

ELECTRON STRUCTURE AND PHOTOPROCESSES IN LASER MEDIA OF COUMARINES

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The electron structure, absorption spectra of K1 and its 3-fluoro-, 3-fluorophenyl-substituted derivatives have been calculated using the PIDO and ESP methods. Detailed analysis of the electron structure of excited states and possible channels of photochemical reactions as well as stereoeffects appeared due to substitution allowed us to produce photostable lasing media efficient in the blue–green spectral region.

The coumarine derivatives are at one of the first places among the most effective laser dyes in the blue–green spectral region known now, but the relation of their structure to spectral parameters of their luminescence and photochemical properties are yet less studied.

The dependence of the fluorescence quantum yield of 7–diethylamine–4–methylcoumarine (coumarine 1–K1) on the solvent polarity has been shown in Ref. 1 to be the curve with the extremum, with the maximum emittance observed in solvents with small polarity, but rather high viscosity. As to the dependence on the structure, the emittance of alkylcoumarines is shown to correlate with the analytically calculated value of the contribution coming from the electron density of electron–donor substituent in the seventh position to the $S_0 \rightarrow S_1$ transition.

Adding of electron–acceptor substituents to pyrone ring can increase the charge transfer (CT) and the efficiency of radiation, but the properties of 3–substituted–7–alkylaminocoumarines are poorly studied, though the third position is one of photochemically active.² Synthesis of 3–substituted–7–aminocoumarines using photochemical reactions with alkyl and aryl halides was mastered in the organic Chemistry Department of the Timiryazev Agricultural Academy under supervision of M.A. Kirpichenok.

It seems to be so that such a substitution has to create the additional channel of radiationless desactivation of C connected with rotation of the group in the third position (see Fig. 1). However, many of the 3–substituted coumarines have high emissivity. With a substituent in the fourth position, the volume phenyl and pyridyl rings in the third position cannot take a position in the molecules plane due to steric barriers. According to the data of X–ray structural analysis, the angles between the bicyclic system of coumarine and the plane of the substituent amount can reach the large ($\sim 60^\circ$) values.⁴ However, the radiationless losses due to rotation around the bond connecting the bicyclic system with the phenyl substituent in a number of solvents can play an essential role if the fourth position is free (substitutes of coumarine 1H). On the other hand, in these systems the flattening to their structure and improving the emissivity is possible due to the increase of the coupling chain and intensification of the charge transfer.

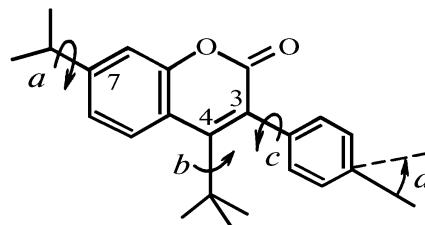


FIG. 1. Four possible channels of energy dissipation in coumarines with an unbound diethylamine group.

The influence of substituents in the third position (fluorine, fluorophenyl, phenyl) on the properties of K1 and K1H has been investigated using the method of partial ignorance of the differential overlap. Comparison of such molecules with 4– CF_3 –substituted derivatives of coumarine 1 allows us to reveal the influence of the unique electron effects of the fluorine atoms on the photon–induced process by the examples of new aminocoumarines with various types and positions of the substitution by fluorine atoms. In this study we have found that fluorination most strongly influences the properties of the excited states because of a strong charge–transfer characteristic of the molecules in these states. Both 4–three–fluoromethyl and 3–fluoro and 3–fluorobenzol substituents influence inductively the distribution of electron density of the remaining part of the molecule by delocalizing the negative charge inside the pyrone fragment. Spectroscopically this is observed as a bathochromic shift and an increase of the oscillator strength of the transition $S_0 \rightarrow S_1$, the dipole moment of a molecule in $S_{1,\pi\pi^*}$ state (see Table I) increases as well. It was also found that introduction into a molecule of K1 dye of the π –fluorophenyl substituent, though nonplane ($\alpha = 60^\circ$) and only low active in coupling but possessing its own system of π –electrons, makes much stronger effect on the position and intensity of the $S_0 \rightarrow S_1$ transition compared to that from simple introduction of a fluorine atom into the third position. Introduction of a phenyl substituent makes the same effect on the spectra. For compounds having no volume CH_3 substituent near the third position (K1H), the flattening of their structure in S_0 state obviously occurs, what is confirmed by calculations made assuming the plane geometry of the 3Ph–K1H molecule (Table I) which better

agree with the experimental data on the $S_0 \rightarrow S_1$ transition. And comparison of experimental data on location of maxima of fluorescence bands for 3Ph-K1 and 3Ph-K1H

molecules allows us to suppose that the planar structure of the latter molecule is kept also in the lower of the excited states.

TABLE I. Spectral characteristics and dipole moments (μ) of substituted coumarines.

Coumarines	Calculation							Experimental data		
	$\mu(S_0)$, D	$S_{1,\pi\pi^*}$			$S_{n\pi^*}$			λ_n , nm	λ_f , nm	ϕ_f
		μ , D	λ , nm	f	μ , D	λ , nm	f			
K1	12.2	13.2	354	0.60	7.2	270	0.000	370	457	0.50
3F-K1	15.5	20.6	358	0.90	9.8	287	0.001	376	476	0.75
3 π F Ph-K1	13.8	18.3	371	1.00	10.0	270	0.003	387	465	0.97
3Ph-K1	11.8	14.6	368	1.00	11.1	273	0.009	375	461	0.86
4CF ₃ -K1	13.1	20.4	374	0.90	10.9	282	0.010	410	510	0.10
K1H	11.9	16.4	359	0.80	6.3	288	0.001	372	461	0.29
3F-K1H	15.3	21.0	365	0.90	10.2	294	0.001	374	490	—
3Ph-K1H plane	12.1	15.2	395	1.22	3.1	348	0.000	398	477.5	0.92
$\alpha = 60^\circ$	11.3	16.3	373	1.04	7.9	277	0.002	—	—	—

Notes. f is the oscillator strength, λ_a and λ_f are locations of the absorption and fluorescence maxima, and ϕ_f is the quantum yield of the fluorescence.

Introduction of substituents under consideration into the molecules K1 and K1H modifies salvation processes, especially, in the excited states, what is confirmed in the experiments by an increase of the Stokes shift (in ethanol 5600 cm^{-1} and 6300 cm^{-1} for 3F-K1 and 3F-K1H in comparison with 5100 cm^{-1} for K1). Thus maximum changes are observed when the fluorine atom is directly introduced into the third position, because just these systems have the highest dipole moments in the excited S_1 state.

Shifts of fluorescence maxima in the case of the (3Ph-K1) and 3 π F Ph-K1 compounds are smaller than for simple 3F-compounds in comparison with their unsubstituted analogs. Here, both the nonplane structure of phenyl substituents of K1 in the third position and a possibility of C-F bond escaping from the plane, play their roles, as was shown by Schastnev and his coauthors.⁵

Substantial redistribution of electron density due to substitutions obviously causes certain changes in the rates of photochemical reactions. The values of molecular electrostatic potentials (MESP)⁶ we have computed by using wave functions of the PIDO method (Table II) can be used as indices of reaction ability in relation to the processes of proton transfer (PT).

First of all, it is necessary to examine the ability of molecules to interact via carbonyl oxygen, what has been shown earlier⁷ to be one of the dominating channels of photochemical transformations. In our earlier study⁸ we have found that fluorination of the methyl group in the fourth position results in a decrease of the MESP on the carbonyl oxygen atom that, in turn, leads to decrease of the probability of protolytic reactions via carbonyl group. Because of a strong electron-acceptor action of the 3F substituent (3F-K1 and 3F-K1H) the minimum of the MESP near the fluorine atom strongly falls down at

excitation both to S_1 , T_1 and $S_{n\pi^*}$, $T_{n\pi^*}$ states becoming the deepest one in the molecule. As a result, the proton-acceptor ability of carbonyl group decreases in comparison with the nonfluorinated analogs (K1 and K1H) (Table II). But the lasing photochemical resistance of 3F-K1 and K1 is the same ($E_{1/2} = 112 - 119$ phot/mole, see Ref. 8), what is explained by multichannel character of coumarines photodegradation. Introduction of a fluorine atom slightly weakens both the bond of one of hydrogen atoms in alkyl chain and in the CH_3 group and the bond of alkyl chain with the nitrogen atom (this is a result of our analysis of bound energies obtained in the course of the program "Bond"⁹). Thus, the positive action of F atom on the photodecay through the channel in the C=O group is compensated for by a growth in the photochemical transformations via other channels. At the same time, appearance of a phenyl ring in this system between the fluorine atom and the rest molecule, though not taking part in coupling, sharply weakens the role of the MESP minimum in the vicinity of this atom in all energy states and does not affect the proton acceptor ability of the carbonyl group (see Table II). Nevertheless, the photochemical resistance of 3 π F Ph-K1 is high ($E_{1/2} = 160$ phot/mole), since the probability of photochemical transformations through the other above-mentioned channels decreases. In addition, the role of stereoeffects in strengthening the photochemical resistance increases (C=O group and the 4th position).

Analysis of theoretical calculations of the structure of the electron-excited states and experimental data obtained for aminocoumarines allowed us to show the importance of $n\pi^*$ state,¹⁰ having the energy 30000–35000 cm^{-1} that is close to the energy of exciting radiation photons of XeCl laser ($\lambda_{\text{le}} = 308$ nm and $\nu = 32500$ cm^{-1}).

TABLE II. The MESP values of aminocoumarines in the ground (S_0) and the excited states.

Coumarines	Proton-acceptor centers	S_0	$S_{1,\pi\pi^*}$	$S_{n\pi^*}$	$T_{1,\pi\pi^*}$	$T_{n\pi^*}$
K1	C = 0	-129	-141	—	-141	—
	*	—	—	-25	—	-32
3F-K1	F	-119	-138	-100	-135	-100
	C = 0	-118	-134	—	-128	—
3 π F Ph-K1	*	—	—	-23	—	-23
	C = 0	-124	-141	—	-139	—
4CF ₃ -K1	*	—	—	-19.9	—	-20
	F	-45	-51	-10.5	-46	-10
K1H	C = 0	-110	-137	—	-134	—
	CF ₃	-76	-96	—	-90	—
3F-K1H	*	—	—	-85	—	-80
	C = 0	-126	-146	—	-143	—
3F-K1H	*	—	—	-30	—	-22
	F	-119	-142	-104	-140	-104
3F-K1H	C = 0	-115	-134	—	—	—
	*	—	—	-21	—	-21

Note. The asterisk denotes the cases of the MESP minimum at the benzol ring.

The $n \rightarrow \pi^*$ transition in coumarine substituents under consideration is sufficiently localized and corresponds to the excitation of n -electrons of oxygen in a carbonyl group to π^* orbitals of carbon atoms in aromatic rings mainly in the third, fourth, fifth, and the seventh positions. So, substitution to these positions essentially influences on the energy of the $n\pi^*$ state. Analysis of the vacant π^* orbitals has shown that the position of the $n \rightarrow \pi^*$ transition strongly depends on the contribution of atom orbitals (AO) of a substituent to π^* -molecular orbitals (MO). For example, the contribution coming from the AO of 3F group to the low π^* orbital exceeds the contributions from the AO of other analyzed substituents by an order of magnitude. As a result, the energy of $n\pi^*$ state of 3F derivatives is lower than that of 3-phenyl-substituted coumarines (Table I). The direct contribution of the AO of CH₃ and CF₃ groups to the formation of the low vacant π^* orbital is not so large, but their inductive influence is essential. This is explained by different contributions of the AO of C₃ and C₄ into this MO. As a result, the energy of $n\pi^*$ level depends even on the influence of the CH₃ group introduced to the molecule (see Table I).

Because of an inessential overlap of the cloud of n electrons with the π system of the molecule the probability of $n \rightarrow \pi^*$ transitions of the coumarines under study is low. Introduction of nonplanar substituents into the fourth position (CF₃), especially of the volume ones into the third position (benzol and fluorobenzol) increases the overlap of the cloud of n electrons with the π^* system of molecules and the oscillator strength of the $n \rightarrow \pi^*$ transition (see Table I) as well as results in appearance of mixed transitions of $n\pi^* + \pi\pi^*$ types.

A strong, sometimes complete, discharging of the initially negatively charged carbonyl oxygen takes place at the $n\pi^*$ state. The charge on the carbonyl oxygen takes the value of + 0.08, $\Delta E(S_0 \rightarrow S_{n\pi^*}) = 0.7$ at the 3F-4CF₃ substitution. Introduction of fluorine atoms via coupling to benzol rings does not increase the transfer of electron density from n electrons $\Delta E(S_0 \rightarrow S_{n\pi^*}) = 0.5$ both in K1 and 3FPh-K1 molecules. This evidences once more the fact that conjugation of 3-fluorophenyl with the whole molecule is too weak.

Analysis of bond energies using the "Bond" program shows strong weakening of C = O bond (by the amount of from 140 to 180 kcal/mol) under excitation to the $n\pi^*$ state. The existence of a volume substituent in the third position decreases this value down to 80 – 120 kcal/mol. Therefore, the probability of transformations according to the mechanism of photodecay involving radicals in the $n\pi^*$ state is lower for 3Ph-substituted K1. In addition, as we have shown earlier¹¹ a decrease of localization of the $n\pi^*$ state on the carbonyl group (as a result of 3CN and 3 pyridyl substitution) also leads to an increase of photochemical resistance ($E_{1/2} = 483$ phot/mol).

Thus, detailed analysis of the electron structure of complex derivatives of coumarines using the methods of quantum chemistry allowed us to take into account the electron structure of molecules in the excited states and possible relationships between various channels of photochemical reactions as well as stereoeffects appearing in substitution, and to produce active media lasing in the blue-green region with a longer lifetime.

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