

# Quantum-chemical study of electronically excited states of protolytic forms of vanillic acid

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## Annotation

The paper describes an analysis of possible ways of deactivation of electronically excited states of 4-hydroxy-3-methoxy-benzoic acid (vanillic acid) and its protolytic forms with the use of quantum-chemical methods INDO/S (intermediate neglect of differential overlap with a spectroscopic parameterization) and MEP (molecular electrostatic potential). The ratio of radiative and non-radiative deactivation channels of the electronic excitation energy is established. The rate constants of photophysical processes (internal and intercombination conversions) occurring after the absorption of light in these forms are evaluated.

Keywords: vanillic acid, INDO/S, MEP, protolytic forms

## Introduction

Vanillic acid (VA) belongs to the class of aromatic hydroxy acids. In the chemical industry, vanillic acid is a promising material for production of polymers due to the presence in the structure of two functional groups (phenolic and carboxyl). The properties of natural vanillines derived from lignin (a component of wood), as well as synthetic vanillines, are determined by the presence in their structure of three reactive groups of oxygen: methoxy, hydroxy, and carbonyl. These groups determine the ionic equilibrium of vanillines in aqueous solutions in the ground and the excited electronic states [1]. The open press contains plenty of articles on the analytical determination of VA in the composition of alcoholic beverages [2, 3], and on the use of VA as inhibitors in testing of the pharmacological action of drugs on animals [4]. Practically, there are no publications on the investigation of the fundamental properties of VA. The article [5] describes the study of hydrogen bonds in derivatives of benzoic acids with the use of the method of IR-Fourier-spectroscopy. The authors have established that proton-acceptor properties of monomers of benzoic acid and its derivatives are formed mainly due to oxygen of the C=O-group. The dominance of the proton-acceptor activity of an oxygen atom of the carboxyl group leads to formation of intermolecular hydrogen bonds of the type O–H...O=C. The type of the substituent introduced into a benzene ring in the *para*- and *meta*-positions relative to the carboxyl group may be useful in synthesis of new aromatic acids with the desired biological activity. There is an imbalance between the applied research on VA and publications on the study of its photophysical and photochemical properties. Therefore, an importance of the knowledge on mechanisms regulating these processes in VA is evident.

The aim of the study is a comparative analysis of photophysical processes occurring in ionic forms of VA in the ground  $S_0$  and the excited  $S_1$  electronic states using quantum chemistry methods.

## Research technique

A 4-hydroxy-3-methoxybenzoic acid (brand "Aldrich") or vanillic acid, or 4-hydroxy-m-anisic acid, 3-monomethyl ester of protocatechuic acid has been studied.

Quantum-chemical calculations have been carried out using the semi-empirical method INDO [6-7] with a preliminary optimization of the geometry using the standard method AM1. This method allows to properly construct an energy diagram of electronic states of different nature and multiplicity, to evaluate the distribution of the electron density in molecules by analyzing the change in charges during the excitation. Moreover, having calculated the rate constants of photophysical processes it is possible to consider ways to deactivate the molecule energy from any of the excited state.

For a correct description of intermolecular interactions (IMI) of polyatomic molecules it is necessary to determine the effectiveness of protonation (or basicity) of each center. For theoretical evaluation of the basicity of compounds the MEP method has been used. The method allows to determine the most probable ways of the proton approach and, therefore, to

obtain the information on the gas-phase basicity of molecules, as well as to take into account specific intermolecular interactions, and to evaluate the reactivity of complex molecular systems. When studying intermolecular interactions it is important to select an atom in the system where formation of H-bonds or protonation is possible. This method is very convenient in a preliminary evaluation of the proton-acceptor ability of complex compounds that have few basic centers in the structure [7].

### Discussion of results

Vanillic acid is a typical benzoic acid and, as the vast majority of acids, can dissociate (Fig. 1). In [8] the ionic forms of VA were experimentally investigated. Table 1 shows the correspondence between the experimental characteristics on the position of bands of ionic forms of VA with the calculated data. In the ground state in the aqueous solution it exists in the anionic form ( $\nu_{\text{absorp.}}=34700 \text{ cm}^{-1}$  and  $39500 \text{ cm}^{-1}$ ), pKa acidity 4.5 (4.54 [9] (pKa (1) = 4.52 (25 °C, water) [10]) in the ground state. Upon excitation, the acidity of VA during the transition from the neutral form to the anionic form decreases  $\text{pKa}^{*F-K}=5.57$ . With an increase of pH to 10 or more there is a deprotonation from the hydroxyl group with formation of the dianionic form, pKa acidity is 11. However, during the transition from the anionic form to the dianionic form in the excited state the acidity increases  $\text{pKa}^{*F-K}=5.43$ . The anionic form is formed during the deprotonation of hydrogen from the carboxyl group COOH in aqueous solution (in the ground state), and at an increase of the solution pH to 10 or more a deprotonation from the hydroxyl group takes place, and the dianionic form is formed.

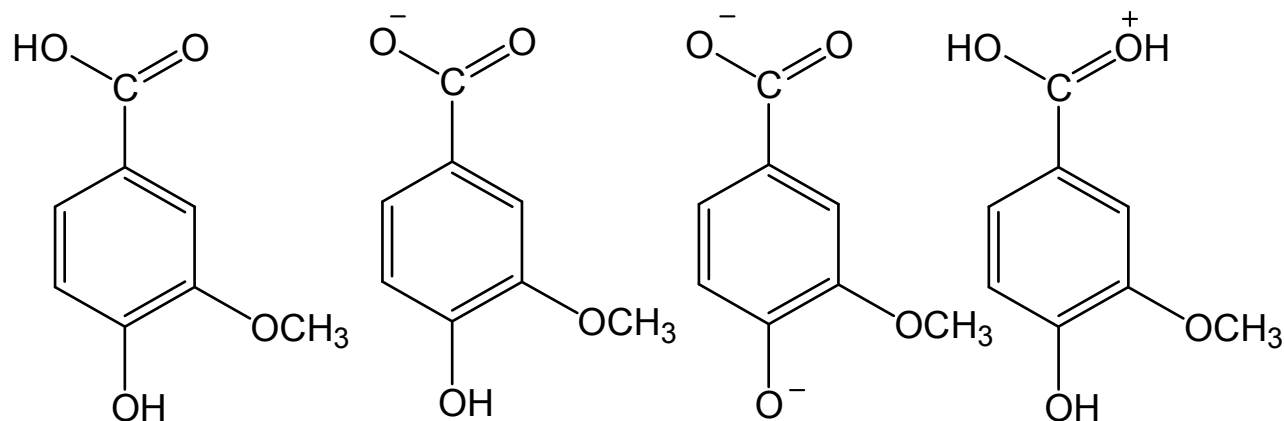


Fig. 1. Protolytic forms of vanillic acid: neutral, anionic, dianionic, and cationic

For a correct performance of quantum chemical calculations it is necessary to set the geometry of the molecule. In the study the molecular geometry was optimized using the standard method AM1. Table 1 shows that there is an agreement of the position  $S_0-S_1$  of the transition with a long-wave absorption band of the corresponding ionic forms of VA, as well as between the calculated and experimental values.

Table 1. Comparison of experimental and calculated absorption bands of vanillic acid

Form	$\nu, \text{cm}^{-1}$ (experiment)	$\nu, \text{cm}^{-1}$ (calculation)
Neutral form (10% $\text{H}_2\text{SO}_4$ )	34000 38400	35063 38576
Anionic form (aqueous solution)	34800 39500	36244 39247
Dianionic form ( $10^{-3}$ NaOH)	33200 35400	33344 35916
Cationic form (90% $\text{H}_2\text{SO}_4$ )	31200 34400	29328 32687

The energies of first bands of all forms of vanillic acid lie in the range from  $29000 \text{ cm}^{-1}$  up to  $36000 \text{ cm}^{-1}$ , and have the nature of the  $\pi\pi^*$  type (Table. 2). The magnitude of a dipole moment depends on the state and the molecule charge

distributed along the molecule. Charged forms (anionic, dianionic, and cationic) have the values of the dipole moment higher than the neutral form. In all forms of the given molecules the long-wave absorption bands have the nature of the  $\pi\pi^*$  type. According to Nurmukhametov classification [11], a molecule belongs to the 5 type and, therefore, should have a high fluorescence efficiency. Experimental data show the opposite result in several forms (see data on the phosphorescence), therefore, we assume that there is a competition between photophysical processes in the molecule.

For the neutral form of VA it should be noted that, as compared to the ground state, in excited states  $\pi\pi^*$  there is an increase of the charge on the carbonyl group; in  $\pi\sigma^*$  states there is a slight decrease. In states with the  $n\pi^*$  nature, both in the neutral form and in negatively charged forms, the charge significantly decreases on carbonyl oxygen and the phenolic group, Table 3.

Table 2. Calculated spectral characteristics of ionic forms of vanillic acid.

Forms	Spectral characteristics			
	$\lambda_{\text{absorp}}$ , nm (wavelength $S_0$ - $S_n$ of the transition)	State (orbital nature)	f oscillator strength	$\mu$ , D ( $\mu\text{O}$ ) dipole moment
Neutral	285	$S_1(\pi\pi^*)$	0,061	6,7 (5,58)
	259	$S_2(\pi\pi^*)$	0,27	8,51
	235	$S_3(n\pi^*)$	0,001	3,42
	228	$S_4(\pi\sigma^*)$	0,002	7,53
Anionic	306	$S_1(\pi\pi^*)$	0,12	16,01 (14,85)
	285	$S_2(n\pi^*)$	0,001	13,73
	262	$S_3(\pi\pi^*)$	0,19	15,32
	249	$S_4(\pi\sigma^*)$	0,002	10,21
Cationic (OHH+)	341	$S_1(\pi\pi^*)$	0,43	14,76 (12,8)
	326	$S_2(n\pi^*)$	0,009	12,85
	306	$S_3(\pi\sigma^*)$	0,099	13,31
	300	$S_4(n\pi^*)$	0,0009	13,06
	256	$S_5(\pi\sigma^*)$	0,007	15,75
Dianionic	300	$S_1(\pi\pi^*)$	0,13	13,26 (12,9)
	264	$S_2(\pi\pi^*)$	0,36	13,61
	250	$S_3(\pi\sigma^*)$	0,002	11,62
	238	$S_4(n\pi^*)$	0,0065	13,47

In the anionic form of vanillic acid in the ground state the electron density is formed as follows. The most electronegative fragment is the carbonyl oxygen, as well as the negative charge on the methoxy group. In the  $S_1$  state there are not many changes in the distribution of charges. In the  $S_2 n\pi^*$  state the electron density flows from the phenolic ring onto the methoxy group. It should also be noted that, as compared to the ground state, in excited states  $\pi\pi^*$  there is an increase of the charge on the carbonyl group, in  $\pi\sigma^*$  states there is a slight decrease. In states with the  $n\pi^*$  nature, both in the neutral or negatively charged forms, the charge significantly decreases on carbonyl oxygen and the phenol group.

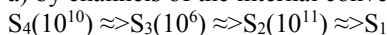
Table 3. Charges of fragments in excited states for ionic forms of vanillic acid

Ionic form of VA	Fragments	-OH carboxyl group	-C=O	PH-OH	-OCH <sub>3</sub>
Neutral	S <sub>0</sub>	0,674	-0,785	0,287	-0,176
	S <sub>1</sub> (ππ*)	0,489	-0,821	0,447	-0,114
	S <sub>3</sub> (nπ*)	0,461	-0,522	0,155	-0,094
Anionic	S <sub>0</sub>	0,028	-0,908	0,048	-0,167
	S <sub>1</sub> (ππ*)	0,027	-0,895	0,030	-0,163
	S <sub>2</sub> (nπ*)	0,025	-0,898	0,371	-0,498
Dianionic	S <sub>0</sub>	-0,023	-0,949	-0,764	-0,264
	S <sub>1</sub> (ππ*)	-0,087	-0,951	-0,664	-0,298
	S <sub>3</sub> (πσ*)	-0,060	-0,936	-0,732	-0,272
Cationic	S <sub>0</sub>	0,705	0,030	0,274	-0,010
	S <sub>1</sub> (ππ*)	0,436	-0,016	0,424	0,157
	S <sub>2</sub> (nπ*)	0,567	0,035	0,238	0,160

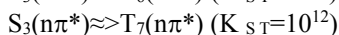
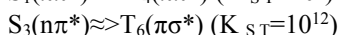
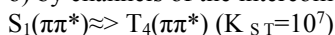
During the transition of a molecule to the excited state there is a deactivation of the energy by channels of internal and intercombination conversions. The schemes of the energy deactivation of excited states in protolytic forms of vanillic acids can be represented as follows:

for the neutral form:

a) by channels of the internal conversion between states:

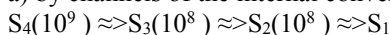


б) by channels of the intercombination conversion:

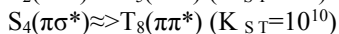


for the anionic form:

a) by channels of the internal conversion between states:

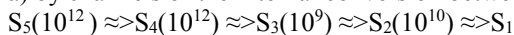


б) by channels of the intercombination conversion:

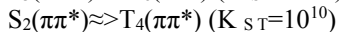
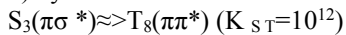


for the dianionic form:

a) by channels of the internal conversion between states:

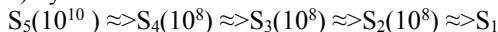


б) by channels of the intercombination conversion:

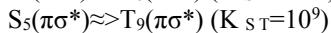
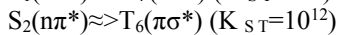
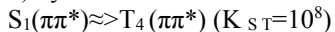


for the cationic form:

a) by channels of the internal conversion between states:



б) by channels of the intercombination conversion:



Estimating the values of constants of nonradiative transitions it can be said that in the neutral form between the singlet states the values of constants are lower by 2- 3 orders of magnitude than between the triplet states. In the anionic form, in  $S_2$  state, the deactivation energy is equally probable:  $S_2 \approx S_1$ , and  $S_2 \approx T_5$ . As compared to other forms, dianion has higher values of both the internal and the intercombination conversions. In the cationic form the calculation of deactivation constants of the excited state has shown that the main channel of decomposition is the intercombination conversion  $S_1 \approx T_4$ . The obtained results are consistent with the experimental results. The fluorescence spectra indicate that the anionic form has the most intense fluorescence, and the cationic form – the lowest.

MEP values were calculated for the state  $S_0$  in the plane  $XY: Z=0$ . According to MEP data, for the neutral form of vanillic acid the minimum value MEP is located in the range of carbonyl oxygen (Fig. 2). The cationic form is formed by protonation of hydrogen to carbonyl oxygen.

For the anionic form the deepest values are located on oxygen of the carboxyl group (Fig. 3).

Fig. 4 shows a chart of MEP minima for the dianionic form of vanillic acid. Deprotonation from the hydroxyl group leads to formation of two almost equal minima around the O- group. The symmetrical arrangement of carbonyl oxygen and the O-carboxyl group makes the attack on these proton centers equally probable. When a molecule is excited in  $S_1$  state, there is a decrease in the basicity on oxygen of the hydroxyl group and its increase on oxygens of the carboxyl group, both in the neutral form and in negatively charged forms. From the abovementioned Figures 2, 3, 4 it is seen that the greatest proton-acceptor ability is possessed by the dianionic form of vanillic acid.

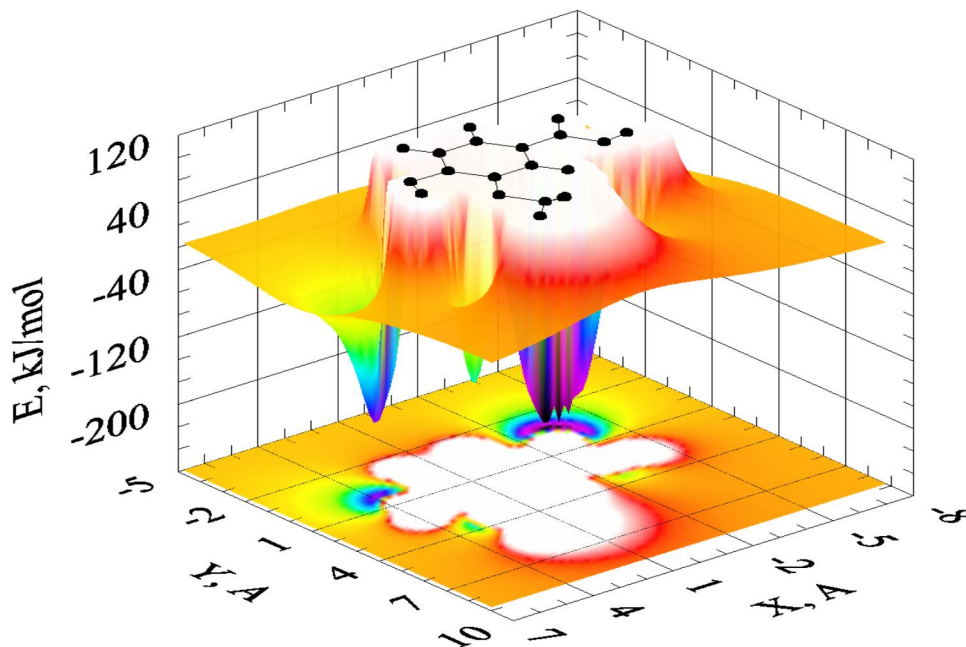


Fig. 2. The chart of MEP values for the neutral form of VA in the plane  $XY: Z=0.00$ .: 1st minimum: the value MEP= 522.66 kJ/mol (the minimum coordinates: X= -3.60 Y= -0.40); 2nd minimum: the value MEP= -139.41 kJ/mol (the minimum coordinates: X= 3.20 Y= 3.80); 3rd minimum: the value MEP= -136.59 kJ/mol (the minimum coordinates: X= 4.00 Y= 0.20).

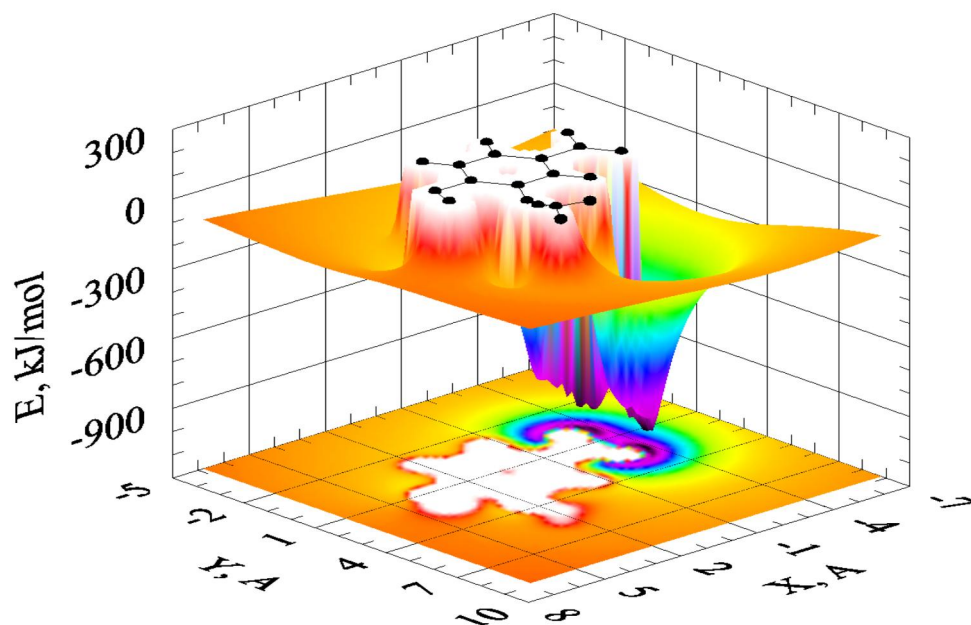


Fig. 3. The chart of MEP values for the anionic form of VA in the state  $S_0$  in the plane  $XY$ :  $Z = 0.00$ : 1st minimum: the value  $MEP = -1200$  kJ/mol (the minimum coordinates:  $X = -3.80$   $Y = 2.20$ ); 2nd minimum: the value  $MEP = -1100$  kJ/mol (the minimum coordinates:  $X = -3.80$   $Y = 0.00$ ); 3rd minimum: the value  $MEP = -1020$  kJ/mol (the minimum coordinates:  $X = -3.60$   $Y = -0.40$ ).

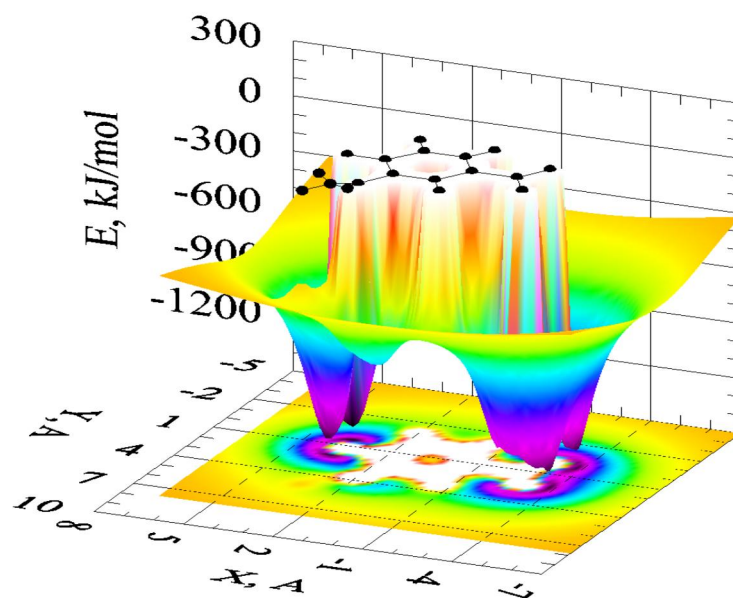


Fig. 4. The chart of MEP values for the dianionic form of VA in the plane  $XY$ :  $Z = 0.00$ : 1st minimum: the value  $MEP = -1300$  kJ/mol (the minimum coordinates:  $X = 3.60$   $Y = 0.40$ ); 2nd minimum: the value  $MEP = -1250$  kJ/mol (the minimum coordinates:  $X = 3.80$   $Y = 2.00$ ); 3rd minimum: the value  $MEP = -1100$  kJ/mol (the minimum coordinates:  $X = -3.80$   $Y = 2.20$ ).

## Conclusion

MEP values set the probable protonation center in Thus, from the abovementioned results it follows that the applied in the study methods for calculation of spectral characteristics of vanillic acid give a good description of photophysical processes occurring in the neutral or the ionic form of the molecule. The results obtained in this study are consistent with the experimental data.

The carried out analysis of the nature of electronically excited states shows that the long-wave  $\pi\pi^*$  transition of the neutral form of vanillic acid is formed by means of a transfer of the charge from the phenol part and the methoxy group onto the carbonyl group of molecules. It should also be noted that, as compared to the ground state, in excited states  $\pi\pi^*$  there is an increase in the charge on the carbonyl group, in  $\pi\sigma^*$  states there is a slight decrease. In states with the  $n\pi^*$  nature, both in the neutral and in negatively charged forms, the charge significantly decreases on carbonyl oxygen and the phenol group the molecule and, thus, we confirm the basicity of the protonation center. The symmetrical arrangement of carbonyl oxygen and the O-carboxyl group makes the attack of the proton on these centers equally probable. When the molecule is in  $S_1$  state there is a decrease in the basicity on oxygen of the hydroxyl group and its increase on oxygens of the carboxyl group, both in the neutral form and negatively charged forms. The most proton-acceptor ability is possessed by the dianionic form of vanillic acid.

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