Initial steps of photosynthetic water splitting by associates of porphyrin

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Abstract

Photochemical and spectral properties of dimeric forms of *meso*-tetraphenylporphine (TPP), associated *meso*-tetra(*p*-aminophenyl) porphine (TAPP) and *meso*-tetra(*N,N,N*-trihexadecyl-4-aminophenyl)porphine (TTAP), which produce donor–acceptor complexes, are investigated by absorption, luminescence, and Raman spectroscopy. Three different protonated dimers of TPP observed in the ground state, according to fluorescence spectra, reveal only two different porphyrin dimers in the excited state and have maxima of emission bands at 693 and 730 nm. Low-temperature measurements of TPP dimers solutions at 77 K after illumination show EPR signal with g-factor of free electron and $\Delta H_{pp} = 0.7$ mT. The differential absorption spectrum of the solution is somewhat similar to spectrum of π-cation radical of TPP. Visible light illumination of associated TTAP in water containing small amount of dimethylformamide (DMF) produces irreversible changes at room temperature. The corresponding differential spectrum of the photoinduced changes exhibits mainly 692 nm band overlapping with broad band in the 460–800 nm region with the maximum at about 620 nm. According to fluorescence spectra of the TPP dimers, interaction between low- and high-energy dimeric forms of porphyrin (with the maxima of Soret bands at 465 and 403 nm, respectively), takes place in the excited state. Similar behavior can be possible for aminoporphyrins but interpretation of their spectra in this respect meets difficulties because of donor–acceptor interactions in the association complexes. Most probably the interactions bring about electron transfer photoreaction between TPP dimers and in the case of TTAP dimeric (or associated) similar forms too. It is proposed that the electron transfer photoreaction involves water and utilizes it as an electron donor in the case of TPP dimers and a sacrificial electron donor in the case of associated TTAP. Unordinary vibrational bands observed in the resonance Raman spectra of TAPP and TTAP support this unusual behavior of the aminoporphyrins. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Dimers; Associates; Porphyrins; Donor–acceptor complexes; Water splitting; Blue light excitation.

1. Introduction

Mimicking of the processes of photosynthetic water splitting is nowadays an area of intention of many researchers interested in the problem of solar energy conversion. Numerous works in this area are devoted to the study of photochemical processes in model systems mimicking the properties of photosystem II with the use of assembling manganese ions [1–6]. It is usually proposed that such artificial systems have to mimic the main steps of photosynthetic water splitting right up to oxygen evolving that takes place in the oxygen evolving complex in biological photosystem. Although actually, the main principles of the structural assembly of the artificial complex are still unknown but some advances in this direction allow to hope that the problem will be solved. At the same time, there are the data elucidating the problem from the other side, the main are the

following. Our previous results demonstrate formation of radical ions of *meso*-tetra(*p*-aminophenyl)porphine (TAPP) after visible light illumination although the properties of the photoinduced product are rather unusual [7]. It is known that π-cation radical of porphyrin has the width (peak-to peak) of EPR signal equaled 0.7 mT [8], but the corresponding EPR spectra of TAPP had abnormally broadened signals. In particular, for the photoinduced radical cation the width of the EPR signal was about 1 mT although this porphyrin had associated state, i.e. a higher extent of the association than the dimer. Usually, unpaired electron in porphyrin dimer has $\sqrt{2}$ decreased width of the corresponding EPR signal as compared to that of the monomer. Hence, we assumed that abnormally broadening of the EPR signals can be due to the interaction between aminoporphyrin radical ion and solvent molecules, for instance, water molecules. Furthermore, the results of the study of interaction between water and aminoporphyrin pigments in donor–acceptor systems suggest a photoactivation of water molecules involved in the structure of these complexes [9]. In connection of this, the following

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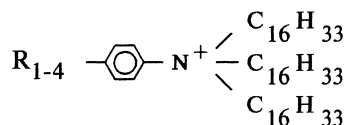*E-mail address:* avu@audaltsov.home.bio.msu.ru (A.V. Udal'tsov)

Compounds
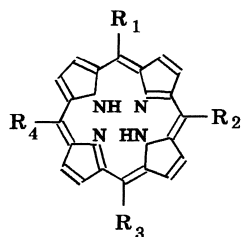
meso-tetraphenylporphine : R_{1-4}

meso-tetra(p-aminophenyl)porphine : R_{1-4} — NH$_2$

meso-tetra(N,N,N-trihexadecyl-4-aminophenyl)porphine :

R_{1-4} — N$^+$ — C$_{16}$H$_{33}$ / C$_{16}$H$_{33}$ \ C$_{16}$H$_{33}$

Scheme 1.

assumption arose. The initiating of the water splitting processes, i.e. the seizing of the first electron from two water molecules, from which oxygen molecule is released at the final step, can be occurred in manganese free donor–acceptor complexes formed by aminoporphyrin. At the same time, if this photoreaction will be irreversible in that case the initial step can produce a driven force for the whole process of water splitting. This assumption prompted us to carry out the experiments to test the possibility of the initial process in associated aminoporphyrin and between porphyrin dimers too.

In the present work photochemical properties and spectral characteristics of protonated dimeric forms of meso-tetraphenylporphine (TPP) and associated TAPP and meso-tetra(N,N,N-trihexadecyl-4-aminophenyl)porphine (TTAP), which produce donor–acceptor complexes, are investigated by absorption, luminescence, and Raman spectroscopy.

2. Experimental

Synthesis of the compounds presented in Scheme 1 was carried out according to the procedures described elsewhere [10–11]. Dimethylformamide (DMF) and other organic solvents were additionally purified by conventional methods [12]. The purified DMF contained about $0.3 \, \text{mol} \, l^{-1}$ water while quantity of water in purified triethylamine (TEA) was less than $0.09 \, \text{mol} \, l^{-1}$ estimated on IR spectra. For the preparation of aqueous-organic solutions distilled water was used.

UV–VIS spectra of porphyrin solutions were recorded with a Specord M-40 spectrophotometer or Hitachi 557 in low-temperature measurements. Photochemical reactions were studied under illumination of porphyrin in water–DMF solutions with a 150 W halogen lamp at room temperature and use of a suitable filter to cut off ultra-violet region or with a direct sun light. Photoinduced changes at 77 K in glassed porphyrin solution containing 50% of glycerol were studied under steady-state illumination of the solution with a 300 W halogen lamp. Fluorescence spectra were obtained with the setup described elsewhere [13]. The measurements were carried out under the same conditions as earlier [14]

except for the excitation. The excitation in the region of Soret band was provided by monochromatic light with a half-width of 12 nm separated from xenon lamp with the use of monochromator. Fluorescence spectra were completely calibrated using the known spectral sensitivity of the equipment. EPR spectra were recorded with a spectrometer RE 1307 (USSR) of 3 cm range in standard quartz ampoule. A 400 W xenon lamp was used for steady-state illumination of the frozen porphyrin solution. Raman spectra of porphyrin solutions were obtained using the setup described in [15]. Excitation was provided by a He-Cd laser into the Soret band ($\lambda_{ex} = 441.6 \, \text{nm}$) or an argon laser ($\lambda_{ex} = 514.5 \, \text{nm}$). A spectral slit width of $4 \, \text{cm}^{-1}$ was used for registration. Raman spectra were recorded in the case of two ranges of porphyrin concentrations, high and medium. In the case of the high concentration, it was higher than $1.4–2.5 \times 10^{-4} \, \text{mol} \, l^{-1}$ and in the case of the medium, the concentration was within $2.5–7.0 \times 10^{-5} \, \text{mol} \, l^{-1}$. All measurements were carried out at 298 K except for light-induced absorption and EPR measurements of TPP dimers at 77 K.

3. Results

3.1. Photochemical properties of associated aminoporphyrin in water containing small amount of organic component

Previous results suggest that abnormally broadening of EPR signals of aminoporphyrin can be due to the interaction between porphyrin radical ions and possibly water molecules. This assumption prompted us to fulfill similar photochemical experiment but in aqueous environment with small amount of organic component. Absorption spectra of TTAP presented in Fig. 1 display irreversible bleaching of Soret band and the band with the maximum at 718 nm under steady-state illumination with the visible light. The bleaching is accompanied by the irreversible growth of the absorption in the 500–670 nm region. Besides, the bleaching of the Soret band leads to appreciable (by 4 nm) hypsochromic shift of its maximum. Similar appreciable shift of the maximum is also noted for the broad 718 nm band. The inset
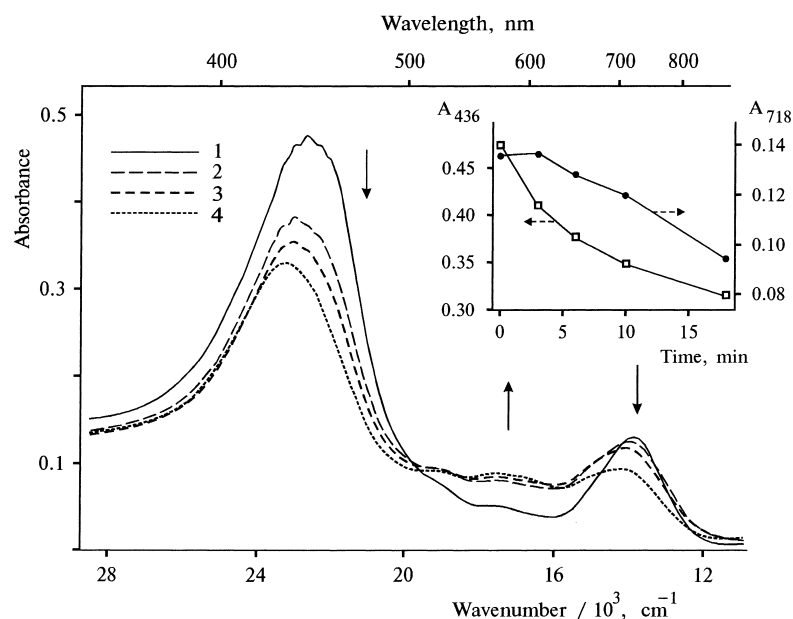
Fig. 1. Absorption spectra of TTAP in water : DMF (95 : 5, v/v) under steady-state visible light illumination ($\lambda > 400$ nm): 0 (1), 6 (2), 10 (3), and 17 min (4). The inset shows kinetics of absorption in the maxima of the bands at 436 and 718 nm. The solid arrows indicate the absorption changes under illumination.
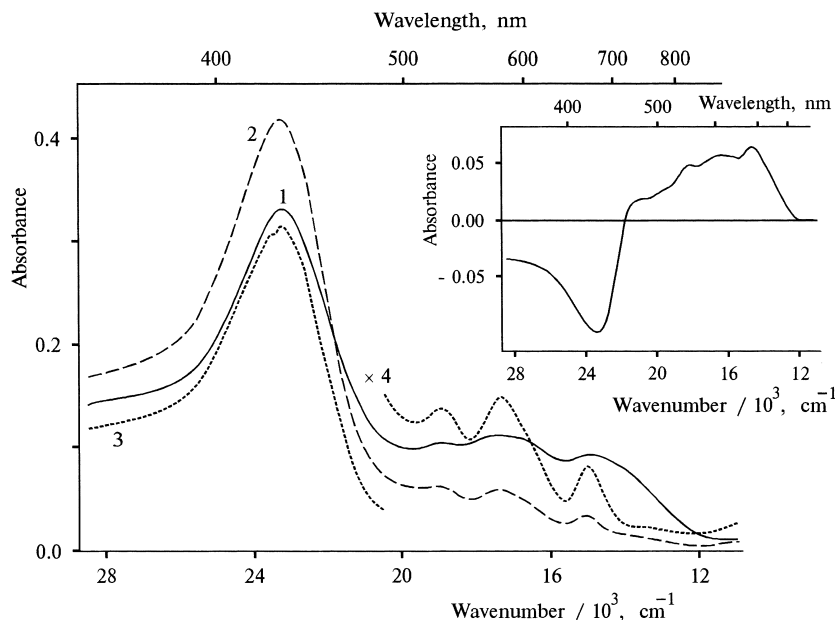

Fig. 2. Absorption spectra of TTAP in water : DMF (97 : 3, v/v): after illumination with the visible light ($\lambda > 400$ nm) (1), the same solution but in the presence of 0.02 mol l^{-1} TEA (2), and not illuminated solution in the presence of 0.02 mol l^{-1} TEA (3). The inset shows differential spectrum, see details in the text.

shows kinetics of the bleaching for the both absorption bands under this steady-state illumination. Although, the photoreaction occurs irreversibly but the products are proved to be able to reversible reduction. Addition of minor amount of TEA to the porphyrin solution after the illumination leads to apparently complete recovering of the Soret band while the broad absorption in the 460–800 nm region disappears (Fig. 2, compare curves 1 and 2). The inset shows differential

spectrum, the spectrum of TTAP solution after illumination minus the same solution but in the presence of 0.02 mol l^{-1} TEA. This spectrum exhibits the red band with the maximum at 692 nm overlapping with very broad absorption in the 460–800 nm region with the maximum at 620 nm and two shoulders at 486 and 558 nm. These shoulders are proved to be close to maximum and a shoulder in the differential spectrum of associated TAPP dication [7]. But the shoulders in
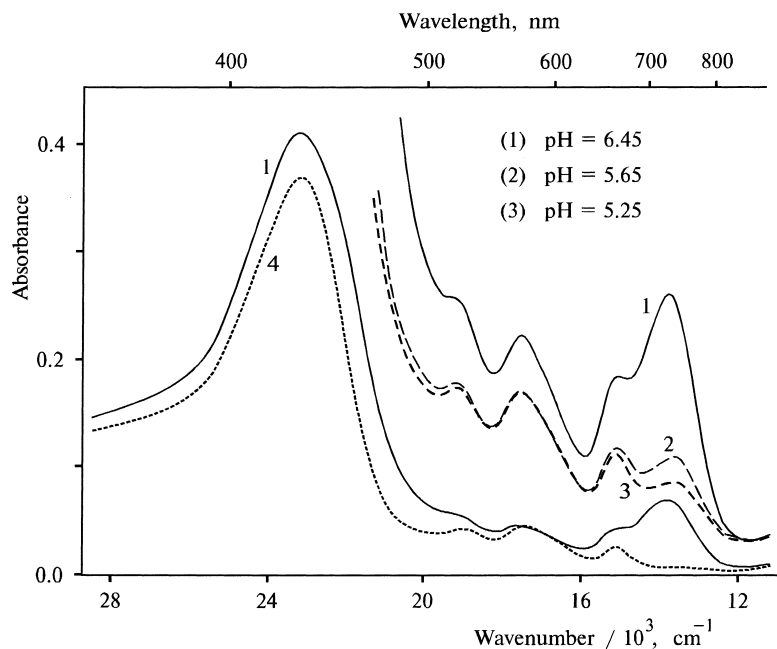
Fig. 3. Absorption spectra of TTAP in water : DMF (97 : 3, v/v) under 2–3 min sunlight exposure: before illumination (1), after the first exposure (2), after the second exposure (3), and not illuminated solution in the presence of $0.02 \, mol \, l^{-1}$ TEA (4).

the spectrum (Fig. 2, the inset) are shifted by 12 nm to the blue and by 8 nm to the red (the former and the latter, respectively) as compared with the maximum and the shoulder in the spectrum of the porphyrin dication. It is interesting that the addition of TEA with the same concentration to the same porphyrin solution but not illuminated gives the other spectrum (Fig. 2, curve 3). The latter differs from that in the case of the illuminated porphyrin solution (curve 2).

Hence, irreversible photoreaction occurs under steady-state illumination of TTAP associated in solution and some positively charged forms of porphyrin are accumulated in the solution during the illumination, according to differential spectrum. The products of the photoreaction are reduced by a suitable electron donor such as TEA.

It is interesting that TTAP associated in these solutions is proved to be very sensitive to usual sun light, the action of which results in similar effect. However, in the case of illumination in the electrochemical cell with a chlorine-argentum electrode, the decrease of the band with the maximum at 732 nm is observed that is accompanied by the decrease of pH of the solution (Fig. 3, curves 1–3). Note that in this case there is no increase of absorption somewhat similar to broad absorption in the 500–670 nm region observed in Fig. 1. The addition of TEA to the initial not illuminated solution of porphyrin leads to similar effect as in the case of 5% (v/v) concentration of DMF, namely, all bands in the spectrum (curve 4) are proved to be essentially less in magnitude as compared with the initial spectrum (curve 1).

Hence, in the case of a suitable electrode, when there is the possibility of leaving of electron from the porphyrin associate, no increase of absorption is observed in the spectrum under steady-state illumination. At the same time the

irreversible photoreaction is accompanied by decrease of pH that means release of protons in the solution. This behavior of the photoreaction suggests deprotonation of porphyrin and apparently participation of water in these processes as an electron donor in the case if water is involved in protonation of the porphyrin.

3.2. Assignment of the products of photochemical reaction in associated aminoporphyrin

All these above spectra show a broad Soret band that suggests associated state of porphyrin in solutions. The presence of amino groups on the phenyl rings of porphyrin molecules brings about donor–acceptor interaction between these molecules [14]. Therefore, similar dimeric (or associated) forms of porphyrin but without amino groups can help identification the products of the above photoreaction. Fig. 4 shows absorption spectra of protonated forms of TPP, where the spectrum (curve 1) has been assigned to doubly protonated TPP dimer and the other two forms with the maxima of Soret bands at 403 and 465 nm in the spectrum (curve 2) were assigned to singly protonated dimers with different configurations [16]. It is proposed that the dimer with the maximum at 465 nm has *trans* NH-configuration on protonated porphyrin molecule as a stable tautomeric form of the dimer where porphyrin molecules are maintained via hydrogen bonds of two water molecules involved in the dimeric complex [17]. While the dimer with the maximum at 403 nm appears to be less stable and, therefore, has *cis* NH-configuration on protonated porphyrin molecule. In the presence of poly-(methacrylic acid) the spectrum of the three
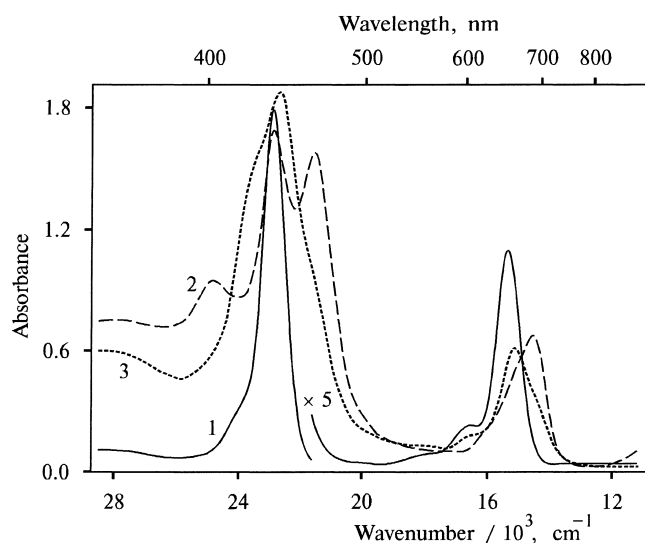
Fig. 4. Absorption spectra of TPP in 50% aqueous solution of acetone (v/v) (1); and in water : acetone : dioxane (90 : 5 : 5, v/v) in the presence of 0.4 N HCl (2) and in the presence of 0.01 M poly-(methacrylic acid) (3).

dimeric forms is strongly changed (curve 3) that suggests the carboxylic groups serves as a centers for additional complexing most probably between different porphyrin dimers and interaction between them.

Hence, interaction between different dimeric forms of TPP results in transformation of the three well-resolved bands into one broad Soret band. Meanwhile, it is quite possible that donor–acceptor interactions in the case of the presence of amino groups on phenyl rings of porphyrin enhance the complexing between porphyrin molecules, as a result of which appreciable tracks of a structure of Soret band are removed completely (see below). In this case structure in Soret band region can be apparently found in differential spectra.

Spectra of water-organic solutions containing protonated dimeric forms of TPP demonstrate the presence of mainly three different dimers but concentration of each component can be different in the different solutions. This allows to calculate the spectrum of singly protonated TPP dimers by subtraction of the different spectra when concentration of singly protonated dimers in the one solution prevails that in the other but the concentrations of doubly protonated dimer are close. The resultant differential spectrum (the spectrum of TPP dimers in water-glycerol-tetrahydrofuran minus the spectrum in water-ethanol solution presented in [18]) is displayed in Fig. 5 , curve 1. This spectrum exhibits two Soret bands with the maxima at 403 and 465 nm, a shoulder at 635 nm and the band with the maximum at 694 nm. On the other hand, subtraction of the spectrum (Fig. 3, curve 4) from the spectrum (Fig. 3, curve 1) gives the spectrum presented in Fig. 5, curve 2, in which three bands with the maxima at 416, 457, and 732 nm are clearly pronounced. This spectrum suggests similar interaction between different forms of the aminoporphyrin (apparently dimeric forms) as in the case of interaction between dimers of TPP in the presence

of poly-(methacrylic acid) (Fig. 4, curve 3). In the region of Soret band this spectrum are proved to be very similar to differential spectrum obtained for the photoactive dimeric forms of TAPP bound with copolymer [19]. The latter differential spectrum, where macromolecular carboxyl groups can influence on the properties of the porphyrin in the region of quasi-allowed electron transitions, is shown in this figure too (Fig. 5, curve 3).

We will call dimeric forms with the maxima of Soret band at 403 ($24\,810\,cm^{-1}$) and 465 nm ($21\,500\,cm^{-1}$) (Fig. 5, curve 1) as a high- and low-energy dimers of singly protonated porphyrin, respectively. The same terms will be applied to similar forms in the spectra with $\lambda_{max} = 416$ and 457 nm in the Soret band region (curve 2) and with $\lambda_{max} = 411$ and 446 nm (curve 3), nevertheless these bands are some shifted as compared with the dimeric forms of TPP. The similarity of the spectra (curves 2 and 3) means that the high- and low-energy dimers of TTAP (with $\lambda_{max} = 416$ and 457 nm in Soret band region) can be also photoactive and involved in the photoreaction registered by absorption spectroscopy (Fig. 1 and Fig. 3). Meanwhile in the case of the high- and low-energy dimers of TAPP bound with copolymer, no accumulation of reduced viologen is observed if burn-off of the porphyrin dimers, i.e. the photoactive dimeric forms, occurs under preliminary steady-state illumination in the absence of electron donor and acceptor [19]. Hence, only photoactive dimeric forms of porphyrin provide the possibility of electron transfer reaction in these systems. This and other results [7,20] suggest that unusual photochemistry takes place when singly protonated porphyrin dimers can serve as an excitation energy trap and generate electron transfer reaction in the both TPP and the aminoporphyrin systems. Regarding the associated TTAP, the band with the maximum at 692 nm in the spectrum (Fig. 2, the inset) corresponds to the band with the maximum at 694 nm in the spectrum (Fig. 5, curve 1), while assignment of the broad band in the 460–800 nm region with the maximum at 620 nm meets difficulties. However, if the positive changes in the spectrum (Fig. 2, the inset) correspond to associated porphyrin dication [7] but with different location of positive charges or more high extent of association of porphyrin molecules, in this case the band with the maximum at 620 nm should be assigned to monocation of high-energy dimer of porphyrin, i.e. the other photoactive dimeric form.

Hence only one band in the spectrum of the products of the irreversible photoreaction in associated TTAP appears to be identify on this stage of the study. According to the spectra, low-energy singly protonated dimeric form of porphyrin with the maximum at 692 nm is the one from the accumulated forms in the solution during the illumination. As we propose this low-energy form of singly protonated porphyrin dimer has *trans* NH-configuration in the protonated porphyrin. This form is transformed under illumination from corresponding dimer (or associate) with the maximum at 720–730 nm, i.e. possibly strongly solvated and/or hydrated species.
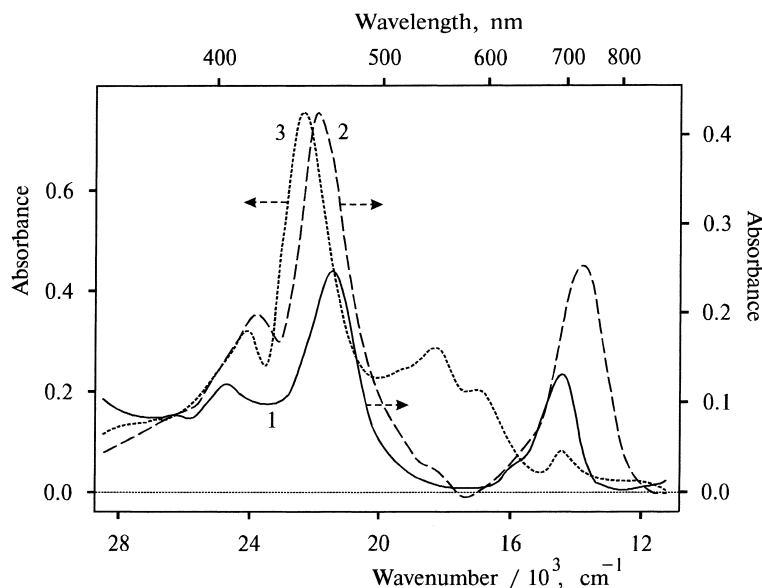
Fig. 5. Differential spectra, the spectrum calculated for dimeric forms of TPP (see details in the text) (1); the spectrum of TTAP in water : DMF (97 : 3, v/v) minus the same solution but in the presence of $0.02 \, \text{mol} \, l^{-1}$ TEA, (2); and the spectrum of TAPP bound with copolymer in DMF-water (90 : 10, v/v) before illumination minus the same solution after 22 min illumination with visible light, (3) [19].

3.3. Photochemical properties of protonated dimeric forms of TPP in comparison with associated aminoporphyrin

The above results prompt us to pay special attention to protonated dimeric forms of TPP which are similar on the spectral properties to the photoactive forms of the aminoporphyrin. Fig. 6 shows absorption spectra of singly and doubly protonated dimeric forms of TPP and associated aminoporphyrins. As mentioned above, Soret bands in the spectra (Fig. 6, panel A) has been assigned to doubly protonated ($\lambda_{\text{max}} = 437$ nm) and two singly protonated TPP dimers of different configurations ($\lambda_{\text{max}} = 403$ and 465 nm) which have different orientation of neighboring molecules in dimer [16]. In the case (Fig. 6, panel A) the bands of doubly protonated dimer and low-energy form of singly protonated dimer ($\lambda_{\text{max}} = 465$ nm) are red shifted by 2–4 nm as compared with the spectrum (Fig. 4, curve 2). So, the maxima in the Soret band region are noted at 403, 439, and 467 nm and in the red region two shoulders at 638 and 656 nm, respectively, and maximum at 698 nm. The most great absorption band in these water-organic solutions is revealed for the low-energy form of singly protonated TPP dimer with the maxima at 467 and 698 nm (Fig. 6, panel A).

According to the absorption spectra of TAPP and TTAP in DMF (Fig. 6, panel B), these porphyrins are present in associated state. As mentioned above, different associated forms of porphyrin interacting in the donor–acceptor complex produce one broad Soret band without any appreciable structure. Although the donor–acceptor interactions bring about specific spectrum in the region of quasi-allowed electron transitions that occurs due to nucleophiles, i.e. the amino groups [14]. In the spectrum of TTAP the Soret band is much more broadened as compared with that of TAPP while

the bands in the quasi-allowed electron transitions are some red shifted that denotes the higher extent of association of TTAP molecules (curve 2). Absorption spectra of TTAP associated in DMF and in water containing small amount of DMF considerably differ each from other (compare Fig. 6, panel B, curve 2 and Fig. 1, curve 1). The broad red band of the latter looks like as a strongly solvated or hydrated associates of porphyrin as compared to the former. It was found earlier that values of pK'_{eq}, i.e. reverse logarithm of equilibrium constant of protonation/deprotonation reaction for aminoporphyrins in the excited state, are located in the alkaline region of pH [21]. Therefore, TTAP associated in water containing small amount of DMF can be protonated under usual day light, for instance, on the step of preparation of the solutions. Hence, according to the spectra (Fig. 1, curve 1 and Fig. 5, curve 2) strongly solvated/protonated state of the porphyrin can be kept partly in the ground state too apparently due to stabilization by hydroxyl counter-ion or by macromolecular carboxyl groups in the case of TAPP bound with copolymer (Fig. 5, curve 3). It should be noted that porphyrins in these solutions possess a quantum yield of fluorescence comparable with monomeric TPP [22].

Well-resolved Soret bands of dimeric forms of TPP allow to study features of emission spectra under selective excitation. Fluorescence spectra of protonated dimeric forms of TPP presented in Fig. 7 are changed with the change of wavelength of excitation. Under selective excitation ($\lambda_{\text{ex}} = 403$ and 437 nm), maximum of the main emission is observed in the spectra (curves 1 and 2) at 693 nm and a shoulder in the 700–760 nm region is noted too. However, under excitation at 465 nm the maximum is observed at 730 nm and at the same time a shoulder at 693 nm (curve 3). Hence, it means that three different protonated forms regis-
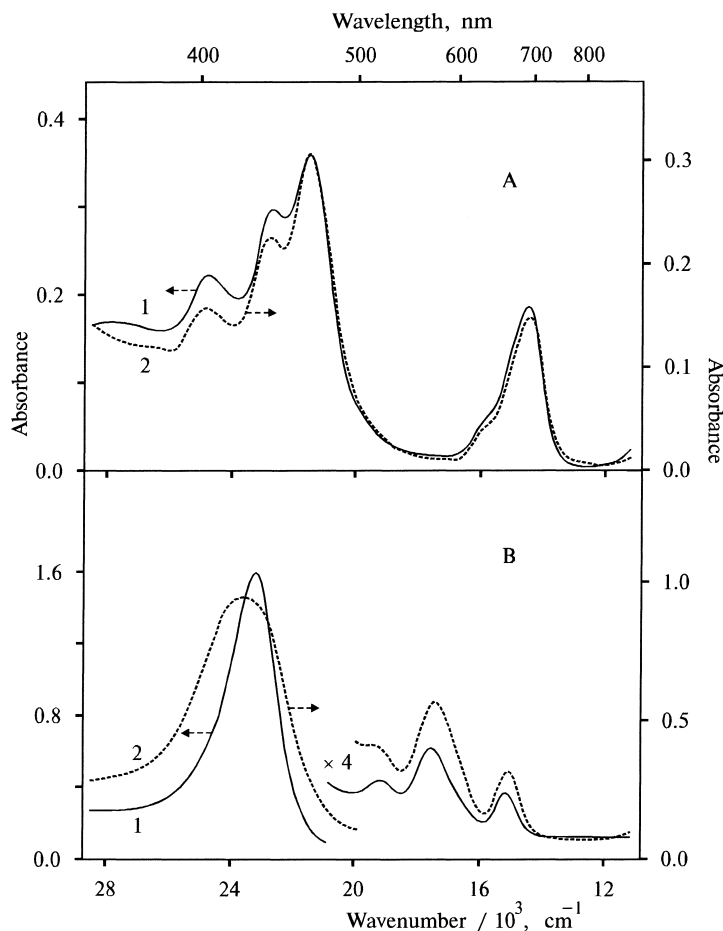
Fig. 6. Absorption spectra of TPP (panel A): in water-tetrahydrofuran (86 : 4, v/v) in the presence of 0.4 N hydrochloric acid, (1); and in water-glycerol-tetrahydrofuran (86.5 : 10 : 3.5, v/v) in the presence of 0.4 N hydrochloric acid, (2); and (panel B): TAPP, (1); and TTAP, (2) in DMF.

tered in the ground state are revealed as two different forms under transition in the excited state. The appearance of the shoulder with the maximum at about 730 nm in the case of $\lambda_{ex} = 403$ or 437 nm suggests that the fluorescence with the maximum at 693 nm can be absorbed by the low-energy dimeric form of porphyrin, the absorption maximum of which is located at 698 nm.

This effect can be seen clear in the case of analogous water-organic solution but in the absence of glycerol when different fluorescent states are observed more pronounced (Fig. 8, panel A). Under excitation at 403 and 437 nm, two maxima or maximum and a shoulder of the main emission are noted at 693 and 730 nm (curves 1 and 2), while under excitation at 465 nm only one maximum at 732 nm and two shoulders at 693 and about 800 nm are observed in the spectrum (curve 3). Note that in the both cases (Fig. 7 and Fig. 8, panel A), the 403 nm excitation produces more pronounced shoulder or maximum at 730 nm in the fluorescence spectra as compared to the excitation with 437 nm. Furthermore, only shoulder at 730 nm is noted in the spectrum (Fig. 7, curve 1) in the presence of glycerol in the solution, while the maximum at 730 nm is observed in the spectrum (Fig. 8, panel A, curve 1) in the absence of glycerol. Hence, the
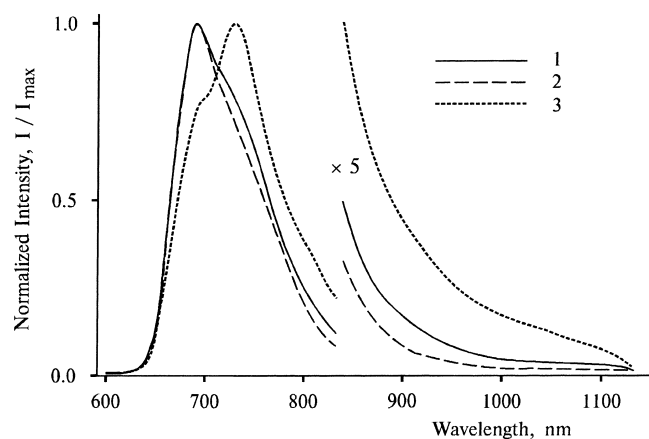

Fig. 7. Fluorescence spectra of TPP in water-glycerol-tetrahydrofuran (86.5 : 10 : 3.5, v/v) in the presence of 0.4 N hydrochloric acid under excitation of 403 nm, (1); 437 nm, (2); and 465 nm, (3).

increase of the viscosity of the environment considerably decreases the ability of the low-energy dimeric form of TPP in the trapping of excitation energy under close conditions. This behavior can take place when the low-energy dimeric form of porphyrin as the acceptor of the excitation energy
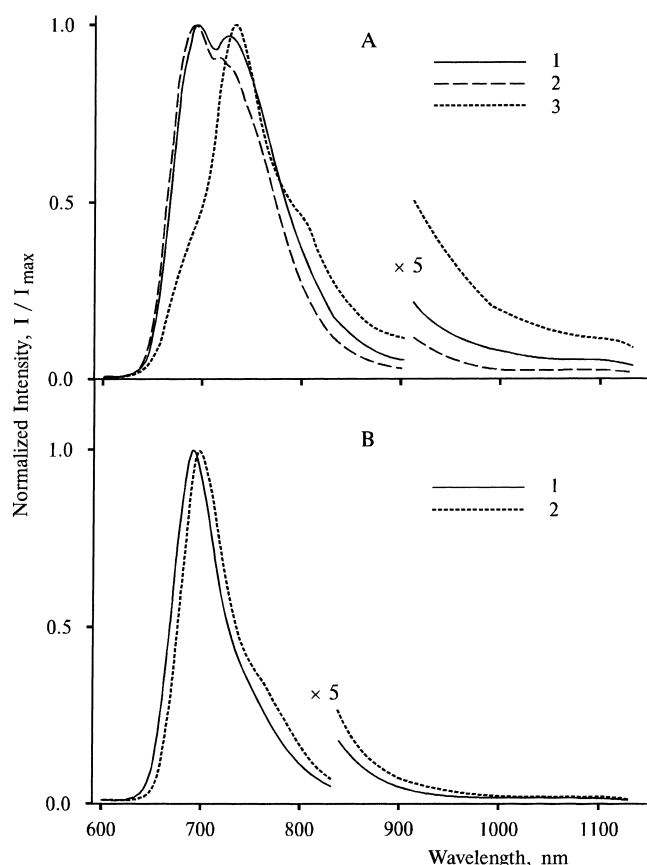
Fig. 8. Fluorescence spectra of TPP, panel A: in water-tetrahydrofuran (86:4, v/v) in the presence of 0.4 N hydrochloric acid under excitation of 403 nm, (1); 437 nm, (2); and 465 nm, (3); and under excitation at the maximum of the Soret band, panel B: in 50% aqueous solution of acetone (v/v) in the presence of 0.4 N hydrochloric acid, (1); and TAPP in DMF, (2).
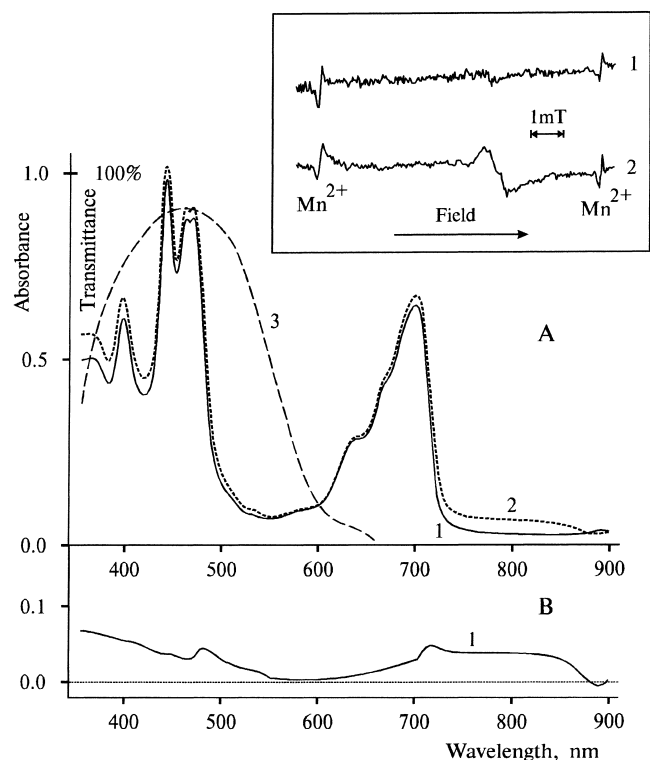

Fig. 9. Absorption spectra of TPP in water-glycerol-tetrahydrofuran (44:50:6, v/v) in the presence of 0.4 N hydrochloric acid at 77 K (panel A): before illumination (1); after 12 min illumination (2), and transmittance of the light filter used for the illumination (3); (panel B): differential spectrum (the spectrum, panel A, curve 2 minus the spectrum curve 1). The inset shows EPR spectra of TPP in water-tetrahydrofuran (92:8, v/v) in the presence of 0.4 N hydrochloric acid at 77 K before illumination (1) and after 10 min illumination (2).

apparently changes its own configuration or near local surrounding in the result of the fast photoprocess in the dimeric form. Anyway, the fact is that the increase of the viscosity of the solution prevents the highly effective transfer of excitation energy in the case of Fig. 7 and is different from Fig. 8, panel A.

In the case of presence only one dimeric form in the solution, namely, doubly protonated dimer of TPP with the maxima at 437 and 654 nm in the absorption spectrum (Fig. 4, curve 1), a considerably narrower emission band with the maximum at 693 nm as compared with the previous spectra is noted in the fluorescence spectrum (Fig. 8, panel B, curve 1). This spectrum indicates that the fluorescence state of doubly protonated TPP dimer is located higher by $730 \, \text{cm}^{-1}$ as compared to that of the low-energy singly protonated dimer. Note that all spectra have near IR-emission tail among which singly protonated dimeric forms possess more intense emission in the near IR region. The presence of shoulder at about 800 nm in the spectrum on excitation at 465 nm (Fig. 8, panel A, curve 3) suggests that the interaction between high- and low-energy dimeric forms is accompanied by electron transfer. Similar shoulder in the analogous region is observed in

the fluorescence spectrum of TAPP (Fig. 8, panel B, curve 2). Formation of radical ions has been revealed for this porphyrin in the same solution earlier [7]. Furthermore, kinetics of fluorescence decay of the aminoporphyrins was proved to be dual-exponential and obeyed to description by reversible electron transfer in the excited state [23].

Hence according to the fluorescence spectra, the selective excitation of three different protonated dimeric forms of TPP reveals only two different fluorescent states of dimer, one of which is doubly protonated dimer of TPP with the maximum of main emission at 693 nm, while the other low-energy configuration of dimeric form of porphyrin has the maximum of the main emission at 730 nm.

Interaction between different dimeric forms of protonated TPP involving water molecules in their complexes [17] suggests the possibility of electron transfer between them according to fluorescence spectra. Fig. 9 shows absorption spectra of TPP dimers in the presence of 50% (v/v) glycerol before and after 12 min illumination of the glassed solution with the filtered light into Soret band region at 77 K (panel A). The differential spectrum, the spectrum (curve 2) minus the spectrum (curve 1), is presented in Fig. 9, panel B. The latter is somewhat similar to the spectrum of π-cation radical of TPP [24], although the characteristic features of

the spectrum (panel B) appears to be due to the interaction of porphyrin with water. Small changes observed in the absorption spectrum can be associated with negative affect of glycerol on the interaction between different dimeric forms of porphyrin and as a consequence on the electron transfer reaction. The EPR spectrum (the inset, curve 2) exhibits the signal localized between third and fourth lines of manganese (II) after illumination of the TPP dimers in not glassed solution, i.e. without glycerol. The signal has g-factor of free electron and $\Delta H_{pp} = 0.7$ mT, these characteristics of the signal correspond to cation radical of TPP [8]. Note that the sensitivity of the EPR spectrometer was not sufficient to register the radical cation under illumination of glassed solution of TPP in the presence of 50% (v/v) glycerol.

Hence, illumination of TPP dimers in solution at 77 K produce porphyrin radical cation according to absorption and EPR spectra. At the same time these results are still not support completely our hypothesis about electron transfer reaction from the low-energy porphyrin dimer containing *trans* NH-configuration to the high-energy dimer containing *cis* NH-configuration on protonated porphyrin. Therefore only further study can elucidate this question. However, in our opinion the fact of appearance of main fluorescence with the maximum at 693 nm on excitation at 403 nm denotes preferable stabilization of the dimer with the *cis* NH-configuration in the excited state by additional protonation of porphyrin with the formation of doubly protonated state. But the additional protonation for water-porphyrin dimeric complex [17] means involvement rather proton of a water molecule bound with the porphyrin than the migration of proton from outside to the complex. From this point of view, we propose that electron transfer photoreaction mainly occurs from the low-energy TPP dimer with *trans* NH-configuration on singly protonated porphyrin to the high-energy dimer with *cis* NH-configuration. The latter dimer transforms rapidly into doubly protonated state under the excitation before electron transfer or maybe synchronically. It is possible that similar behavior can take place in the case of TTAP in water containing small amount of DMF when strongly solvated/hydrated low-energy porphyrin dimer (or associate) donates electron to high-energy form and transforms into corresponding singly protonated dimer.

3.4. Vibrational properties of dimeric and associated porphyrins under selective excitation

Resonance Raman spectra of dimeric and associated forms of porphyrins demonstrate unordinary peculiarities. Considerable changes are revealed in the spectra of TAPP associated in DMF at a high concentration of porphyrin under different excitation ($\lambda_{ex} = 514.5$ and 441.6 nm), Fig. 10, curves 1 and 2, respectively. New bands, among which it should be noted 1607 and 1900 cm^{-1} bands, are observed in the spectrum (curve 2). However, with the decreasing of porphyrin concentration, the 1900 cm^{-1} band disappears although the 1607 cm^{-1} band retains in the spectrum [9]. Additionally, the intensity of porphyrin bands in relation to that of solvent strongly increases in the spectrum (curve 2) as compared with this ratio in the spectrum (curve 1). In the spectrum of protonated dimeric forms of TPP, some new weak bands are noted with the increase of the porphyrin concentration (curve 3) as compared to the spectra obtained earlier [17]. Although, these new bands can be associated with the assembling of the dimeric forms that is observed in the solution. However, no appreciable new bands in the region higher the 1607 cm^{-1} band are revealed in the spectrum. Two strong and very broad 1901 and 1962 cm^{-1} bands are built up in the spectrum of TTAP at a medium concentration of porphyrin than TAPP but with a higher extent of association (curve 4). It is interesting that 1086 cm^{-1} band characterizing solvent vibrations is also broadened and increased in magnitude in this spectrum as compared to similar band in the spectra (curves 1 and 2). Characteristics of the other bands in the spectrum (curve 4) except for some changes in weak bands are kept the same as in the spectrum (curve 2). Although, the band of deformations of water (1660 cm^{-1}) is masked by the wing of the broad and intense 1901 cm^{-1} band.

Hence, new 1901 and 1960 cm^{-1} bands (± 2–3 cm^{-1}) are built up in the resonance Raman spectrum of TTAP at a medium concentration of porphyrin but with a high extent of association, while the 1900 cm^{-1} band is only revealed in the spectrum of TAPP at a high concentration of porphyrin. The presence of long hexadecyl groups in the structure of TTAP molecules is apparently favorable condition for assembling of this porphyrin and appearance of unordinary peculiarities.

To understand the nature of unordinary vibrational characteristics in the resonance Raman spectra of associated aminoporphyrins, we applied to very simple model system, i.e. amine containing small amounts of water. Fig. 11 shows infrared spectra of TEA containing 0.09 and 0.46 mol l^{-1} water (curves 1 and 2, respectively). These both spectra exhibits two unordinary bands of weak intensity at 1805 and 1938 cm^{-1}, but the intensity of which is not almost changed with the increase of water concentration. It is quite possible that these bands are related to combination vibrations of water which are becoming appreciable in the surrounding of alkaline-dissociated water contacting with amine. The concentration of the alkaline-dissociated water is defined according to the equilibrium constant. Therefore, the intensity of the combination vibrations appears to be almost unchanged. In this work we have not the aim to identify these bands but the fact is obvious that 1805 and 1938 cm^{-1} bands are related to some vibrations of unusually polarized water molecules, for instance, to deformation + translation (for the former band) and deformation + libration (for the latter). Anyway, 1901 and 1960 cm^{-1} bands observed in the resonance Raman spectrum of TTAP look like similar to the 1938 cm^{-1} band in the IR spectra of TEA-water thin layer. Meanwhile strong intensity of these bands suggests involve-
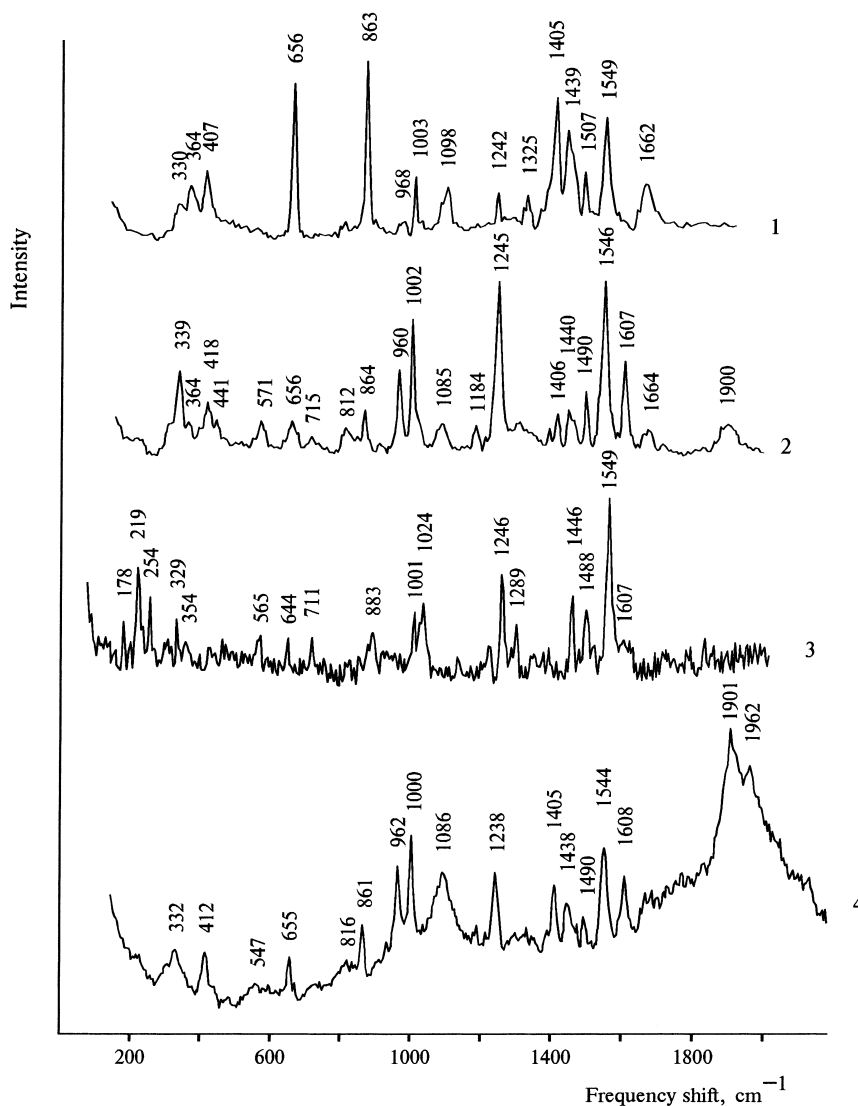
Fig. 10. Resonance Raman spectra of TAPP at a high concentration in DMF with excitation at 514.5 nm, (1), and 441.6 nm, (2); TPP in water-glycerol-tetrahydrofuran (86.5 : 10 : 3.5, v/v) in the presence of 0.4 N hydrochloric acid ($\lambda_{ex} = 441.6$ nm), (3); and TTAP in DMF ($\lambda_{ex} = 441.6$ nm), (4).

ment of water in the interaction between associated aminoporphyrin molecules under excitation.

Hence, the strong and broad 1901 and 1960 cm^{-1} bands have the nature of origination similar to aliphatic amine in the presence of water traces. These bands are apparently built up in the result of resonance interactions under selective excitation of porphyrin and perhaps characterize some strongly polarized intermediates accumulated under interaction of porphyrin with water.

4. Discussion

Unordinary broadened EPR signals of radical ions of associated TAPP [7] suggest unusual interaction between products of photoinduced electron transfer reaction. As evidenced earlier, water is involved in the donor–acceptor complexes formed by associated aminoporphyrins in thin films that was revealed by electronic and infrared absorption spec-

troscopy [25,26]. Hydration of the thin film containing minor amount of water resulted in a certain increase in absorption in the 670–800 nm region with the maximum at 750 nm. Moreover, a new broad emission band with the maximum at about 840 nm was found in the fluorescence spectrum of the thin film in the presence of water traces. But no emission of Q_x electron transition was observed in the spectrum. Additionally, later study established direct water molecules participation in the donor–acceptor complex with aminoporphyrin [9], vibrational characteristics of which in the region of water translations was found similar to water-tetraphenylporphine dimeric complex [17]. These main unusual results are the background for unordinary photochemistry of the aminoporphyrins and allow us to propose that the trapping of excitation energy by broad and intense charge transfer band with the maximum at 750 nm can produce electron transfer from water molecules involved in the complex.
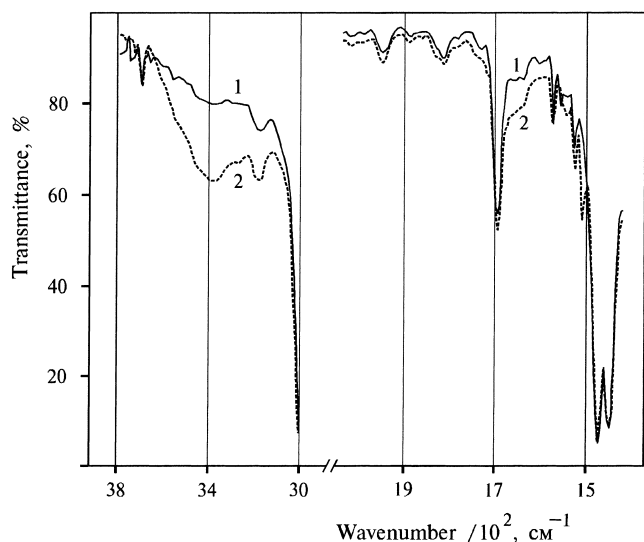
Fig. 11. Infrared spectra of TEA in the presence of small amount of water at the concentration of $0.09 \, \text{mol} \, \text{l}^{-1}$ (1) and $0.46 \, \text{mol} \, \text{l}^{-1}$ (2), optical pathway is $50 \, \mu\text{m}$.

It is quite possible that singly protonated dimeric forms of porphyrin can involve the bound water molecules in the photoprocess too. But in this case it is apparently needed an additional energy supply, since the maximum of the overlapped bands of singly protonated porphyrin dimers (Fig. 5) is blue shifted by 20–55 nm as compared with that of red band in thin films of aminoporphyrin. Possibly this additional energy supply can be provided in the case of illumination into Soret band region when the energy of exciton interactions is close to the energy of deformational vibrations of water [7]. Although in the case of singly protonated TPP dimers the low-temperature measurements demonstrate photoinduced formation of radical cation but these experiments apparently does not still exclude another mechanism of the formation of cation radical. In this way a theoretical consideration can help us to find a background for electron transfer photoreaction in the case of singly protonated dimers.

Under usual conditions π-electron structure of porphyrin monocation is unstable [27] but in the case of singly protonated dimeric form of porphyrin, the stabilization of the π-electron structure in the ground state occurs due to co-ordination of neighboring porphyrin molecule via water molecules with the formation of hydrogen bonds [17]. As a result of it, for the water molecules bound in the structure of water-porphyrin dimeric complex favorable conditions of involvement into donor–acceptor interaction with porphyrin are produced. Hence, although π-electron structure of the configurations of the singly protonated porphyrin dimers is stabilized in the ground state, however, this π-electron structure is destabilized in the excited state. Generally speaking, there are only two possibilities for the π-electron structure of the dimeric monocation of porphyrin to be stabilized in the excited state. In dependence from the configuration of the porphyrin dimer, a water molecule bound with the dimer can lend a proton or an electron to the pro-

tonated porphyrin molecule. Therefore, π-electron structure of porphyrin macrocycle in the excited state is stabilized by lending of proton from the bound water molecule in the one configuration with formation of doubly protonated state or electron in the case of the other configuration of porphyrin dimer.

Hence, only two different configurations of porphyrin dimers can exist in the excited state. One of which is doubly protonated dimeric form with the maximum of main emission at 693 nm while the other has the maximum of the main emission at 730 nm. However, the latter is photochemically activated dimeric form since accepts the electron in the excited state and, therefore, presents as the neutral dimer on the whole. It means that protonated nitrogen atom in the porphyrin macrocycle can be reduced and, therefore, the porphyrin contains H$^\bullet$. In the case of the presence of the another dimeric form of porphyrin in the solution, electron transfer takes place in the result of the interaction between them. Hence, the excitation into the low-energy dimeric form of porphyrin monocation ($\lambda_{ex} = 465$ nm) leads to the fast electron transfer to doubly protonated dimer. Therefore, the shoulder at about 800 nm in the fluorescence spectrum is rather a recombination fluorescence. Hence, the energy loss for the reversible electron transfer can be estimated, the value of which in this case equals to $1200 \, \text{cm}^{-1}$. It is interesting that proton transfer under selective excitation into high-energy dimeric form of porphyrin monocation ($\lambda_{ex} = 403$ nm) occurs under similar energy loss. Stokes shift observed for this form is $1240 \, \text{cm}^{-1}$. It should be noted that according to the maxima of the emission at 693 and 730 nm (Fig. 8, panel A), any selective excitation ($\lambda_{ex} = 403$ or 437 nm) produces the fluorescence of both possible configuration of dimeric form of porphyrin due to the interaction between these different forms. Although, the interaction between different singly protonated dimeric forms ($\lambda_{ex} = 403$ nm) is proved to be some more effective as compared with the interaction between low-energy singly protonated and doubly protonated dimers ($\lambda_{ex} = 437$ nm), compare curves 1 and 2. This fact suggests the presence of some synchronization in the generating of the different charges in the high- and low-energy dimeric forms of porphyrin in the excited state. The consideration can be useful for elucidation of electron transfer processes both between TPP dimers and between aminoporphyrin forms.

As we propose, similar processes of electron transfer can take place in the case of TTAP in water containing small amount of DMF. But in this case according to the spectrum (Fig. 1, curve 1) strongly solvated/hydrated associate (possibly dimer) with the maximum of red band at 720–730 nm transforms under steady-state illumination into singly protonated dimer of the aminoporphyrin with the maximum at 692 nm, according to the differential spectrum (Fig. 2, the inset). At the same time, the high-energy dimeric form of TTAP with the shoulder at 635–638 nm transforms into broad band with the maximum at 620 nm. It is possible that the latter product contains electron delocalized between two

protons in the macrocycle in *cis* configuration. In the difference from aqueous solutions of TTAP containing 3–5% (v/v) DMF, no changes are observed under illumination of this porphyrin in DMF in the presence of minor amount of water. However, blue light excitation ($\lambda_{ex} = 441.6$ nm) leads to the considerable changes in the resonance Raman spectra as compared with the other excitation ($\lambda_{ex} = 514.5$ nm). These changes are apparently associated with the same processes which takes place under interaction between different dimeric (associated) forms of porphyrin. Although physical processes of interaction between low- and high-energy dimeric forms takes place, however, the photochemical reaction is not realized since there is no protonated forms of porphyrin. In this situation the changes observed in the resonance Raman spectra look like an activation of water molecules bound in porphyrin dimeric (or associated) complex [9]. Note, that the energy gap between photoactive dimeric forms of TTAP in the spectrum (Fig. 5, curve 2) estimated from the maximum at 416 and 457 nm is about 2000 cm^{-1}. This value is very close to the broad and intense 1901 and 1962 cm^{-1} bands observed in the spectrum of TTAP in DMF (Fig. 10, curve 4). On the other hand, it is quite possible that the two latter bands are built up in the result of splitting under blue light excitation of similar 1938 cm^{-1} band observed in the IR spectrum of the simple system (Fig. 11).

Hence, electron transfer reaction taking place in solutions of TPP dimers suggests the real possibility to utilize water as an electron donor and, therefore, the initial steps of water splitting. Although, apparently more effective photoreaction proceeds in associates of TTAP in water containing small amount of DMF that also occurs between low- and high-energy forms of porphyrin as we propose. It is quite possible that this initial step of electron transfer between two different dimeric forms can generate a driven force for the overall process of water splitting.

5. Conclusion

The results presented above show photoinduced changes in solutions of dimeric forms of TPP at 77 K and in water-DMF solutions of TTAP at room temperature. The changes of the former correspond to radical cation of porphyrin with g-factor of free electron and $\Delta H_{pp} = 0.7$ mT. However, the radical cation can interact with water according to differential absorption spectrum. At the same time, fluorescence spectra under selective excitation show interaction between different dimeric forms of protonated TPP. It is proposed that the interactions bring about electron transfer reaction between them. The efficiency of the photoreaction in solutions of protonated TPP dimers appears to be low since the protonation is occurred with exogenous proton added to the solution. In the case of photoreaction of TTAP associates in water containing small amount of DMF, the irreversible changes are observed since protonation of the

porphyrin appears to be to pK'_{eq} located in alkaline region of pH. According to differential spectrum we propose that the irreversible photoreaction proceeds between similar low- and high-energy dimeric (or associated) forms of porphyrin because of main characteristics of the spectrum are analogous to those of the corresponding dimers of TPP. These data and unusual results of resonance Raman spectroscopy of TTAP in DMF containing water traces, when behavior of the aminoporphyrin in the excited state is apparently reminiscent alkaline dissociation of water bound with the aminoporphyrin, allow us to suggest involvement of water in the photoreaction as a sacrificial electron donor. From this point of view the photoreaction in the electrochemical cell with chlorine-argentum electrode is considered as leaving of electron from water activated with low-energy porphyrin dimer to the electrode that is accompanied by release of proton in the solution. The electron transfer photoreaction between different dimers of TPP most probably occurs with involvement of water as the electron donor too but not sacrificial.

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