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SPECTROSCOPY OF CONDENSED MATTER

Spectral-Luminescent Properties of Charged Forms of Some Substituted Benzaldehydes

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Abstract—The spectral-luminescent properties of the charged (anionic and cationic) forms of three biologically active substituted benzaldehydes, namely, *o*-anisaldehyde (2-methoxybenzaldehyde), syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde), and vanillin (3-methoxy-4-hydroxybenzaldehyde), are studied by quantum-chemical methods. Calculations show that the S_1 state of the charged forms of the studied molecules, in contrast to the neutral forms, is of the ππ* type, and its localization is similar to the localization of the S_2 (ππ*) state of the neutral molecules (anisaldehyde and vanillin) or of the S_3 (ππ*) state of syringaldehyde. According to the calculation results, the spectral range of 240–420 nm contains no new absorption bands corresponding to electronic transitions differing in nature and localization from the electronic transition of the neutral molecules. The calculated fluorescence characteristics of the charged forms of the studied molecules show that the radiative decay rate of the charged forms is considerably higher than that of the neutral forms, which is related to the different orbital nature of the S_1 state in the neutral and charged forms. Analysis of the calculated and experimental data on the fluorescence of the studied substituted benzaldehydes in alcohol solutions reveals that the fluorescence at 410 nm belongs to the cationic forms. Vanillin and syringaldehyde may also exhibit weak fluorescence of their anionic forms.

Keywords: substituted benzaldehydes, spectral-luminescent properties, quantum-chemical methods
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INTRODUCTION

The problem of creation of effective medical drugs based on benzaldehydes and their biologically active hydroxy-substituted derivatives requires knowledge of their physicochemical properties depending on various factors, in particular, on the medium properties. An important feature of this class of compounds is their ability to form charged protolytic forms (anions and cations) with intra- and intermolecular hydrogen bonds depending on the properties of the environment (solvent, matrix, additives, etc.). It is known that excitation of a molecule changes its properties due a change in the charge density distribution with respect to the ground electronic state. This leads to a change in the physicochemical properties of compounds [1]. One of the methods of studying physicochemical properties and their variations is to study the absorption and fluorescence spectra of materials [2]. Therefore, the study of the spectral-luminescent properties of benzaldehydes and their charged forms is topical.

At the first stage, we measured the absorption spectra of the studied benzaldehydes in hexane and ethanol. We succeeded in measuring the fluorescence of these compounds only in ethanol [3]. The experimental study of benzaldehyde molecules was performed without creating special conditions for obtaining the charged forms, because of which it was hardly possible to unambiguously assign the measured absorption and fluorescence spectra to particular protolytic forms. This assignment requires a detailed consideration of the spectral-luminescent properties of these compounds in media with different donor–acceptor properties, as well as of the results of quantum-chemical calculations. The results of the quantum-chemical calculation of the neutral forms of these compounds are presented in [3]. Analysis of the obtained experimental and theoretical results allowed us to conclude that the neutral forms of the studied substituted benzaldehydes are not responsible for the observed fluorescence of their solutions in ethanol.

In the present work, we perform quantum-chemical calculations of the spectral-luminescent properties of the charged forms (anionic and cationic) of three substituted benzaldehydes, namely, 2-methoxybenzaldehyde (*o*-anisaldehyde), 3-methoxy-4-hydroxy-

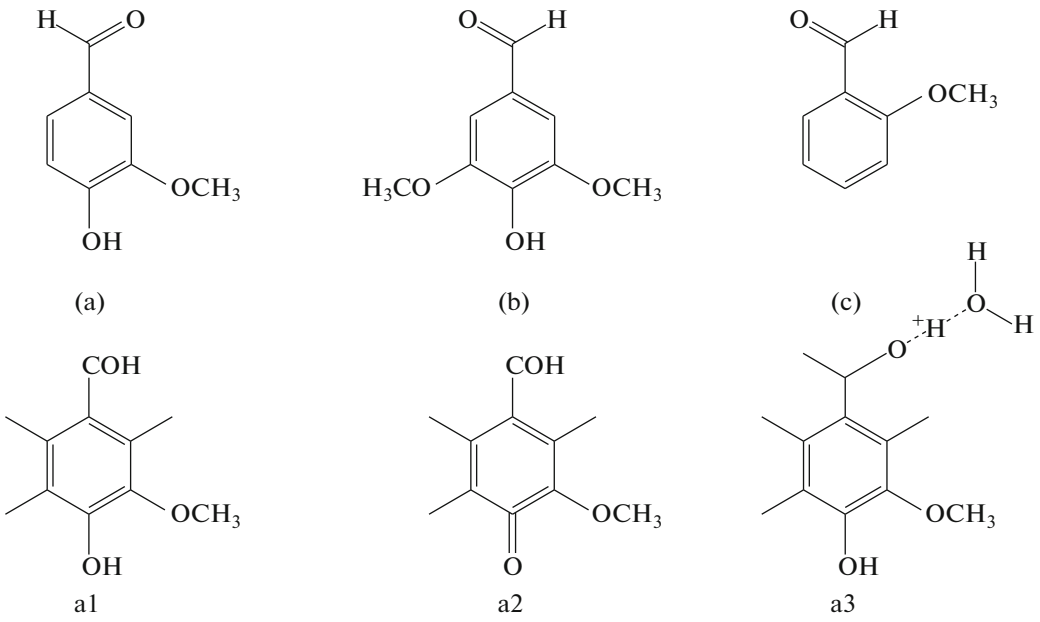

Fig. 1. Structural formulas of substituted benzaldehydes studied: (a) vanillin, (b) syringaldehyde, and (c) *o*-anisaldehyde, as well as of protolytic forms of vanillin given as an example: (a1) neutral form ($q = 0$), (a2) anionic form ($q = -1e$), and (a3) cationic form ($q = 1e$).

benzaldehyde (vanillin), and 3,5-dimethoxy-4-hydroxybenzaldehyde (syringaldehyde) (Fig. 1).

Note that the main aim of our studies of the spectral-luminescent properties of biomolecules is to determine the interrelation between their electronic structure, spectroscopic properties, and pharmacological function [4].

METHOD OF INVESTIGATION

We synthesized the studied substituted benzaldehydes at Belarus State University and measured their absorption and fluorescence spectra at the Institute of Physics, National Academy of Sciences of Belarus. The absorption spectra of the compounds in hexane and ethanol with a concentration of 10^{-4} mol/L were measured on a Cary-500 Scan UV-Vis-NIR spectrophotometer (Varian, United States). The corrected fluorescence and fluorescence excitation spectra were measured using an upgraded SDL-2 spectrofluorimetric complex (LOMO, Soviet Union) based on excitation and recording monochromators MDR-12 and MDR-23, respectively. The complex was controlled by a personal computer as described in [5]. A DKsSh-120 xenon lamp was used as an excitation source. The light signal passed through a monochromator was recorded by an FEU-100 photomultiplier (230–800 nm) in the photon counting mode. The fluorescence quantum yields of ethanol solutions were estimated by the relative method. A solution of quinine in 0.1 N sulfuric acid (quantum yield $\gamma = 0.55$) was used as a reference solution.

The theoretical study of the dependence of the spectral-luminescent properties of polyatomic molecules on their chemical and electronic structures is an important problem of the theory of the electronic structure of molecular systems. This problem in many cases cannot be solved using only the experimental (empirical) basis. The physicochemical (including spectral-luminescent) characteristics of molecules reflect the properties of their electronic shells, which are determined by the chemical structure of the compounds. On the other hand, the dependence of the electronic structure of a molecule on its molecular structure can be correctly studied only using quantum-chemical methods.

Let us briefly remind how the calculated theoretical values are related to the experimentally measured characteristics of the absorption (emission, fluorescence) spectra. The main characteristic is optical density $D(\nu) = \varepsilon(\nu)Cl$, where $\varepsilon(\nu)$ is the decimal molar extinction coefficient (L/mol cm), C is the concentration of molecules (mol/L), l is the layer thickness (cm), and ν is the wavenumber (frequency, energy) (cm^{-1}). The intensity of the bands of electronic spectra are usually characterized by dimensionless value f (oscillator strength) calculated using the heuristic formula

$$f = 4.32 \times 10^{-9} \int \varepsilon(\nu) d\nu.$$

Radiative (absorption or emission) or nonradiative electronic transitions (internal conversion or intersystem crossing) occur between the electronic-vibrational (vibronic) states of the molecule. In the theoret-

ical context, this ensures the fulfillment of the conservation law during the electronic transition. At the same time, according to the Franck–Condon principle, the geometrical characteristics of the initial vibronic state (thermodynamically equilibrium vibrational distribution) are retained during the electronic transition. This means that the electronic transition energies determined by quantum-chemical calculations correspond to the maxima of the corresponding absorption (emission) bands. An electronic absorption band can be usually approximated by a Gaussian curve with particular halfwidth $\Delta\nu$. Assuming that $\Delta\nu \approx 5000\ \text{cm}^{-1}$, we obtain the approximate relation $f \approx 10^{-5}\varepsilon(\nu_{max})$, which is useful for comparing the theoretical (f) and experimental ($\varepsilon(\nu_{max})$) characteristics of spectra.

In the present study, the quantum-chemical calculations were performed by the intermediate neglect of differential overlap (INDO) method using the software package and original parameterization developed specially for investigating the problems of photonics of polyatomic organic compounds at the Department of Photonics of Molecules, Siberian Physical Technical Institute, Tomsk State University.

The used variant of the INDO method allows one to calculate the energies and oscillator strengths of electronic transitions, the electron density distributions on atoms and molecular fragments, and the change in the electron density upon electronic excitation with respect to the ground state. The rate constants of radiative decay (k_r), nonradiative transitions (internal conversion, k_{ic}), and intersystem crossing (k_{ST}) were calculated by the method described in [7], have an estimation character, and make it possible to determine the tendencies in changes of the fluorescence quantum yield ($\gamma = k_r/k_r + k_{ic} + k_{ST}$) in series of similarly constructed compounds [8].

The ground-state geometry of the compounds studied was optimized by the AM1 method [9]. To calculate the charged forms, we applied the following molecular models. Changes in the geometry of anionic forms are limited by changes in the length of chemical bonds so as not to disturb the valence of the atoms of the molecule. Cations (protonated forms) were modeled as complexes with the hydrogen bond between the molecules of substituted benzaldehydes and a proton solvated by a methanol molecule (Fig. 1). For adequate modeling of cationic complexes, we used molecular electrostatic potentials (MEPs) [10, 11], which allowed us not only to identify the most efficient electron-acceptor center in the molecule, but also to determine the proton attachment site.

For correct calculation of the emission spectrum, we determined the excited state geometry from the change in the electron density on the P_{AB} chemical bonds of the studied molecules occurring upon excitation with respect to the ground state (according to Mulliken [12]). We used the known linear relationship between the chemical bond length and population. Then, the change in the bond length due to the transition to the excited state can be described as

$$\Delta R^*_{AB} = -k\Delta P^*_{AB},$$

where ΔP^*_{AB} is the change in the bond population due to the transition of the molecule from the ground to the excited state. Coefficient $k = 0.46$ was found from the change in the length of the C–C bonds of benzene upon the $S_0 \rightarrow S_1$ transition [13].

It should be noted that the spectral-luminescent properties of the charged forms of substituted benzaldehydes are insufficiently studied. The experimental data on the absorption and fluorescence spectra of vanillin [14] and on the absorption spectra of anionic vanillin and syringaldehyde published in monograph [15] can be considered as the most complete.

RESULTS AND DISCUSSION

The detailed experimental study of the charged forms of vanillin performed in [14] showed that the absorption and fluorescence spectra of the aqueous solution of vanillin strongly depend on the solution PH. Vanillin can exists in three protolytic forms (neutral, anionic, and cationic) (Fig. 1) depending of the solution PH. The anionic form of vanillin is formed in the ground state as a result of proton detachment from the hydroxyl group (pH > 7.2) as the weakest, which is evidenced by the lower population (P_{AB}) of the O–H bond in the studied compounds compared to other C–H bonds ($P_{O-H} = 0.572e$, $P_{C-CH_3} = 0.766e$, $P_{Cap-H} = 0.890e$, $P_{C-H(COH)} = 0.773e$ [3]).

The cationic form appears as a result of protonation (pH < –1) of the oxygen atom of the aldehyde group, which has higher acceptor properties than the other oxygen atoms of the molecules. Since the proton-acceptor properties of ethanol as a solvent are close to those of water and, in addition, ethanol often contains some amount of water, we may suggest that cationic forms are present in the ethanol solutions of the studied substituted benzaldehydes, which follows from both the absorption and fluorescence spectra. In particular, the experiment in [14] showed that the absorption spectra of aqueous solutions of vanillin contain simultaneously the bands of the neutral and anionic forms of vanillin. The authors of [16] studied the influence of the composition of water–ethanol solvent on the oxidation of vanillin on a platinum electrode by dc voltammetry and came to the conclusion that the electrochemical oxidation in an alkaline medium either is preceded by deprotonation or the deprotonation and oxidation processes occur simultaneously. This conclusion indirectly confirms the presence of the bands of not only neutral but also anionic forms of vanillin in the absorption spectrum of the solution.

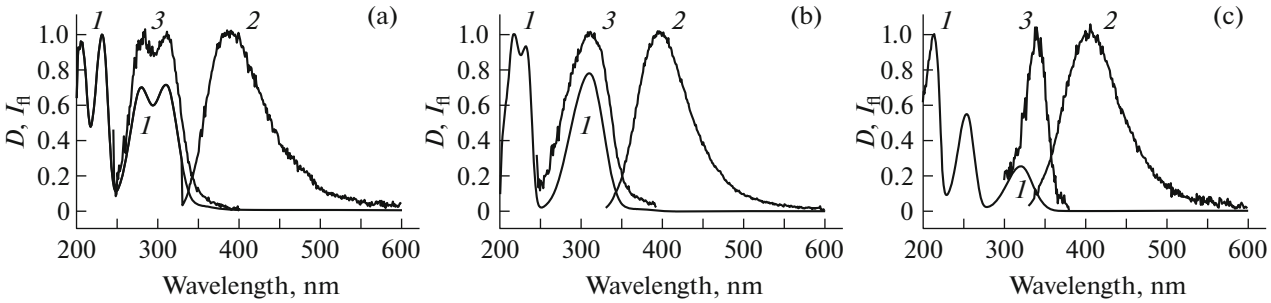

Fig. 2. (*1*) Absorption (*D*), (*2*) fluorescence, and (*3*) fluorescence excitation spectra of (a) vanillin, (b) syringaldehyde, and (c) *o*-anisaldehyde in ethanol. The excitation wavelength is 330 nm; the recording wavelength is 410 nm. Spectra *2* and *3* are given in relative units.

The formation of charged (anionic and cationic) forms should also be expected in alcohol solutions of syringaldehyde, whereas *o*-anisaldehyde can exist only in two (neutral and cationic) forms due to the absence of carboxyl groups.

Figure 2 shows the experimental absorption and fluorescence spectra of the studied compounds in ethanol.

Absorption Spectra of Charged Forms

Table 1 lists the calculated characteristics of the absorption spectra of the charged forms of vanillin, *o*-anisaldehyde, and syringaldehyde in comparison with their neutral forms and the experimental absorption spectra of the anionic forms. The spectra of the anionic forms of vanillin and syringaldehyde are measured in alkaline ethanol solution [15]. Calculations show that proton detachment from the hydroxyl group in the anionic form leads to a strong decrease in the energy of the $n\pi^*$ transitions and an increase in the energy of the $n\pi^*$ states.

Analysis of the calculated characteristics of the absorption spectra of the neutral and anionic forms of vanillin reveals that the spectrum of the charged form in the range of 240–420 nm contains one band fewer than the spectrum of the neutral form and the spectrum of the charged form is shifted to longer wavelengths with respect to the spectrum of the neutral form. Analysis of the molecular orbitals (MOs) in the configuration forming the long-wavelength band in the absorption spectrum of the vanillin anion showed that this band is formed by one $S_0 \rightarrow S_1(\pi\pi^*)$ transition and is similar to the band of the $S_0 \rightarrow S_2(\pi\pi^*)$ transition in neutral vanillin with a lower energy but a higher intensity. The experimental absorption spectrum of anionic vanillin exhibits between the two bands a plateau with a slight bend at 395 nm [15], which, in its orbital nature, corresponds to the $S_0 \rightarrow S_3(\pi\pi^*)$ transition of neutral vanillin.

According to the calculation results, the long-wavelength band in the absorption spectrum of anionic syringaldehyde is formed by two electronic transitions corresponding to the $S_0 \rightarrow S_3(\pi\pi^*)$ and $S_0 \rightarrow S_5(\pi\pi^*)$ transitions of the neutral molecule. Comparison of the calculated and experimental absorption bands of the anionic forms of vanillin and syringaldehyde reveals a satisfactory agreement between them, which allows us to expect good agreement with experiment for the cationic forms as well.

The long-wavelength band in the absorption spectrum of cationic *o*-anisaldehyde is formed by two electronic transitions, $S_0 \rightarrow S_1(\pi\pi^*)$ and $S_0 \rightarrow S_2(n\pi^*)$. The localization of the molecular orbitals forming the $S_1(\pi\pi^*)$ state of cationic *o*-anisaldehyde allows us to suggest that this state correspond to the $S_2(\pi\pi^*)$ state of the neutral molecule. The long-wavelength band in the absorption spectrum of cationic vanillin is formed by the $S_0 \rightarrow S_1(\pi\pi^*)$, $S_0 \rightarrow S_2(n\pi^*)$, and $S_0 \rightarrow S_3(\pi\pi^*)$ electronic transitions, while the $S_1(\pi\pi^*)$ and $S_3(\pi\pi^*)$ states of the cationic form correspond to the $S_2(\pi\pi^*)$ and $S_4(\pi\pi^*)$ states of the neutral form, respectively (Table 1). The state of affairs in the spectrum of syringaldehyde cation is similar to that for vanillin.

Note that the absorption spectra of the charged forms of the studied substituted benzaldehydes in the range of 220–240 nm have no additional bands with the MO localization different from that for the neutral forms. The calculation results for anionic vanillin and syringaldehyde agree well with the experiment (Table 1).

The proton detachment from the hydroxyl group negatively charges the molecules of substituted benzaldehydes, but a large part of the negative charge is localized on the oxygen atom that remained after the proton detachment from the hydroxyl group (Table 2).

The other part of the negative charge enhances the acceptor properties of the benzene ring and the aldehyde and methoxy groups in the $\pi\pi^*$ states of vanillin and syringaldehyde anions.

Table 1. Experimental and theoretical characteristics of the absorption spectra of protolytic forms of benzaldehydes

Calculation									Experiment
neutral form			cationic form			anionic form			anionic form [15]
state	E_i, cm^{-1}	f	state	E_i, cm^{-1}	f	state	E_i, cm^{-1}	f	λ_{max}, nm (E_{max}, cm^{-1})
o-Anisaldehyde									
$S_1(n\pi)$	25240	0.0	$S_1(\pi\pi)$	26330	0.138				
$S_2(\pi\pi)$	32170	0.215	$S_2(n\pi)$	30810	0.0				
$S_3(\pi\pi)$	36040	0.142	$S_3(\pi\pi)$	34060	0.208	Anionic forms are absent			
$S_5(\pi\pi)$	42330	0.590	$S_6(\pi\pi)$	42120	0.476				
$S_7(\pi\pi)$	45630	0.162	$S_{11}(\pi\pi)$	49550	0.538				
$S_{12}(\pi\pi)$	49450	0.286	$S_{12}(\pi\pi)$	50310	0.210				
Vanillin									
$S_1(n\pi)$	27490	0.0	$S_1(\pi\pi)$	27880	0.229	$S_1(\pi\pi)$	28830	0.586	355 (28170)
$S_2(\pi\pi)$	32820	0.120	$S_2(n\pi)$	31460	0.0	$S_2(n\pi)$	29380	0.0	
$S_3(\pi\pi)$	34940	0.162	$S_3(\pi\pi)$	31650	0.251	$S_3(\pi\pi)$	31440	0.156	300 (33300) (bend)
$S_5(\pi\pi)$	41560	0.647	$S_5(\pi\pi)$	39108	0.360	$S_6(\pi\pi)$	37630	0.028	255 (39220)
$S_7(\pi\pi)$	44190	0.316	$S_6(\pi\pi)$	41840	0.069	$S_9(\pi\pi)$	41950	0.157	
$S_{11}(\pi\pi)$	47520	0.205	$S_{10}(\pi\pi)$	47108	0.421	$S_{13}(\pi\pi)$	46660	0.374	
Syringaldehyde									
$S_1(n\pi)$	27810	0.0	$S_1(\pi\pi)$	24480	0.032	$S_1(\pi\pi)$	26500	0.513	370 (27030)
$S_2(\pi\pi)$	30290	0.032	$S_2(\pi\pi)$	27290	0.491	$S_2(\pi\pi)$	29020	0.131	
$S_3(\pi\pi)$	32050	0.278	$S_3(n\pi)$	33030	0.0	$S_3(n\pi)$	29390	0.0	
$S_5(\pi\pi)$	32500	0.407	$S_5(\pi\pi)$	37790	0.101	$S_9(\pi\pi)$	38840	0.150	255 (39220)
$S_8(\pi\pi)$	40650	0.530	$S_7(\pi\pi)$	40980		$S_{13}(\pi\pi)$	44480	0.353	
$S_{12}(\pi\pi)$	45730	0.110	$S_{10}(\pi\pi)$	44150		$S_{15}(\pi\pi)$	47220	0.090	
$S_{13}(\pi\pi)$	46620	0.278	$S_{12}(\pi\pi)$	44660					

E_i is the energy of a purely electronic transition, and f is the oscillator strength of this transition.

The benzene ring in the cationic forms of the studied compounds exhibits stronger acceptor properties than in the anionic forms, especially in the $n\pi^*$ state (Table 3).

The situation with the $COHH^+$ group of the cationic forms of the studied molecules is more complicated, i.e., the acceptor or donor properties of this group in the excited states change with respect to the neutral forms. For example, in the S_0 state of the neutral forms, the COH group exhibits acceptor properties in all the compounds, while the COHH+ group becomes a donor. Or, for example, the COH group is an acceptor in the $S_2(\pi\pi^*)$ state of the neutral form and sharply decreases its acceptor properties in the $S_1(\pi\pi^*)$ state of the cationic forms.

Fluorescence of Charged Forms

The experimental and calculated characteristics of the fluorescence of the molecules studied are presented in Table 4. According to these data, all the substituted benzaldehydes studied in this work exhibit weak fluorescence at $\lambda_{fl} = 410$ nm with quantum yields of 0.022, 0.012, and 0.008 (*o*-anisaldehyde, vanillin, and syringaldehyde). The main difference of the absorption and fluorescence spectra of the charged forms from the corresponding spectra of the neutral forms is the orbital nature of the S_1 state. The S_1 state in the neutral forms has the orbital nature of the $n\pi^*$ type [3], which explains the absence of fluorescence. The S_1 state in the charged forms has the orbital nature of the $\pi\pi^*$ type (i.e., inversion of the $n\pi^*$ and $\pi\pi^*$

Table 2. Electron density distribution in anionic forms of substituted benzaldehydes upon excitation

State	Electron density on molecular fragments, *e*			
	benzene ring	COH group	O_{OH}	$OCH_3(1)$ and $OCH_3(2)$ groups
Vanillin anion				
S_0	+0.128	–0.225	–0.746	–0.157
$S_1(\pi\pi)$	+0.372	–0.659	–0.618	–0.095
$S_2(n\pi)$	–0.124	+0.047	–0.784	–0.140
$S_6(\pi\pi)$	+0.086	–0.273	–0.587	–0.023
Syringaldehyde anion				
S_0	+0.277	–0.232	–0.746	–0.152, –0.147
$S_1(\pi\pi)$	+0.511	–0.658	–0.630	–0.112, –0.111
$S_2(\pi\pi)$	+0.063	–0.240	–0.595	–0.116, –0.111
$S_3(n\pi)$	+0.036	+0.003	–0.780	–0.127, –0.131

Table 3. Electron density distribution in cationic forms of substituted benzaldehydes upon excitation

State	Electron density on molecular fragments, *e*			
	benzene ring	$COHH^+$ group	OH group	$OCH_3(1)$ and $OCH_3(2)$ groups
o-Anisaldehyde cation				
S_0	+0.490	+0.542	–	–0.032
$S_1(\pi\pi)$	+0.874	–0.022	–	+0.148
$S_2(n\pi)$	+0.907	+0.106	–	–0.013
$S_3(\pi\pi)$	+0.662	+0.201	–	+0.138
Vanillin cation				
S_0	+0.580	+0.528	–0.051	–0.057
$S_1(\pi\pi)$	+0.881	–0.037	+0.014	+0.142
$S_2(n\pi)$	+0.960	–0.002	+0.015	+0.027
$S_3(\pi\pi)$	+0.452	+0.319	+0.038	+0.191
Syringaldehyde cation				
S_0	+0.557	+0.618	–0.067	–0.049, –0.059
$S_1(\pi\pi)$	+0.882	+0.001	–0.074	+0.078, +0.113
$S_2(\pi\pi)$	+0.492	+0.077	+0.065	+0.119, +0.247
$S_3(n\pi)$	+0.525	+0.271	+0.043	+0.052, +0.109

states occurs), which is responsible for the fluorescence.

The experimental spectra in ethanol formally yield the value of the Stokes shift of the fluorescence of uncharged substituted benzaldehydes in the range of 6900–7900 cm^{-1}. However, this Stokes shift was determined without allowance for the existence of the $S_1(n\pi)$ state, which does not manifest itself in the absorption spectrum. Taking into account that the calculated energy of the $S_1(n\pi^*)$ state lies within the range of 26000–27000 cm^{-1}, the Stokes shift in the studied uncharged forms does not exceed 2500 cm^{-1}, which testifies to insignificant structural reconstructions of absorbing molecules after excitation.

The coincidence of the positions of the absorption and fluorescence excitation peaks of vanillin and syringaldehyde allows us to conclude that the observed fluorescence band of these compounds belongs to one type of particles of each molecule. A considerable difference between of the absorption and fluorescence excitation spectra (~1800 cm^{-1} for the long-wavelength band position) was recorded for *o*-anisaldehyde. This difference can be explained by the presence of two conformers with close fluorescence character-

Table 4. Fluorescence characteristics (band peak λ_{fl} and quantum yield γ) of protolytic forms of substituted benzaldehydes

Calculation							Experiment (ethanol)	
pompound	protolytic form	λ_{fl}, nm (cm^{-1})	k_r, s^{-1}	$k(S_1-S_0)$, s^{-1}	$k(S_1-T_i)$, s^{-1}	γ	λ, nm (E_{fl}, cm^{-1})	Γ
o-Anisaldehyde	Neutral	386 (25670)	3×10^4	10^{-7}	4×10^{11}	$>10^{-4}$	410 (24390)	0.022
	Cationic	381 (26220)	9×10^7	2×10^5	2×10^9	0.035		
Vanillin	Neutral	376 (26600)	2×10^2	10^{-7}	8×10^{10}	$>10^{-4}$	410 (24390)	0.012
	Anionic	372 (26860)	3×10^8	1×10^5	6×10^{11}	5×10^{-4}		
	Cationic	419 (23870)	8×10^7	2×10^6	2×10^9	0.038		
Syringaldehyde	Neutral	378 (26600)	2×10^2	10^{-7}	2×10^{10}	$>10^{-4}$	410 (24390)	0.008
	Anionic	387 (25840)	2×10^8	10^{-7}	6×10^{11}	4×10^{-4}		
	Cationic	420 (23810)	8.3×10^7	1×10^6	2.5×10^9	0.032		

istics (λ_{fl}, γ) in the solution. The optimized geometry of this molecule gives the conformer presented in Fig. 1. In our opinion, another molecular configuration can also exist, in which the COH group is rotated by 180° with respect to the C–COH bond. Calculations showed that the conformers of *o*-anisaldehyde have different absorption centers, which leads to different positions of the long-wavelength peaks in the absorption and fluorescence excitation spectra. The calculated fluorescence peaks of the conformers are closely positioned ($\lambda_{fl1} = 389$ nm, $\lambda_{fl2} = 382$ nm), the energy difference between them being less than 500 cm^{-1}.

We compared two calculated characteristics (fluorescence band position and quantum yield) with the experiment. The best correspondences between the calculated fluorescence energy and the experimental fluorescence peak was obtained for the cationic forms of vanillin and syringaldehyde. This coincidence is worse for *o*-anisaldehyde. The calculated fluorescence quantum yield is higher for the cationic forms than for anionic ones, which suggests that the fluorescence at 410 nm experimentally observed in ethanol solutions of substituted benzaldehydes belongs to the cationic forms of the considered compounds.

In summary, the analysis of the experimental and calculated data (Table 4) allows us to conclude that the fluorescence of vanillin, *o*-anisaldehyde, and syringaldehyde observed at a wavelength of 410 nm belongs to the cationic forms of these compounds. Note that vanillin and syringaldehyde may also exhibit a very weak fluorescence of the anionic form.

CONCLUSIONS

1. Based on the results obtained, we can conclude that the absorption spectrum of the charged forms in the range of 240–420 nm is formed by electronic transitions of the same localization and orbital nature as the absorption spectra of the neutral forms. The difference consists only in intensity and the low-energy shift of the spectrum of the charged forms.

2. Inversion of the $n\pi^*$ and $\pi\pi^*$ states in the charged forms of the studied compounds with respect to the neutral forms takes place. The charged forms of 2-methoxybenzaldehyde (*o*-anisaldehyde), 3-methoxy-4-hydroxybenzaldehyde (vanillin), and 3,5-dimethoxy-4-hydroxybenzaldehyde (syringaldehyde) are responsible for their fluorescence in ethanol.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. F. Weller, Naturwissensch. **42**, 175 (1955).
2. M. Mohapatra and A. K. Mishra, Photochem. Photobiol. Sci. **18**, 2830 (2019). doi 10.1039 /c9pp00294d
3. O. K. Bazyl', V. Ya. Artyuhov, G. V. Mayer, P. P. Pershukevich, M. V. Bel'kov, O. I. Shadyro, and S. N. Samovich, Opt. Spectrosc. **127**, 242 (2019). https://doi.org/10.1134/S00304006X
4. G. B. Tolstorozhev, G. V. Mayer, M. V. Belkov, and O. I. Shadyro, Russ. Phys. J. **59**, 544 (2016). https://doi.org/10.1007/s11182-016-0804-x
5. E. S. Voropai, M. P. Samtsov, M. E. Rad'ko, K. N. Kaplevskii, P. P. Pershukevich, M. V. Bel'kov, and

F. A. Ermalitskii, in *Laser and Optoelectronic Technology, Collection of Articles,* Ed. by I. S. Manak (Akad. Upr. Prezidente RB, Minsk, 2006), No. 10, p. 200 [in Russian].

6. V. Ya. Artyukhov and A. I. Galeeva, Russ. Phys. J., No. 11, 949 (1986).
7. G. V. Mayer, V. G. Plotnikov, and V. Ya. Artyukhov, Russ. Phys. J. **59**, 513 (2016). https://doi.org/10.1007/s11182-016-0801-07
8. V. Ya. Artyukhov, T. N. Kopylova, L. G. Samsonova, N. I. Selivanov, V. G. Plotnikov, V. A. Sazhnikov, A. A. Khlebunov, G. V. Maier, and M. V. Alfimov, Russ. Phys. J., No. 10, 1096 (2008).
9. www.cambridgesoft.com.
10. E. Scrocco and J. Tomasi, Adv. Quantum Chem. **11**, 115 (1978).
11. V. Ya. Artyukhov, J. Struct. Chem. **19**, 364 (1978).
12. R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
13. G. Herzberg, *Molecular Spectra and Molecular Structure* (Wan Nostrand, Toronto, New York, London, 1969).
14. O. V. Vusovich, Extended Abstract of Cand. Sci. Dissertation (Tomsk, 2016). http://ams.tsu.ru/TSU/QualificationDep/co-searchers.nsf/72A8038F9DD1EB9C472580B300309353/$file/%D0%92%D1%83%D1%81%D0%BE%D0%B2%D0%B8%D1%87_%D0%9E.%D0%92._%D0%94%D0%B8%D1%81%D1%81%D0%B5%D1%80%D1%82%D0%B0%D1%86%D0%B8%D1%8F.pdf.
15. J. M. Skourikhin, *Chemistry of Cognac and Brandy* (De-Li Print, Moscow, 2005) [in Russian].
16. K. G. Bogolitsyn, N. L. Ivanchenko, E. F. Potapova, and A. N. Shkaev, Khim. Rastit. Syr'ya, No. 1, 11 (2006).

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