

Experimental and quantum-chemical study of excited electronic states of vanillin protolytic species

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Received February 4, 2002

Spectral and luminescent properties of vanillin protolytic species are studied, as well as the effect of inter- and intramolecular proton transfer on the spectral characteristic of molecules under study in the ground S_0 and excited S_1 electronic states.

A wide variety of photochemical reactions can be considered from the position of acid-base interactions. To assess the acid-base interactions means to understand the essence of a chemical reaction and to have a possibility of controlling it.¹ Ferster found and proved that for some fluorescing systems the acid-base equilibrium in the excited state has no time to establish completely.² To prove this theory, he used the method of electronic fluorescent spectroscopy.

Along with experimental methods, the applied quantum-chemistry methods received wide utility. Quantum-chemical calculations help to explain some photochemical processes from the viewpoint of the theory of molecular orbitals and thus to establish the relationship between spectral-luminescent properties and molecular structure.³

In this paper, we consider the effect of inter- and intramolecular proton transfer (PT) processes on the spectral properties of molecules under study in the ground S_0 and excited electronic states, as well as the spectral-luminescent properties of vanillin protolytic species. Vanillin falls in the group of wide-spread natural phenols.⁴ Photochemical reactions of vanillin proceed through the acid-base equilibrium.⁵ The study of protolytic species is interesting from the viewpoint of proton transfer, since their structure includes simultaneously the phenol group increasing the acidity in the excited state ($pK_a > pK_a^*$) and the carbonyl group, which becomes more basic in the excited state ($pK_a < pK_a^*$).

Experimental and quantum-chemical methods of study

Electronic absorption spectra were recorded with a Specord M-40 double-beam spectrophotometer, and

fluorescence spectra were recorded with a Hitachi-850 spectrofluorimeter. Aqueous solutions of 3-methoxy-4-hydroxybenzaldehyde (vanillin) having the concentration of 10^{-4} mol/l with different additives of H_2SO_4 , HCl, and NaOH were under study. The values of pH were measured with a 673 pH-meter. The absorption spectra in the ground state were used to draw titration curves and to calculate the values of acidity and basicity pK_a . In the excited Frank-Condon state, pK_a^{*F-C} was calculated as $pK_a^{*F-C} = pK_a - 0.625\Delta\nu/T$, where $\Delta\nu$ is the difference between peaks of two protolytic species.²

For quantum-chemical calculations of spectral characteristics of multiatomic organic molecules, we used the semi-empiric Intermediate Neglect of Differential Overlap (INDO) method.⁶⁻¹⁰ The PNDO method allows one to construct the correct energy diagram of electronic states of different origin and multiplicity in complex aromatic and heterocyclic compounds, to estimate the distribution of electronic density in molecules, and to analyze charge variation at excitation. The efficiency of the processes of intercombination conversion was determined based on the matrix elements of spin-orbit interaction in the one-center approximation.⁸ The computer program developed by Artyukhov and Maier was used for calculation of matrix elements of the spin-orbit interaction; this program allows estimation of the rate of singlet-triplet conversion K_{ST} (Refs. 8-10).

Results and discussion

In the ground state, we separated three protolytic species (anion, cation, and neutral forms; see Figs. 1 and 2). The neutral form exists with small additives of sulfuric acid at pH = 3-4. The values of acidity pK_a equal 7.2 for the ground state and -0.5 for the excited S_1^{*F-C} state. From the values of pK_a and pK_a^{*F-C} , it can be concluded that the protolytic equilibrium in the

excited state shifts toward lower pH, that is, the vanillin acidity increases in the S_1^* state. In the aqueous solution, the anion exists along with the neutral form; this spectrally manifests itself as a bend in the longwave part of the absorption curve. As alkali is added, this bend turns into the anion absorption band and the absorption of the neutral form disappears. Anion fluorescence is observed in the region of 405 nm, and the neutral form fluoresces at the wavelength of 330 nm. The anion is formed through proton removal from the hydroxyl group.

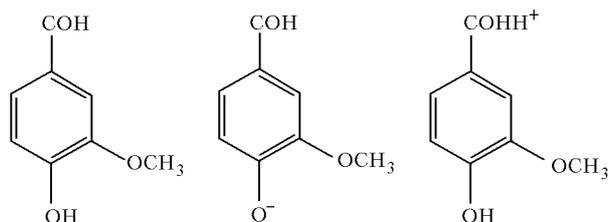


Fig. 1. Vanillin protolytic species.

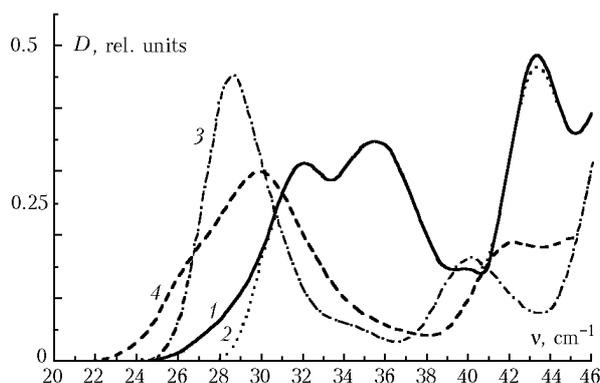


Fig. 2. Vanillin absorption spectra: aqueous solution (1), neutral form (2), anion (3), and cation (4).

The values of basicity pK_a of vanillin with additives of mineral acids were calculated. In the ground state, the cation was obtained at very large additives of sulfuric acid ($pK_a < -1.0$); in the excited state, the cation can be obtained much more simply (at acid additives $\sim 10^{-3}$ – 10^{-2} M). The cation is produced through attachment

of proton to carbonyl oxygen. This indicates that the vanillin basicity in the excited state increases. Actually, in the excited state $pK_a^{*F-C} = 5.4$.

Due to the presence of the hydroxyl and carbonyl groups in the structure of the studied molecule, vanillin possesses acid properties in the ground state (absorption of the neutral form and anion is mostly seen) and basic properties in the excited state. The cation form fluoresces in the region of 425 nm at small additives of sulfuric acid.

The quantum-chemical calculation of the absorption spectra shows that the longwave $\pi\pi^*$ -transition of the neutral species is formed by the charge transfer from the phenol part and methoxy group to the carbonyl group of the molecule (Table 1 and 2). It is seen from Table 1 that in the excited $S_1(\pi\pi^*)$ state, with the wavelength of 318.3 nm, a charge at the phenol ring and methoxy group decreases, while a charge at the carbonyl group increases. In the $S_2(n\pi^*)$ state, the charge distribution over fragments changes significantly at excitation, and the electron density is transferred to the phenol part ($\Delta q = 0.224$). As to the $S_4(\pi\sigma^*)$ state, the electron density is re-distributed through the charge transfer from the methoxy group to the phenol ring ($\Delta q = -0.140$ and $\Delta q = 0.115$). From analysis of the dipole moment values in the ground and excited states of the vanillin molecule, we can see that they decrease at excitation to the $n\pi^*$ state and increase in the $\pi\pi^*$ and $\pi\sigma^*$ states.

It can be also seen from the obtained energy level diagram that as the neutral form transits into the excited state, the molecule can deactivate through the channels of both internal and intercombination conversion. The most probable energy deactivation is the following:

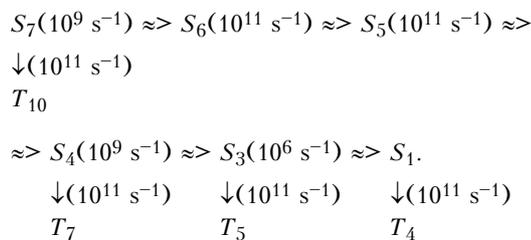


Table 1. Charges of fragments of vanillin protolytic species, e

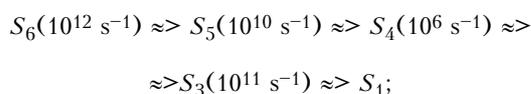
Fragment	Neutral form			Anion			Cation		
	S_0	S_1	S_2	S_0	S_1	S_2	S_0	S_1	S_2
Phenol ring	0.152	0.328	-0.072	-0.669	-0.224	-0.618	0.512	0.999	1.072
Carbonyl group	-0.093	-0.428	-0.001	-0.228	-0.775	-0.377	0.621	-0.026	-0.002
Methoxygroup	-0.059	0.100	0.073	-0.104	0.019	-0.005	-0.132	0.027	-0.070

Table 2. Spectral-luminescent properties of vanillin protolytic species as calculated by the PNDO/S method

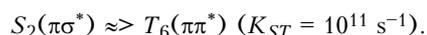
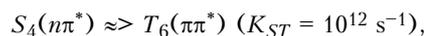
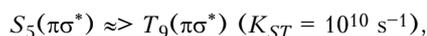
Neutral form				Anion				Cation			
λ , nm	f	μ , D	Origin	λ , nm	f	μ , D	Origin	λ , nm	f	μ , D	Origin
318	0.19	7.9	$S_1, \pi\pi^*$	366	0.49	18.7	$S_1, \pi\pi^*$	377	0.11	16.2	$S_1, \pi\pi^*$
306	0.00	2.9	$S_2, n\pi^*$	317	0.00	16.3	$S_2, \pi\sigma^*$	320	0.43	17.7	$S_2, \pi\pi^*$
289	0.23	9.1	$S_3, \pi\pi^*$	314	0.14	11.3	$S_3, \pi\pi^*$	262	0.00	18.2	$S_3, \pi\sigma^*$
285	0.00	4.9	$S_4, \pi\sigma^*$	288	0.00	8.3	$S_4, n\pi^*$	247	0.08	22.9	$S_4, \pi\pi^*$
323	0.00	2.9	$T_4, n\pi^*$	303	0.00	8.3	$T_8, n\pi^*$	239	0.00	21.3	$T_9, n\pi^*$
–	–	5.4	S_0	–	–	10.5	S_0	–	–	25.8	S_0

The calculated distribution of the electron density in the anion form indicates that the $S_0 \rightarrow S_1$ transition, as well as in the neutral form, is connected with the charge transfer from the phenol ring and methoxy group to the carbonyl group. The situation is just similar for the S_2 and S_4 states. The charge at the phenol ring decreases in both S_1 and S_2 states. The charge at the carbonyl group increases (from -0.228 to -0.775 and from -0.228 to -0.337 e). The electron density at the methoxy group decreases by 0.1 e in the both states. The obtained values of the dipole moments suggest that a tendency to the decrease in the excited $n\pi^*$ states is observed. The energy can deactivate through the following channels:

(a) internal conversion between the states:

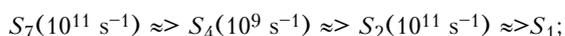


(b) intercombination conversion between the states:

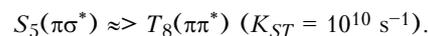
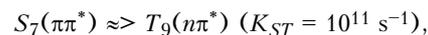
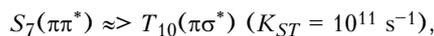


In the cation form, the electron density in $S_1(\pi\pi^*)$ is transferred from the phenol ring and methoxy group to the carbonyl group. In $S_2(\pi\pi^*)$ the charge is transferred from the phenol ring and carbonyl group to the methoxy group. From analysis of the charge distribution over fragments in the cation, we can say that the charge at the phenol ring increases, while the charge at the carbonyl group and methoxy group decreases. As compared with other forms, the dipole moment in the cation decreases in all states ($\pi\pi^*$, $\pi\sigma^*$, $n\pi^*$). Similarly to the neutral and anion forms, we can draw the scheme of energy deactivation in the excited states, which looks as follows:

(a) through the channels of internal conversion between the states:



(b) through the channels of intercombination conversion between the states:



Thus, the calculation by the PNDO/S method shows that the dipole moment in the all protolytic species is directed along the long molecular axis. The charged species (anion and cation) have higher dipole moments in both ground and excited states. The charge transfer direction keeps the same in all species in the first $\pi\pi^*$ transition. The experimental data indicate that for all protolytic species the fluorescence intensity depends on the excitation wavelength. At fluorescence excitation to the shortwave part of the spectrum (~ 250 nm), its intensity decreases sharply. Due to the states of the $\pi\sigma^*$ type located in this region, intense introversion with the triplet $\pi\pi^*$ states is observed, which can be the cause of this dependence.

Acknowledgments

This work was supported by the Ministry of Education, Grant No. E 00-12.0-235.

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