently a strong effect of concentration on the position of the ASE laser spike, and the assumed intermolecular dipolar field effect seems to follow the expected variation with intermolecular separation. Excitation photon saturation leads to an asymptotic limit at the highest concentration used. All the points were read for the Nd:YAG driving laser energy at the maximum value of 15.5 mJ used (cf. Figure 7).

Variation of ASE Laser Spike with Input Laser Energy

The third variable available to test the idea of an intermolecular dipolar field effect is the energy magnitude of the pumping laser, which would vary the transient concentration of excited high dipolar field molecules. The third harmonic of the Nd:YAG pulsed laser was used (355 nm, 10 Hz repetition rate). Figure 7 presents the ASE laser spike for fisetin in dioxane at 298 K with successive laser pulse energies of 4.5, 5.0, 8.0, 10.5, 13.0, 14.5, and 15.5 mJ. It would have already been noted in Figures 3 and 4 that the ASE laser spike for fisetin is pronouncedly *asymmetrical*, with a broad onset on the short λ side and the normal steep onset on the long λ side. In contrast, the ASE laser spike for 3-HF (**I**, Scheme 1) in Figure 3 is relatively *symmetrical*, with a steep onset on both sides as is generally the case for unshifted ASE laser spikes.

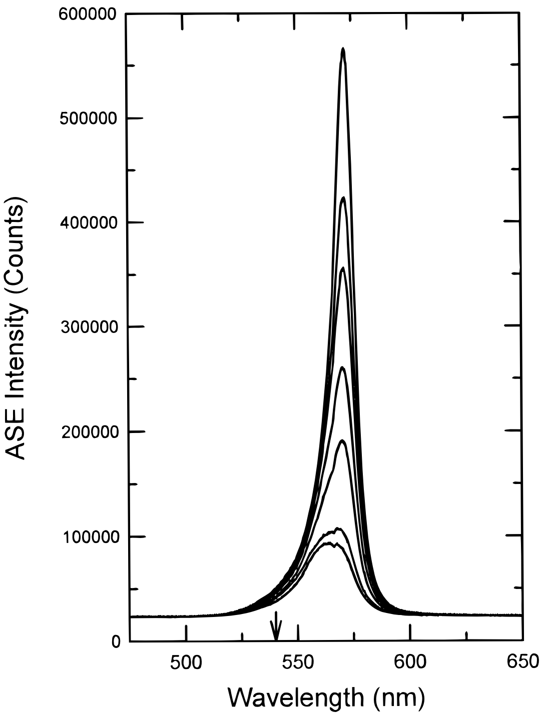


Figure 7. Input Nd:YAG laser pulse energy in generation of the ASE laser spike for fisetin (**III**, Scheme 1) in dioxane at 298 K. Successive input pulse energies are 4.5, 5.0, 8.0, 10.5, 13.0, 14.5, and 15.5 mJ. The arrow marks the position of the PT fluorescence Franck−Condon maximum for an expected unperturbed ASE laser spike for fisetin.

Not only is the gradually sloping character of the short λ foot of the fisetin ASE laser spike pronounced but also at the lowest pulsed laser energies, there is a complexity of the spectral structure, with dual contour, for the ASE laser spike in dioxane at 298 K. The expected position for the unperturbed laser spike is marked by the arrow (Figure 7). We believe that there is a profound molecular significance in these features. It is clear that the shape of the laser spike develops and simplifies with increasing laser energy until at the highest laser energy the laser spike maximum is reinforced at the maximum value of the λ-shift. Nevertheless, the asymmetrical foot of the ASE laser spike is still present in Figure 7 even at 15.5 mJ.

We interpret the complexity of the ASE laser spike for fisetin in dioxane, which is most evident in that case because of the large λ-shift of over 1000 cm^{-1} to the red, as arising from statistical variations of the dipolar field around the reference S_1' molecule, which gives rise to the induced emission wave train. Figure 8 illustrates a sampling of this system. A very dilute solution finds the excited reference molecule $(S_1')^0$ (double oval) surrounded only by solvent. As the concentration increases, the excited reference molecule is surrounded by several excited molecules $(S_1')^{**}$. At the highest S_1' concentration, or highest laser energy, the reference excited molecule is surrounded by many excited molecules $(S_1')^{n*}$. Thus, a series of (S_1') substates would exist, with the statistically most perturbed molecule giving rise to the lowest excited substate $(S_1')^{n*}$, in the strongest dipolar field. We reiterate that the *transition moment* would then be perturbed by the *permanent zwitterion dipoles* of the S_1' PT (or S_0') state.

Although other research indicates that for fisetin the zwitterion dipole magnitude may be equally very large for both tautomer singlet states involved in the PT fluorescence, S_1' and S_0', the interpretation given above depends on the ultrarapid depopulation of the S_0' population by the picosecond time scale reverse proton-transfer to S_0. Thus, a reference S_1' molecule that initiates an induced emission wave train is either in the field of other S_1' excited molecules in the extreme case (with dipole moment $\vec{\mu} \approx 10-12$ D exerting the extreme dipolar field perturbation) or in the field of normal tautomer ground-state molecules S_0, which would have an order of magnitude lower dipole moment (e.g., $\vec{\mu} \approx 2-3$ D).

The succession of the S_1' substates illustrated in Figure 8 indicates the strong possibility of energy transfer between the

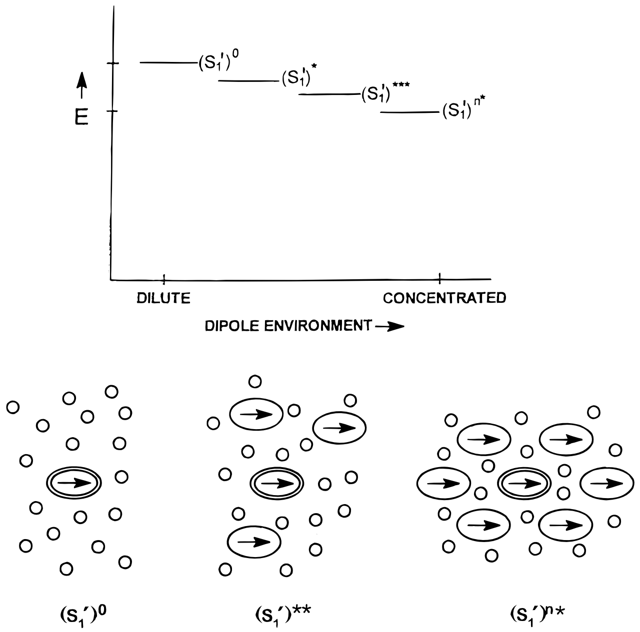


Figure 8. Schematic diagram illustrating proton-transfer-tautomer S_1' substates under successively increasing dipolar field perturbation. The double oval indicates the reference molecule in the laser train.

various substate species. In this concept we can assume that at the limiting high molecular concentrations used and the highest population inversion achieved, the energy transfer is much faster than the nanosecond fluorescence emission of the S_1' PT state. Even though the dense packing of excited molecules around a reference S_1' molecule may represent a small fraction of the S_1' reference molecules, its lowest energy position would make that molecule act as a trap for intermolecular energy transfer. Thus, the dominant ASE laser spike would shift to lowest energy, with the largest λ red-shift, even if the most perturbed species is not the most abundant.

Interpretation of the Polyhydroxyflavone PT Properties

A mutual dipolar perturbation effect has been presented here as the basis for the unorthodox ASE laser spike shift for proton-transfer fluorescence in the polyhydroxyflavones. It has been shown that starting with the monohydroxyflavone, 3-HF (**I**, Scheme 1), progressive addition of $-$OH groups to the 3-HF flavone skeleton has the effect of enhancing the ASE laser spike shift. We have attributed this shift to the generation of a large permanent electric dipole in the S_1' state (Figure 1) arising from the *zwitterion* structure of the proton-transfer tautomer and the large population inversion at the highest driving laser energy. The $-$OH group at the 3-position on the A-ring (benzpyrone ring) of the ground-state flavonol has the principal role of providing for the proton transfer in the excited state within the $-$OH to O=C$-$ hydrogen bond.

The additional $-$OH groups provide considerable additional electron-donating capacity, the 3,4′,7-trihydroxyflavone (**II**, Scheme 1) having a pair of such extra $-$OH groups at the opposite ends of the flavonol and the fisetin (**III**) having a third additional $-$OH in the B-ring. These electron-donating groups extend the π-electron pool of the flavonol, offering the potentiality of generating a giant dipole in the PT tautomer *zwitterion* forms.

The variation of ASE laser spike displacement of 150, 740, and 1070 cm^{-1}, respectively, from 3-HF to fisetin (structures **I**$-$**III**) suggests the possibility of calibrating a dipole moment scale for the transient S_1' state of the PT tautomer from the ASE laser spike shift. Theoretical quantum mechanical calculations of the S_1' state dipole moment, although not with absolute accuracy, would possibly allow a fair relative quantification. Once a reference point is established, either by an independent experimental determination or a sufficiently reliable scaled theoretical calculation, a calibration plot of $\Delta\tilde{\nu}_{\mathrm{ASE}}$ vs $\vec{\mu}$ could be established.

In contrast to the extreme variation of ASE laser spike wavelength with solvent variation (cf. Figure 4), it is necessary to point out the startling observation also evident in Figure 4 that the *proton-transfer fluorescence* $\lambda_{\max}$ itself is totally immune to the solvent dielectric constant variation. This is an apparent contradiction. If the large ASE laser spike shift is attributable to a giant dipole in the S_1' excited state, why is there not a comparable large solvent dipolar-relaxation effect in the fluorescence position itself in polar solvents? This unusual circumstance is the subject of another current research from this laboratory[17] in which our basis rests on the unique aspects of the excitation dynamics of the PT fluorescence four-state system compared with normal absorption and fluorescence two-state molecular spectroscopy.

Transient absorption spectroscopy could be an alternative basis for interpretation of the present unorthodox ASE laser spike wavelength shifts. It is necessary to compare the present interpretation of the ASE laser spike shift from the PT fluorescence FC maximum with the contrary idea of a simple underlying transient absorption as the origin of the λ-shift. If a transient absorption underlay the PT fluorescence, it could shift the apparent maximum of the fluorescence with the ASE laser spike then displaced to the new position. A consideration of the ASE laser spike shift with molecular substitution, molecular concentration, solvent polarity, and driving laser energy could be assumed to be parallel to analogous shifts of the transient absorption bands for a given system. In fact, the ASE laser spike shift for fisetin was assumed in our earlier study[15] to be based upon a transient $T_1 \rightarrow T_n'$ absorption. However, the low-energy and very broad $T_1 \rightarrow T_n$ absorption bands reported for some organic molecule laser dyes had seemed to limit this possibility as a source of perturbation of the laser spike position.[18]

Recent research on the ASE laser spectroscopy of some dimethylaniline-substituted aromatics, especially a *N*,*N*-dimethylaniline pyrene derivative, have shown that the ASE laser spike is shifted to the *minimum* between two transient absorption bands in various solvents.[19] The wavelength of the CT fluorescence band of this type of molecule is very solvent-polarity sensitive and the transient absorption spectra are similarly so. The presentation made is convincing, and the “negative” transient absorption can constitute the residual fluorescence, whose apparent maximum can then give a simple normal coincidence with the ASE laser spike position, as observed.

Transient picosecond time-resolved spectra are available for the molecules covered in the current research, not only for 3-hydroxyflavone (3-HF, which is a 2-phenyl-3-hydroxychromone) but also for 2-methyl-3-hydroxychromone, 3-HC. Table 1 summarizes the results for 3-HF.

To test the idea of transient absorption effects on the position of the ASE laser spike, we compare the *minimum* in the transient absorption with the ASE spike wavelength (both in bold face type, Table 1). The transient absorption spectra for 3-HF observed by Parthenopoulos and Kasha[21] in formamide solution are analogous to the results for 3-HF in cyclohexane recently reported by Ormson et al.,[22] indicating very small solvent effects on the PT tautomer states. By comparison of the *minimum* in the transient absorption at 545 nm with the ASE laser spike

TABLE 1: Comparison of Transient Absorption with Proton-Transfer Fluorescence in 3-Hydroxyflavone (3-HF) and ASE Laser Spike

$S'_1 \rightarrow S'_{n,m}$ Transient Absorption (nm)

solvent	λ_1(max)	λ_{min}	λ_2(max)	ref
cyclohexane	453	**525−42**	610	(at 150 ps) 1986, ref 20
formamide	460	**545**	610 (at 50 ps)	(at 50 ps) 1990, ref 21
cyclohexane	456	**530−40**	∼575 (at 100 ps)	(at 100 ps) 1995, ref 22

$S'_1 \rightarrow S'_0$ Proton-Transfer Fluorescence and ASE Laser Spike (nm)

	fluorescence	ASE laser spike	ref
formamide	525		21
acetone	526		15
methylcyclohexane	526	**532**	this laboratory

position in hydrocarbon solvent, the frequency shift would be 662 cm^{-1} for this effect to be valid. We present in this paper an observed frequency shift of 150 cm^{-1} for 3-HF in dioxane (the data of Table 1 indicate a frequency shift of 215 cm^{-1} for the less polar solvent methylcyclohexane). These data indicate that the ASE laser spike shift observed for polyhydroxyflavone probably may not have its fundamental origin in a shift of the PT fluorescence caused by transient absorption. However, the case of 3-HF is not a good test because it exhibits the smallest ASE laser spike shift of the cases studied in this paper.

If a transient absorption band strongly overlaps with a fluorescence band directly, the absorption yields a parasitic term[3,16] to the stimulated emission cross section and the ASE laser spike is quenched. This proved to be the case for 2-methyl-3-hydroxychromone[16] and for a dimethylaniline pyrene[19] in one solvent (acetonitrile).

It is also notable that in prototype cases of single-structure phenyloxazoles there is observed a zero-shift of the ASE laser spike from the fluorescence FC maximum for those nonproton-transfer molecules studied.[4] It will be interesting to discern whether this arises from a complete absence of a transient absorption in the fluorescence region or from a negligible change of dipole moment in the S_1 vs the S_0 state (of the nonproton-transfer case).

In our continuing research on flavonols we shall pursue further rapid transient absorption spectroscopy and related dynamic studies. It will be interesting to discern why the transient absorption minimum defined the ASE laser spike position so clearly for the dimethylanilinopyrene molecule charge-transfer states[19] but seems to fail to do so for the proton-transfer tautomer states of polyhydroxyflavones. A critical feature may lie in differences in the competitive excitation dynamics in the two systems.

Conclusion

It is clear that use of normal absorption and fluorescence spectroscopy, even with the added intricacies of the PT tautomer state and the CT state excitation, fails to reveal all the aspects of the chemical physics of the excitation dynamics of the unorthodox PT and CT excited states. The use of ASE laser spectroscopy reveals hidden characteristics of the excitation dynamics, which ordinary stationary-state spectroscopy conceals. Obviously, understanding the full nature of the excitation process requires inputs from both types of spectroscopic research.

There is a number of flavonols available both as natural products isolated from the plant world[23] and numerous synthetic derivatives. The derivatives have been also actively pursued as ideal radiation scintillator probes[24] because of the huge PT fluorescence red-shift from the UV excitation region. For the same reason, studies of their binding to serum albumens as ideal protein-fluorescence probes have been initiated.[25,26] The intense and broadening interest in the role of flavonoids in human health physiology[27] and their role as antioxidants in radiation biology[28] make the electronic structure and spectroscopic behavior of these complex molecular electronic systems both fascinating and compelling.

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