UV-VISIBLE SPECTRA OF PEROXOTITANATE COMPLEXES

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Comparative analysis of calculated (subject to solvent influence in PCM model) and experimental UV-visible spectra of peroxotitanate complexes in solutions at various conditions of occurrence. It has been shown that the change of complex composition, dependent on the solution pH value, leads to the change of characteristic absorption bands of UV-visible spectra in the wavelength range exceeding 320 nm. The tendency of the absorption bands in solution spectra to shift is correlated to the change of calculated spectra in accordance with the monomer complex unit. It has been suggested that the color of the complex solution in weakly acidic and neutral media is related to appearance of hydroperoxy-bonds between titanium atoms.

Keywords: peroxotitanate complexes, electronic absorption spectra, PCM, TD–DFT.

Introduction

At present the syntheses of catalytic materials on the basis of green technology have acquired a special significance and popularity in terms of ecological compatibility and possibility of controlling the synthesis process. Oxides of titanium, magnesium, zirconium, silicon are widely used as such materials, both individually and in mixed compositions.

Previously titanium alkoxides were used as handy precursors (initial substances) for the synthesis of titania-based catalysts. As they are toxic, nowadays the attention of researchers is directed at study and development of appropriate synthesis techniques with the use of other precursors: titanium citrate, oxalate and peroxide complexes [1]. The state of titanium peroxide complexes in aqueous solutions has been studied experimentally in considerable detail in papers [2–4], but their precise composition is unknown so far, as it strongly depends on the synthesis conditions, primarily on the solution pH and the ratio "hydrogen peroxide – titanium". At that the understanding of the state and structure of peroxide complexes in precursor solution is important in order to control the following synthesis of titania catalysts. Modern quantum-chemical computational methods can play the supportive role for it, especially *ab initio* methods.

The most widespread use for calculation of the structure and characteristics of both organic and inorganic complexes belongs to Kohn-Sham method (DFT), which provides adequate description of the states of ions, complexes, crystals that correlates to experimental data. Numerous extensions of the method – use of various functionals, atomic basis sets, inclusion of environment for investigated structures – have enabled the description of various classes, states and properties of any elements, including heavy ones (in [5], as an example) and their compounds. Investigation of theoretical electronic spectra with by application of calculation of energy characteristics within the bounds of TD-DFT method [6, 7] is widely used in global practice in an effort of detailed interpretation of observed experimental data. Recently the similar calculations have been carried out in order to determine the state of many oxide materials and their precursors, including titania-based catalysts. Thus, in papers [8–10] calculation methods (DFT) have been used for determination of the properties of peroxide complexes emerging at H_2O_2 application to the surface of titanium and titanium silicate catalysts. Likewise, much information has been extracted concerning occurrence of active centers and their properties, transition complexes at interaction of catalysts with ethylene, ammonia and other compounds, the direction of possible catalyzed reactions. Calculated data concerning the structure of titania doped with nitrogen [11–12] and iron [13] have been given, the laws of changing width of forbidden band have been theoretically explained, as well as the UV-visible spectra at various conditions of synthesis and further material processing.

All abovementioned studies pursue the processes on the completely formed phase interface, at that the theoretical investigation of the state and the properties of titania precursors, which greatly influence the formation of the spatial structure of the solid phase, has been practically ignored.

In order to account for the influence of medium (solvent) on the studied substances the clarifying models are invoked, within which various types of solvate-solvent interaction are considered: dipole-dipole, dipole-induction, dispersion and so on. One of such models (COSMO, [14]) was previously used to investigate the interaction of some titanium tungstate complexes with hydrogen peroxide and the properties of the obtained peroxy compounds. The results were in good agreement with the experimental properties, they had certain prognostic ability in relation to their oxidizing properties. In recent decade the precise numerical polarized continuum model (PCM) has been developed [15, 16]. Within the model a solvent is considered as an isotropic medium characterized by some physical constants, at that the specific interactions are not taken into account in an explicit form. A molecule of a solute is placed in a cavity which forms in this continuous medium. All its atoms are surrounded by spheres with Van der Waals radius. In order to construct the smooth surface necessary for the method convergence, secondary surrounding of minor radius spheres is carried out, with the following triangulation in order to form the surface elements. By means of several iterations the surface charge field of the formed cavity and the free energy of a molecule in a solvent are estimated. The popularity of PCM is explained by speedy calculations of electron states in the environment of the solvent molecules, which is but little less compared to calculations for gas phase. At that the theoretical results and tendencies of changing compound spectra, obtained with the use of this model, most adequately correlate to the dependencies of experimental spectra of the synthesized compounds in solutions and explain their characteristic features. PCM in the simplified version (IEF-PCM) has been used for calculation of the interaction of terminal titanium oxide groups with the aqueous solution of hydrogen peroxide [8], which has been of great help in determination of arrangement of the solvent molecules as ligands in the peroxycomplex structure: by way of hydrogen bonding intermediates are formed with predominantly five-membered cycles. Likewise, the prognosis of the complex catalytic properties with respect to epoxidation reaction has been defined more accurately.

At interaction of titanium compounds with hydrogen peroxide the formation of several possible complex types can occur. Thus, in [2–3] it is noted that the reaction of titanium tetrachloride with hydrogen peroxide in acidic medium produces complexes with one peroxy group of the series $[Ti(O_2)(OH)_x]^{(2-x)+}$ (**I**). We can suggest that during the synthesis of titania peroxide precursors the formation of both the similar complexes and the complexes with peroxy and hydroperoxy group of the series $[Ti(O_2)(OOH)(OH)_x]^{(1-x)+}$ (**II**) takes place – at the great excess (10-100-fold) of hydrogen peroxide. Besides, it is noted in [2–3] that complexes of the series (**I**) are especially inclined to dimerization, as well as to further condensation and addition of new monomeric units. Therefore it is important for us to consider the behavior of such structures surrounded by the molecules of water in the role of a solvent, as immediate precursors during controlled formation of hydrated titania precipitate, which has not been studied previously. Investigation of other complexes of $[Ti(O_2)(OOH)_2]$ type or of the series $[Ti(OOH)_y(OH)_x]^{(4-x-y)+}$ (**III**) is not of interest, as their existence in aqueous solution is not confirmed by the previously published data. Formation of several OOH groups, bonded to titanium, is carried out on the completely formed phase interface: for example, in paper [8] titanium complexes of the series (**III**) have been studied as the active centers on the surface of titanium silicate catalyst. The existence of the complexes with two and three peroxy groups, fully considered in [17], is also of low probability in the conditions described below, for the reason that their formation demands very great excess (by the factor of hundreds) of hydrogen peroxide compared to titanium. On the other hand, the directions of their further oligomerization are analogous to the reaction directions of the series (**I**) complexes.

In its turn, electronic spectroscopy is one of the most accessible and dependable investigation methods of solution compositions. Therefore we aimed chiefly at the following: to establish the existence of the absorption bands in the UV-visible spectra of peroxotitanate complex solutions, related to definite chemical composition and forms, or to explain the absence of such bands within the studied range, considering the possible change of complex composition in a solution with changing pH value. This we plan to carry out by means of comparing the UV-visible spectra of solutions to the electronic absorption spectra of optimized complex forms obtained by way of quantum chemical calculation, taking into account aqueous environment in PCM. We suggest that the consideration of predominating types of bonding for titanium atoms in the calculated complez forms from several monomeric units will give an opportunity to prognosticate the reaction direction of further oligomerization at specific conditions, as well as formation of specific forms of hydrated titania precipitate. The necessary information of occurrence of such forms in a solution we can get from its UV-visible spectrum.

Experimental

In order to obtain peroxotitanate complexes $TiOSO_4 \cdot nH_2O$ (Aldrich) was used. Titanium oxysulfate was dissolved in distilled water at 50 °C, then it was diluted to obtain 50 mL of 0.05 M solution, and hydrolized by 3 M sodium hydroxide. Addition of NaOH was stopped when pH of the reaction mixture reached 5.0. The resulting titanium hydroxide precipitate was centrifuged at 7000 rpm and washed by distilled water until the negative reaction for sulfate. Then titanium hydroxide was dissolved in 10 mL 30 % hydrogen peroxide, and the formed peroxy complex was diluted by distilled water up to 50 mL. The pH value of the obtained solution varied in the range 2.0...2.3, which was the consequence of peroxytitanic acid decomposition. Mole ratio "hydrogen peroxide – titanium" was 35:1. In order to slow down the hydrogen peroxide decomposition process the solution was placed in an ice bath. The UV-visible spectra of solutions were registered with the use of Shimadzu UV-2700 spectrophotometer.

Computational

The present study investigates the electronic spectra of several complexes of the series (**I**) and the neutral complex of the series (**II**), formed at the reaction of hydrogen peroxide with titanium hydroxide precipitate in neutral, acidic and weakly basic media (at $pH < 9$). The complexes have been modeled, beginning from the corresponding monomer, by means of consecutive addition of single-type monomers to each other one by one and to the calculated complex of two monomer units. Monomer units of the complexes are presented in Fig. 1. In the first stage optimization of structure geometry has been carried out through the necessary number of steps until the stationary point with the greatest energy gradient value (not exceeding 0.0001 Hartree/Bohr) has been reached. Frequency analysis of the obtained Hessian for all the structures has shown the absence of imaginary frequencies.

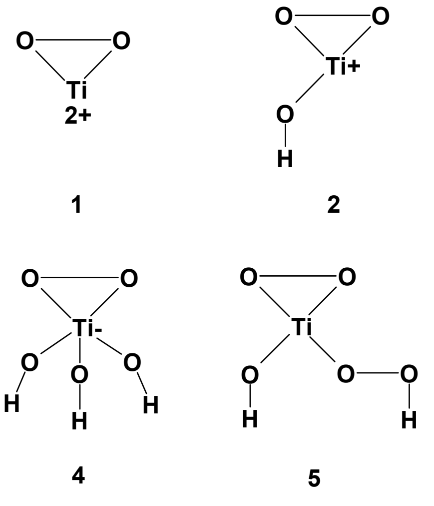


Fig. 1. Monomer units for calculation of spectra of the peroxotitanate complexes

Functionals PBE0 [18] and B3LYP [19, 20] and basis sets: polarized all-electron 6-31G** [21, 22] and pseudopotential LANL2DZ [23] are most often used in the present time, they are the most universal for determination of molecule characteristics of oxides for the elements of periods I–IV. For example, the calculations in [11, 13] and [8, 12], respectively, were carried out with the use of those parameters. At that the combined basis sets were used: the second of the abovementioned for titanium atoms, the first of them for atoms of the remaining elements. Geometry optimization of the studied complexes was carried out by Kohn-Sham method (DFT) with the use of the functional B3LYP on the basis of the basis set 6-31G** for all elements. Influence of water solvent was accounted for by the use of D-PCM model in the basic version with the following parameters: the same coefficient for all parts of the cavity, without calculation of cavitation, repulsion and dispersion energies, at standard temperature 298 K. Van der Waals radii were taken from [24].

In the second stage the energy characteristics of the complex ground state were calculated, with further calculation of excited states and electronic spectra, also accounting for the influence of water solvent. Electronic spectra of the optimized structures were obtained by TD-DFT method. Such a calculation was carried out for 10–40 excited states with the necessary number of iterations and the energy convergence criterion for each state (not exceeding 0.00003 Hartree/Bohr), so that to encompass the spectrum range with the lower bound 220...240 nm. The whole calculation of the optimized structure and energy characteristics was carried out with the program package Firefly 8.0.1 [25].

Results and Discussion

We have considered the electronic spectra of the calculated structures of peroxotitanate complexes of the series **I** $\{[Ti(O_2)(OH)_x]^{(2-x)+}\}_n$ and the neutral complex $[Ti(O_2)(OOH)(OH)]_n$ from the series **II** (in both cases n=1...3). Depending on the acidity the number of OH-groups in the monomer units of the complexes increases with increasing pH. Such an increase of x is related to deprotonation of water molecules, surrounding the complexes [2], and to coordination of hydroxyl groups on titanium atoms. Reasoning from this, the complexes of the series (**I**), where x=0, 1, 2 and 3 (Fig. 1), have been used as the monomer units for the calculation.

In order to estimate the thermodynamic probability of complex formation from various amounts of different monomer units and the possibility of their existence in aqueous solution the energy of monomer units addition to complexes has been estimated (Table 1) on the basis of calculated amounts of free energy in the solvent. It is necessary to note that bond formation between monomers is more probable for neutral monomers **3** and **5**, at that titanium atoms are bonded by oxy- and hydroxy bonds, while monomer units **5** in the complex are bridged through oxygen of hydroperoxy group.

Table 1

Energy of monomer units addition to complexes, kJ/mol

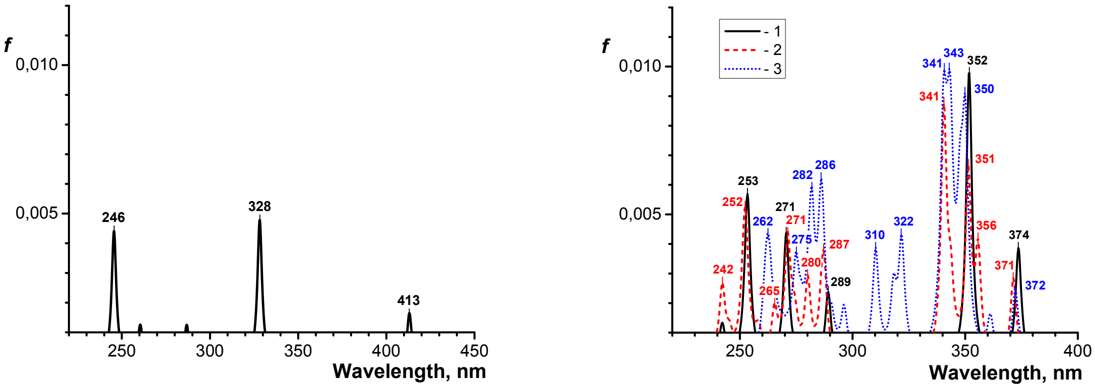
Monomer unit / Number of units in the complex	1	2	3	4	5
One	**229.27**	**14.98**	**–158.15**	**–62.65**	**–157.08**
Two	**465.98**	**–13.00**	**–144.99**	**–86.71**	**–52.99**

Existence of bonded complexes from ionic monomers **2** and **4** is less probable, the monomer units are bonded only by hydrogen bonds. Ions **1** exist in solution solely in the form of hydrated monomers, therefore the electronic spectrum is obtained only for the monomer unit. Likewise, in the context of the sloping potential energy surface for the complex consisting of three monomer units **4** in the used method we can calculate only transition states with one imaginary vibration frequency. The specified data pertain to one of such states with the minimal energy.

For all optimized complex structures the energy values for electron transitions between the ground state and the excited state have been calculated, and the corresponding electronic line spectra in the range from 220–240 nm to absorption with the minimal transition energy (λ_{max}) have been obtained. The calculated spectra of complexes with monomer units from **1** to **5** are shown in Fig. 2–4 (line spectrum is approximated by Lorentz function).

Experimental spectra of the synthesized peroxotitanate complexes (for titanium concentrations 0.05 M; 0.005 M; 0.0005 M) are shown in Fig. 5.

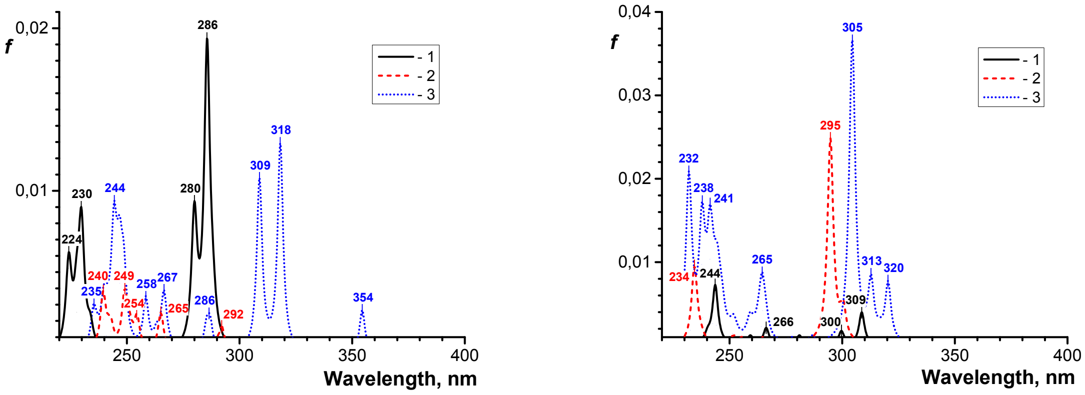
Analyzing the obtained results, first of all we should note that the range of wavelength lower than 300 nm is not informative both for indication of existence of this or that series of complexes in solution and for monitoring oligomerization process and subsequent formation of precipitation phase during hydrolysis of complexes. Our experimental data and previously accomplished studies [2, 26] have shown that in this range the intensive absorption band is observed at all conditions (besides strongly acidic media), at that the band is continuous, smooth, and lacking maxima. Clearly defined absorption maximum within this range (245 nm) appears only for the anatase phase of hydrated titania, that is, after complete hydrolysis of peroxotitanate complex. The calculation of electronic spectra also supports (Fig. 2–4)



a)

b)

Fig. 2. Calculated spectra: a) spectrum of the complex with monomer unit 1; b) spectrum of the complexes with monomer unit 2. Numbers in line designations correspond to the number of monomer units in the complex



a)

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Fig. 3. Calculated spectra: a) spectrum of the complexes with monomer unit 3; b) spectrum of the complexes with monomer unit 4. Numbers in line designations correspond to the number of monomer units in the complex

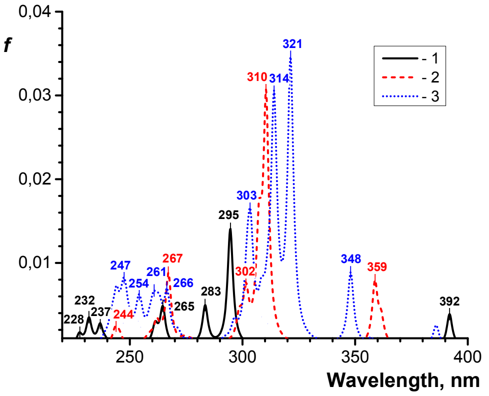


Fig. 4. Calculated spectra of the complexes with monomer unit 5. Numbers in line designations correspond to the number of monomer units in the complex

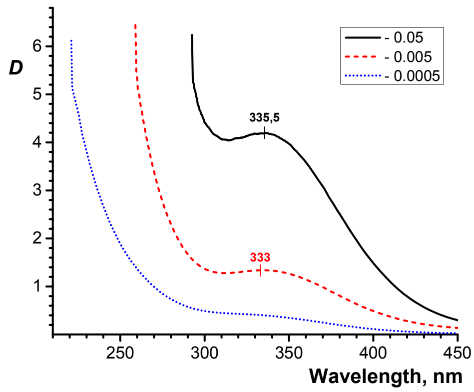


Fig. 5. Spectra of solutions of peroxotitanate complexes at pH 2.3. Titanium molar concentration of solutions is shown in line designations

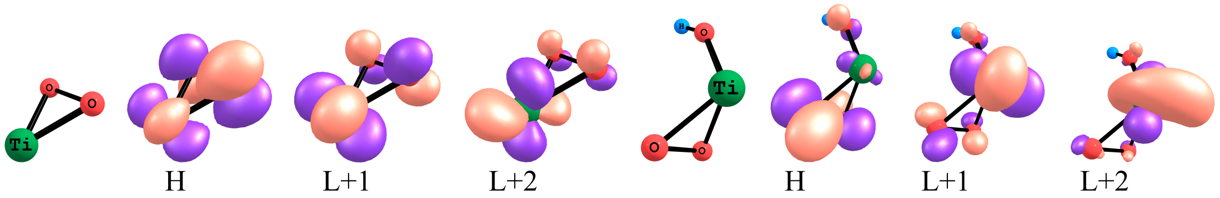
the fact that within the range 240...300 nm the absorption bands with comparable oscillator strengths are situated near enough to each other, which leads to appearance of continuous absorption band with allowance made for band broadening and equilibrium of complexes with different monomer units in the solution.

At the values pH < 1 such a band is observed in the range lower than 240 nm. Therefore for strongly acidic medium (where the complex exists mostly in the form of monomer **1**) it is possible to establish the correspondence between the calculated absorption bands and the experimentally observed ones [26] in a wider range. Thus, two-fold increase of absorbance from 330 to 300 nm corresponds to the calculated band 328 nm, and the right edge of the absorption band for wavelengths lower than 250 nm corresponds to the calculated band 246 nm.

Study of absorption in the range of wavelengths exceeding 300 nm seems important for investigation of the state in the solution of various peroxotitanate forms and their subsequent oligomerization. Experimentally it has been found that light absorption significantly decreases compared to the range of wavelengths lower than 300 nm, but at that the bands with clearly defined maxima changing their position subject to acidity are observed.

For strongly acidic media it has been shown that the complex spectra contain wide absorption bands with maxima at 397 nm [26] and 412 nm [2] and a smooth slope of absorbance up to wavelength 500 nm/ Such spectra determine reddish orange color of the solution. This absorption band corresponds to the calculated line of the monomer **1** spectrum at 413 nm. The spatial parts of the monomer **1** molecular orbitals (MO), which determine excited states of the molecule due to electron transitions between them, are presented in Fig. 6a. Besides, there also is the correspondence of these transitions to the absorption bands in the spectrum with SAP coefficients. SAP squared determine the contribution of each transition into the excited state. It has been found that both abovementioned absorption bands (413 and 328 nm, charge transfer bands) are induced by electron transitions from occupied atomic orbitals (AO) of peroxy group oxygen atoms p_x to vacant AO of titanium atoms D_{xz} and D_{xy}, which (in various combinations) mostly form vacant MO L+1 and L+2 of $(TiOO)^{2+}$ cation. Increasing intensity and widening absorption band of the solution compared to calculated data can be due to a number of causes influencing the electronic state of a complex: more complicated and multivariate type of ion hydration compared to the interactions studied within the bounds of PCM; significant cavitation energy; significant ionic strength of a solution, etc.

Gradual disappearance of the absorption band near 400 nm with increasing pH to 2 is related to transition of the complex from monomer **1** to complexes with monomer units **2** and **3**. At that the maximum smoothly shifts from 412 nm at pH=1 to values 330...340 nm ([2] and Fig. 5) at pH=2.5. The smoothness of the shift points at equilibrium in the solution of monomer forms $(TiOO)^{2+} \leftrightarrow (TiOO)(OH)^{+}$, which shifts to the right with increasing pH. In the range pH 2.5...3.0 the absorption maximum is near 335 nm, and absorbance smoothly decreases up to ~450 nm. So the solution has yellowish orange color. The calculated spectra of complexes with monomer unit **2** reasonably explain the absorption curve of the solution, when the absorption envelope lines are constructed. The most intensive bands are in the ranges 335...360 nm, as well as 370...380 nm (Fig. 2b), while in the range 400...500 nm a few weak absorption bands are present with oscillator strength not exceeding 0.0004 (not shown in the figure). Pictorial representation of MO, the transitions between which determine the solution spectrum, are shown in Fig. 6–7. As the calculations show, the most intensive absorption bands are determined by electron transitions, similar to those mentioned above, namely, the charge transfer transitions. In the case



a) **b)**

Fig. 6. Pictorial representation: a) MO for monomer unit 1. Absorption bands and the corresponding electron transitions: 413 nm: H→L+2 (–*0.98*); 328 nm: H→L+1 (*0.95*); b) MO for monomer unit 2. Absorption bands and the corresponding electron transitions: 374 nm: H→L+2 (*0.98*); 352 nm: H→L+1 (–*0.94*)

of complexes with monomer unit **2** the upper occupied MO are similar to those of $(TiOO)^+$ ion, they are formed from the combination of AO p_x, p_y, p_z of peroxy group oxygen atoms, whereas the lower vacant MO are formed from the combination of the abovementioned vacant AO of titanium atoms D_{xz} and D_{xy}, as well as the vacant AO of titanium D_x^2, D_y^2, D_z^2, and deeper AO of titanium. Calculation-proved increase of oscillator strength for absorption bands in the range near 350 nm for the complexes with monomer unit **2** compared to the band 413 nm for monomer **1** is also consistent with the experimental data [2].

Going from the cationic peroxotitanate complexes to neutral and anionic ones with monomer units **3** and **4**, which means increasing pH of the solution to neutral and weakly basic values, we observe absorption only in the range of wavelengths lower than 320 nm (Fig. 3). The calculated data have also shown that the absorption bands with lower transition energy, if any, are due to the existence in the complex structure of the fragment bonded to others with one bridging bond through the hydroperoxy group oxygen (example in Fig. 8). Therefore one of the appearance causes for such absorption bands in UV-visible spectrum of peroxotitanate complexes at specific conditions (ratio "hydrogen peroxide – titanium" is small and pH > 6) can be the formation of hydroperoxy bonds between titanium atoms in a complex. Formation of one or two hydroxy bonds between monomer units of a complex does not lead to changing spectrum in the range of wavelengths greater than 300 nm. Change of the solution color to maize yellow at changing pH to the abovementioned value, noted by us (and also in [26]), does not contradict the calculated data, though it demands more thorough investigation.

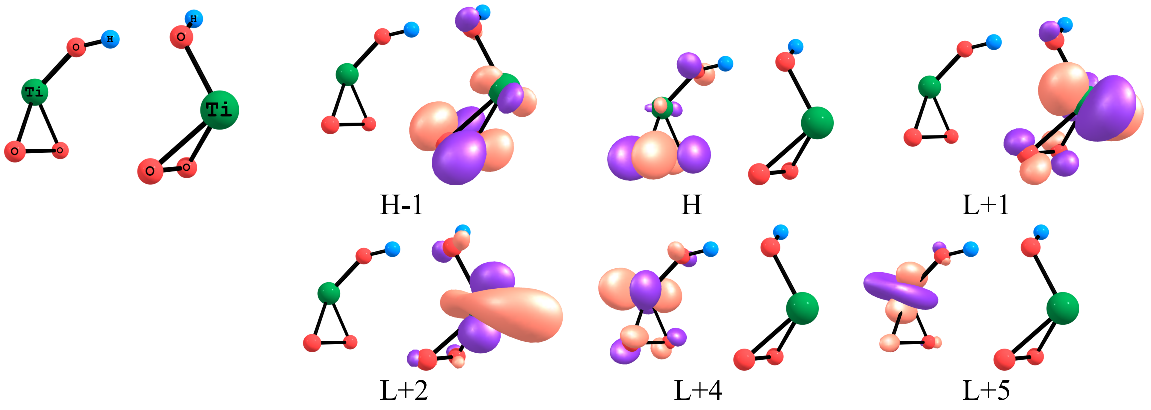


Fig. 7. Pictorial representation of MO for the complexes with two monomer units 2. Absorption bands and the corresponding electron transitions: 371 nm: H→L+5 (*–0.90*), H→L+2 (*0.36*); 356 nm: H–1→L+2 (*0.87*), H→L+2 (*–0.35*); 351 nm: H→L+4 (*0.92*); 341 nm: H–1→L+1 (*0.80*), H→L+2 (*–0.34*)

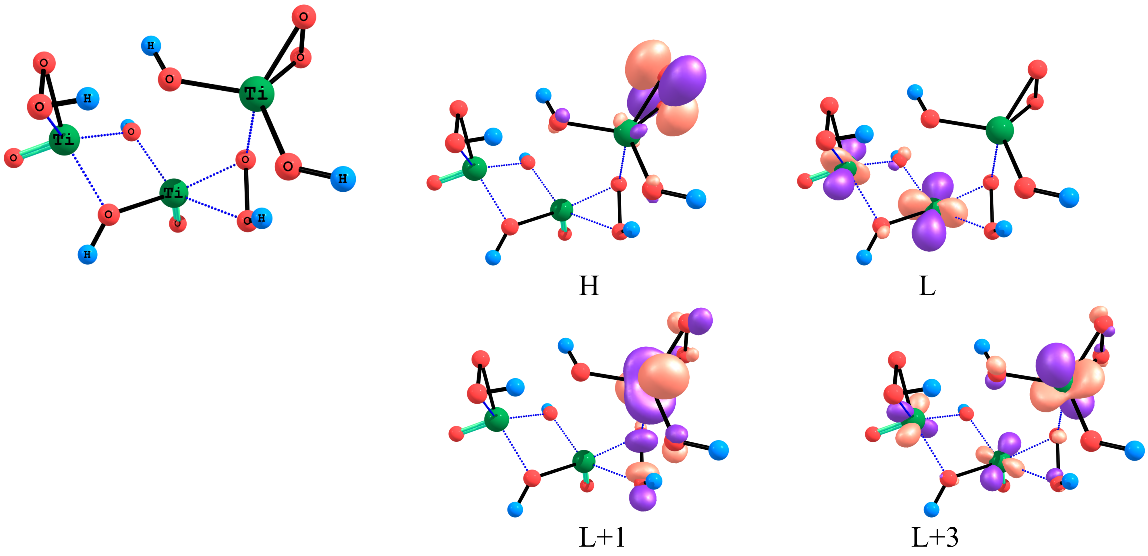


Fig. 8. Pictorial representation of MO for the complex with three monomer units 3. Absorption bands and the corresponding electron transitions:

Use of great excess of hydrogen peroxide during the synthesis of peroxotitanate complexes can lead to coordination of several peroxy groups on one titanium atom (excepting strongly acidic medium), therefore the spectra of neutral complexes of the series (**II**) have been calculated for purposes of comparison. For these spectra it has been shown (Fig. 4) that the range of wavelengths lower than 320 nm is also of low information value because of the great number of intensive closely-spaced absorption bands. As opposed to neutral complexes of the series (**I**), the spectra include intensive bands at 392, 359, 348 nm for one, two, and three monomer units in the complex, respectively. Probably, the yellow color of the peroxotitanate complexes synthesized in [26] up to basic pH values is due to occurrence of the series (**II**) complexes. Analysis of electron transitions (Fig. 9–10) has shown that the presence of these bands is mostly determined by the transitions from the upper occupied MO (combination of AO of the peroxy group oxygen atoms) to the lower vacant MO with its peculiarities. It has been shown that for the series (**II**) such a MO is formed from the combination of not only vacant D-type AO of titanium atoms, but also of p-type AO of the bridging peroxy group oxygen atoms that are specific for the series (**II**). This suggests that the cause of appearance of the abovementioned bands for complexes of the series (**II**) is similar to the cause of coloring for the neutral complexes of the series (**I**). That is, the absorption band near 360 nm can serve as an indicator of existence of bridging hydroperoxy groups in the complex at neutral pH of the solution.

The factor that determines titania precipitation from peroxotitanate complexes is the stability of the hydrogen peroxide excess existing in the solution. Therefore the greatest rate of precipitation should be observed in weakly acidic medium, where peroxide is less stable compared to strongly acidic medium.

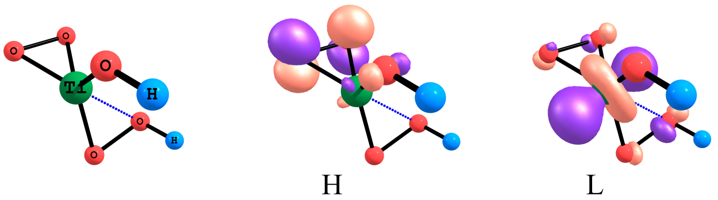


Fig. 9. Pictorial representation of MO for monomer unit 5. Absorption bands and the corresponding electron transitions: 392 nm: H→L (*0.96*)

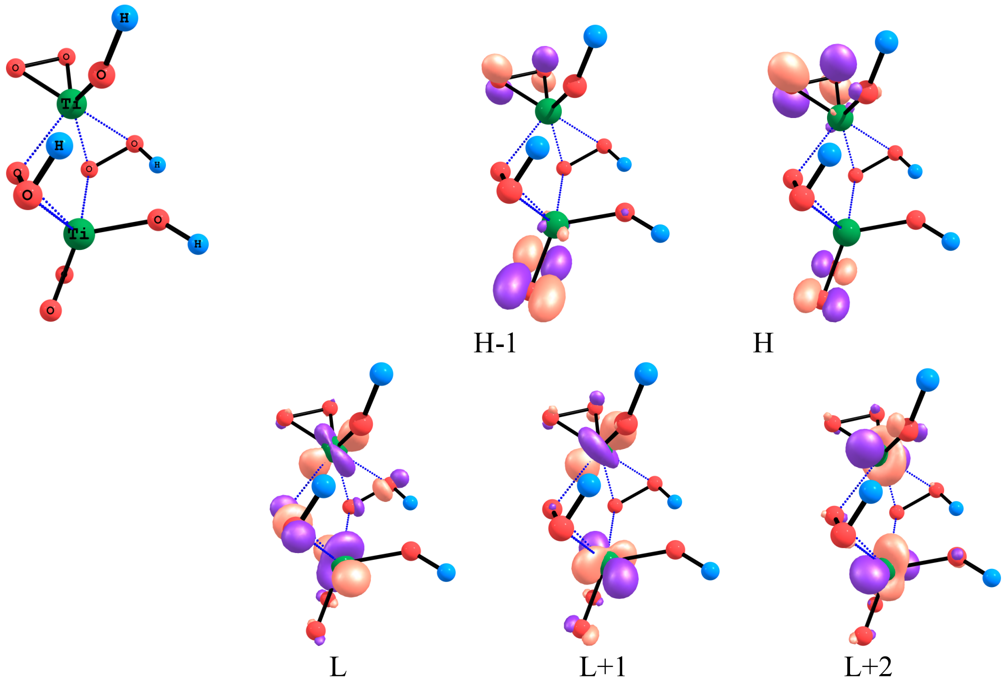


Fig. 10. Pictorial representation of MO for the complex with two monomer units 5. Absorption bands and the corresponding electron transitions: 359 nm: H-1→L (*0.81*); 310 nm: H→L+1 (*0.74*), H–1→L+2 (*–0.43*)

In these conditions the state of peroxotitanate complexes is nearer to the isoelectric point, that is, the probability of occurrence for the complexes formed from monomer units **3** and **5** (at great excess of hydrogen peroxide) is significantly higher. Such complexes are the most capable of oligomerization and, possibly, of hydrolysis that leads to further formation of hydrated titania precipitate. On the other hand, for neutral monomer units the value of the energy of complex formation from three units decreases compared to the complexes of two units (Table 1), which enables the former to occur in solution with less probability than the latter. For the series (**II**) the decrease is much steeper; relative stability of such a complex of two monomer units can determine the stability in time of peroxotitanate complex solutions in wide range of pH values, verified experimentally for the initial ratio "hydrogen peroxide – titanium" more than 10:1 [26].

Understanding how the bonds between monomer units in peroxotitanate complexes are formed and tracking of this process by means of UV-visible spectra analysis makes it possible to estimate probable directions of further oligomerization and hydrolysis reactions, as well as the probability of formation for this or that crystal or amorphous phase, in which the precipitate is formed (anatase, rutile, etc.). Attempts of the estimation with the use only of calculated data were made previously in [17], where polyperoxide complexes were studied. Oligomeric chains in such complexes are formed in two ways: a) two oxygen bridges between titanium atoms, which leads to subsequent formation of the structure of anatase type (octahedrons with common edges) – in the case of minimal and maximal concentration of added hydrogen peroxide; b) one oxygen bridge between titanium atoms, which helps subsequent formation of the structure of rutile type (octahedrons with common tips) – in the case of medium concentration of added hydrogen peroxide. Our research in the spectral characteristics of the solutions of peroxotitanate complexes at various synthesis conditions coupled with calculated data has shown that the use of UV-visible spectra can provide information about occurrence of monomer units of this of that kind in the complexes, as well as about the bonding pattern. We consider the possibility of further application of this information to prognosticate priority ways of the new phase formation in specified environment.

Conclusion

In the present paper the electronic spectra of peroxotitanate complexes formed from five types of monomer units have been investigated. Non-empirical calculations of the optimized complex structures have been carried out by Kohn-Sham method with the use of functional B3LYP and all-electron basis set 6-31G**, with allowance made for influence of water as a solvent in PCM. The calculation of the excited states has been carried out by TD-DFT method. It has been found that the spectra of complexes in the series (**I**) ($[Ti(O_2)(OH)_x]^{(2-x)+}$) have characteristic absorption bands, they are specific for wavelength range higher than 300 nm, namely: 413 nm for $x = 0$ and several bands in the ranges 335...360 nm and 370...380 nm for $x = 1$. It has been shown that the position of the absorption bands in the spectrum of the solution of peroxotitanate complexes at $pH < 1$ corresponds to the calculated spectrum of monomer unit **1**, while the spectrum of the solution at pH 2.0...2.5 corresponds to the calculated spectrum of the complexes with monomer unit **2**. At that the difference between the absorption band maxima and the intensive calculated lines does not exceed 10 nm. In the spectra of neutral complexes of the series (**I**) and (**II**) $[Ti(O_2)(OOH)(OH)]$ the absorption bands in the range 345...400 nm, that determine yellow color of the complexes in neutral medium, can appear subject to bonding between titanium atoms through the hydroperoxy group oxygen. The complex composition is related to the solution pH values and the excess of hydrogen peroxide relative to titanium, at that the tendency of solution spectrum change under varied conditions of complex existence correlates to the change of calculated spectra in accordance with the monomer unit predominating in the composition. Thus, comparison of the calculated electronic spectrum and the UV-visible spectrum of the peroxotitanate complex solution makes it possible to estimate the composition at specific conditions and prognosticate the possible reaction pathways.

Acknowledgments

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УФ-ВИД СПЕКТРЫ ПЕРОКСОТИТАНАТНЫХ КОМПЛЕКСОВ

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Выполнен сравнительный анализ расчётных (с учётом влияния растворителя в модели PCM) и экспериментальных УФ-вид спектров растворов пероксотитанатных комплексов при варьировании условий их существования. Показано, что изменение состава комплексов, зависящего от величины pH раствора, приводит к изменению характерных полос поглощения УФ-вид спектров в области длин волн более 320 нм. Тенденция сдвига полос поглощения в спектрах растворов соответствует изменению расчётных спектров в зависимости от мономерной единицы комплекса. Предположено, что окраска раствора комплексов в слабокислой и нейтральной среде связана с возникновением гидропероксосвязей между атомами титана.

Ключевые слова: пероксотитанатные комплексы, электронные спектры поглощения, PCM, TD-DFT.

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