

PICOSECOND SPECTROSCOPY OF SOME METALLOPORPHYRINS*

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Summary

The energy relaxation process of metal-free protoporphyrin IX dimethyl ester and its compounds with Cu(II), Ag(II), Ni(II), Pd(II), Pt(II), Zn(II), Fe(III) and the heme proteins myoglobin, hemoglobin and cytochrome c were studied by dual-beam picosecond spectroscopy. Excitation at 530 nm, which is in the β visible absorption band for these compounds, revealed that both the metal-free porphyrin and the Zn(II) porphyrin have lifetimes for S_1 which are longer than 1 ns, in keeping with their known fluorescence properties. From the time-resolved spectra after excitation, absorption due to S_1 , T_1 and S_0 could be identified. In addition, a low-lying singlet d-d level was seen for the Ni(II) porphyrin. While the Pt(II) and Pd(II) compounds have intersystem crossing times of less than 8 ps and 20 ps respectively, the Ni(II) compound relaxes from S_1 to S_d in about 10 ps and from S_d to S_0 in 260 ps. The paramagnetic Cu(II) and Ag(II) species have intersystem crossing from 2S_1 to 2T_1 in less than 8 ps followed by an equilibrium of the 2T_1 and 4T_1 states, requiring about 450 ps for the Cu(II) compound and about 12 ps for the Ag(II) compound. An anomalous lengthening of the decay time with increasing excitation intensity was observed for the copper but not for the silver porphyrin. The Fe(III) porphyrins relax with rates faster than 6 ps, which was the resolving time of this experiment. No differences between heme proteins and Fe(III) protoporphyrins in solution were observable within this time resolution.

1. Introduction

The characteristics of electronic excitation and relaxation in porphyrins have been intensively studied over the past 50 years. Because of their biological importance and as large conjugated molecules, the porphyrins have been widely investigated by biologists, chemists and physicists alike. The cyclic tetrapyrrole

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ring of porphyrins can form complexes with more than 50 metals mostly in oxidation states +2 or +3. The visible absorption spectrum, fluorescence spectrum, phosphorescence spectrum and quantitative yields of porphyrins are greatly affected by the formation of these metal complexes [1 - 6]. Theoretical studies on porphyrins and metalloporphyrins have been able to account for the principal features of the visible absorption spectrum and some of the kinetics of the excited states [1, 7 - 11]. In general, it is observed that closed-shell diamagnetic metal ions such as Zn(II) and Mg(II) form complexes with porphyrins which are strongly fluorescent like the metal-free porphyrins. Open-shell diamagnetic metal ions such as Pd(II) or Pt(II) form metalloporphyrins which are only weakly (or not at all) fluorescent but show strong phosphorescence. Paramagnetic ions such as Cu(II) or Fe(II) make metalloporphyrins which are not fluorescent and have barely detectable or no phosphorescence. Obviously then, the mode of relaxation of the excited state of the metalloporphyrins is greatly affected by the central metal ion.

The development of picosecond spectroscopy with the capability of simultaneous wavelength and time resolutions [12 - 14] has made it possible to study visible electronic excitation and decay directly. In order to understand further the mechanisms of energy relaxation in porphyrins, we studied the excited state kinetics of several related metalloporphyrins.

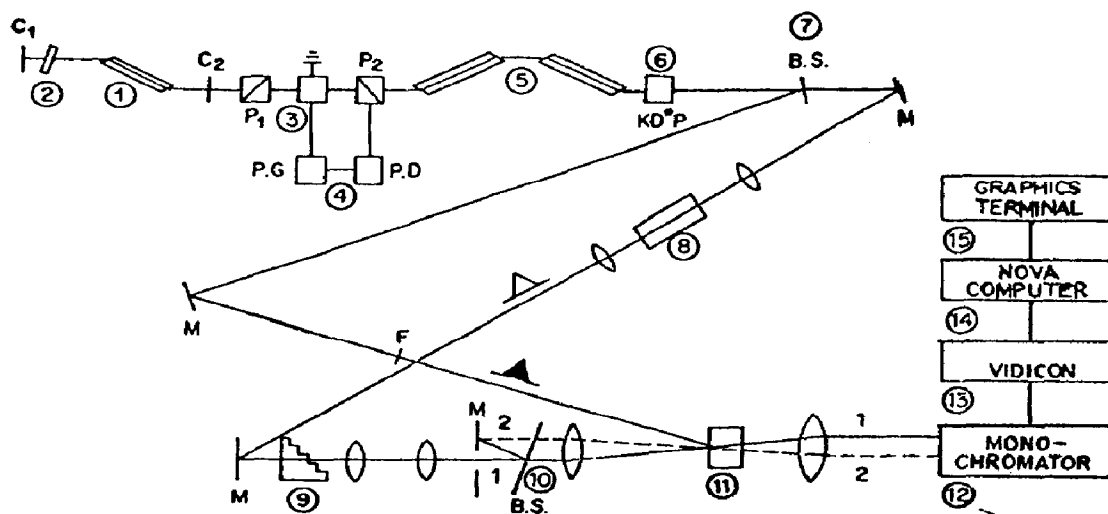


Fig. 1. A schematic representation of the experimental system: 1, Nd³⁺ glass oscillator with cavity mirrors C₁ and C₂; 2, saturable dye absorber cell; 3, Pockels cell positioned between crossed polarizers P₁ and P₂; 4, electronic Pockels cell driver; 5, Nd³⁺ glass amplifiers; 6, second-harmonic generator; 7, beam splitter; 8, broad-band continuum cell containing CCl₄ or cyclohexane; 9, variable delay transmission echelon; 10, double-beam splitter; 11, sample cell; 12, monochromator; 13, optical data digitizer; 14, Nova computer; 15, graphics terminal; M, mirrors; F, filters; ▲, 530 nm (excitation); △, 560 - 1600 nm continuum (interrogating).

2. Methods

The metalloporphyrins were prepared by the methods of Callis *et al.* [15] or Dorough *et al.* [16] and purified when necessary on silicic acid columns with varying proportions of benzene and glacial acetic acid. Hemin and protoporphyrin IX dimethyl ester were obtained from Sigma Chemical Co., St. Louis, MO.

The dual-beam picosecond spectrometer system was that described by Huppert *et al.* [17]. The excitation pulse was a 6 ps, 5 mJ, 530 nm (second-harmonic) single pulse from a pulse train generated by a mode-locked Nd³⁺-YAG laser amplifier. The probe pulse was generated from the exciting pulse by using a small amount of light from a beam splitter and putting it through a continuum generator (CS₂ or D₂O cell).

Optical timing and delay of the probe pulse were obtained by path length adjustments and use of a quartz echelon of known delay times. Detection was accomplished on a Vidicon after dispersion of the probe pulse continuum by a spectrograph. The experimental set-up is shown in Fig. 1. A second frequency doubling of the exciting pulse to 355 nm was accomplished with a KDP crystal and the probe pulse was generated by using part of the 355 nm pulse to pump a tunable dye laser over the range 400 - 480 nm. Since no continuum is generated, this method has time resolution but only at the wavelength of the probe pulse from the dye laser.

3. Results and discussion

3.1. Metal-free protoporphyrin IX dimethyl ester

As seen in Fig. 2, excitation of the metal-free porphyrins at 530 nm results in an increase in absorption at 590 nm due to excited state absorption. Excitation at 355 nm results in a bleaching of absorbance in the Soret band at 405 nm due

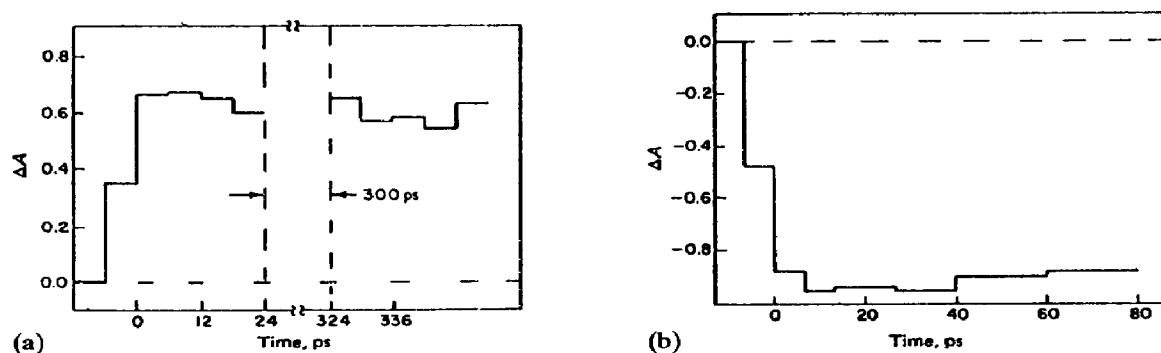


Fig. 2. (a) The absorbance increase at 590 nm as a function of time, observed in hematoporphyrin after excitation at 530 nm with a picosecond pulse. It should be noted that the actual interrogation time was extended to 400 ps. (b) Bleaching kinetics of hematoporphyrin interrogated in the 405 nm region after being excited by a 355 nm pulse (from ref. 17).

to ground state depletion. The excited state persists for more than 1 ns in agreement with the well-known strong fluorescence of metal-free porphyrins.

3.2. Closed-shell diamagnetic metalloporphyrins

Zn(II) protoporphyrin IX dimethyl ester represents a metalloporphyrin with a closed-shell diamagnetic metal (d_{10} electronic configuration). Excitation at 530 nm resulted in loss of absorption at 560 nm due to depletion of the ground state Q band and an increase in absorption at 480 nm due to absorption by the excited state. Like the metal-free porphyrin, Zn(II) protoporphyrin has a lifetime of the excited state of more than 1 ns. This long-lived excited state is expected since zinc porphyrins are strongly fluorescent [18]. Absorption of the excited state $S_1 \rightarrow S_n$ extends from at least 480 to above 600 nm with the ground state bleaching at the Q bands causing the net absorbance to be decreased at those points. For most of the metalloporphyrins observed in this study, the Q band ground state bleaching exceeded the broad but low intensity excited state absorbance at the Q band maxima. Thus, although the $S_1 \rightarrow S_n$ excited state absorbance extends across the Q bands, the Q band depletion (absorbance decrease) exceeds the excited state absorbance at the maxima of the Q band (0-0, 0-1) transitions.

3.3. Open-shell diamagnetic metalloporphyrins

The series of $d_8 2+$ metal ions Ni(II), Pd(II) and Pt(II) were chosen to examine the heavy metal effect in an isoelectronic group. Excitation of the Pt(II) protoporphyrin IX dimethyl ester at 530 nm results in a long-lived bleaching at 550 nm (Fig. 3) and a long-lived absorbance increase at 480 nm (not shown). The time courses for both the bleaching and the absorbance increases are identical. Since the platinum porphyrins are non-fluorescent but strongly phosphorescent, we assign the long-lived (more than 1 ns) component to the triplet state. Since there is no short-lived component to the decay process, the S_1 state must either have a very low absorption cross section or rapidly decay to the T_1 level.

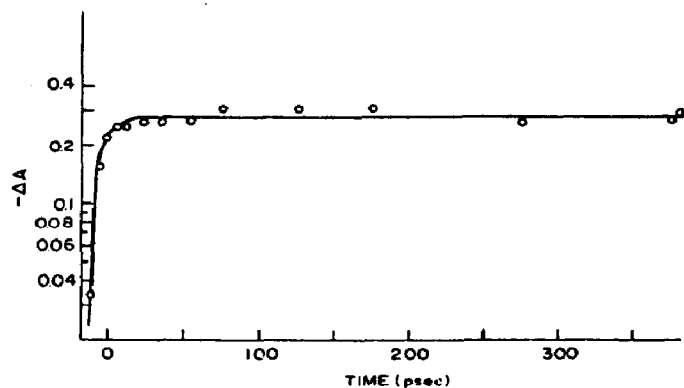


Fig. 3. A semilogarithmic plot of absorbance change ΔA vs. time for platinum protoporphyrin IX dimethyl ester excited at 530 nm and interrogated at 550 nm (from ref. 19).

The Pd(II) protoporphyrin IX dimethyl ester complex does have a biphasic decay of the excited state. As seen in Fig. 4, excitation at 530 nm results in a strong bleaching at 560 nm which has a short-lived component with fairly low absorption cross section and a long-lived component which shows little decrease over the 350 ps of observation. Subtraction of the long-lived component gives the decay rate for the short-lived component which is about 20 ps. The same kinetics for the absorbance *increase* at 480 nm result from 530 nm excitation. Since the palladium complexes of porphyrins are weakly fluorescent and strongly phosphorescent, it can be assumed that, since the quantum yield of palladium porphyrin fluorescence is about 2×10^{-4} and assuming a natural lifetime of 60 ns, the lifetime of S_1 must be about 20 ps. The assignment can be made that the short-lived component is the S_1 state and the long-lived component (more than 1 ns) is the T_1 state.

Excitation of the Ni(II) protoporphyrin dimethyl ester at 530 nm results in different kinetic behavior from that of palladium and platinum complexes. The absorbance increase at 480 nm is shown in Fig. 5. There is a biphasic decay with the fast component being about 10 ps and the slower component being 250 ps. The bleaching kinetics at 560 nm are monophasic with a decay time of 270 ps, as seen in Fig. 6. There is therefore a rapidly decaying excited state which does not repopulate the ground state as monitored at 560 nm. On the basis of theoretical calculations [20, 21] there should be a low-lying S_d or T_d state of this complex. Because the lifetime of the long-lived state is 250 ps, it is more probable that this state is the S_d rather than the T_d , since there is neither fluorescence nor phosphorescence in the visible range in Ni(II) porphyrins.

3.4. Open-shell paramagnetic metalloporphyrins

In order to ascertain the influence of unpaired electrons on the excited state kinetics of metalloporphyrins, the Cu(II) and Ag(II) complexes were studied. Excitation of the Cu(II) protoporphyrin IX dimethyl ester at 530 nm resulted

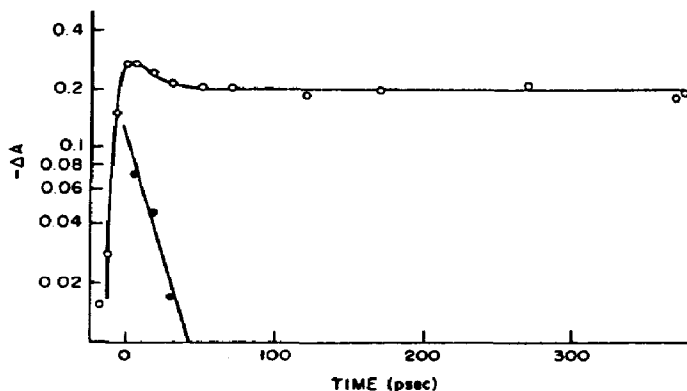


Fig. 4. A semilogarithmic plot of absorbance change ΔA vs. time after excitation at 530 nm observed for palladium protoporphyrin IX dimethyl ester at 560 nm and 292 K. The full circles were obtained from the open circles after subtraction of ΔA of the long component which decays in the time range 0 - 400 ps after excitation. (From ref. 19.)

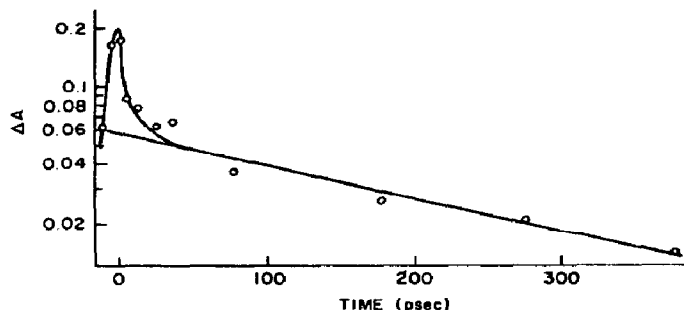


Fig. 5. The optical density change observed at 480 nm for nickel protoporphyrin IX dimethyl ester excited at 530 nm (from ref. 19).

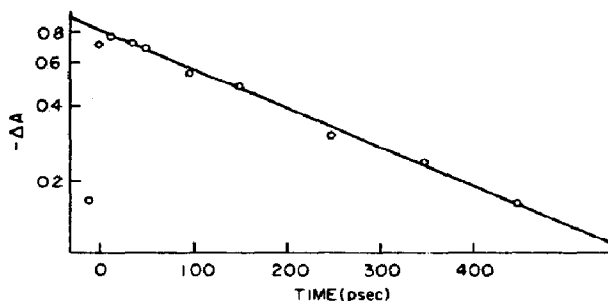


Fig. 6. The optical density change observed at 560 nm for nickel protoporphyrin IX dimethyl ester excited at 530 nm.

in a biphasic bleaching at the Q band at 570 nm and a similar biphasic absorption increase at 480 nm. The time constant of the shorter phase is about 450 ps while that of the longer-lived component is more than 1 ns for both bleaching (depletion of the ground state) and absorbance increase (absorbance of the excited state). Ag(II) and Cu(II) porphyrin complexes should have singlet states with doublet levels (2S_0 , 2S_1 etc.) and triplet states with doublet and quartet levels (2T_1 , 4T_1 etc.) [9]. Since the copper porphyrins are not fluorescent but are weakly phosphorescent, the most probable explanation for the decay rates is that the 2S_1 state relaxes very rapidly (in less than 6 ps) to the 2T_1 state by intersystem crossing. Equilibrium is established with the 4T_1 state (slightly lower in energy) in 450 ps which is our first observable decay rate. The long-lived decay rate of more than 1 ns must then be the combined transition from 2T_1 and 4T_1 to 2S_0 . This assignment is compatible with the known phosphorescent lifetime at room temperature of 1 μ s for copper porphyrins [4].

For the Ag(II) protoporphyrin IX dimethyl ester, excitation at 530 nm also gave biphasic kinetics. The absorbance increase at 480 nm had an initial decay of 12 ps and a very low absorbance lasting more than 1 ns. The same kinetics are seen with the 560 nm bleaching. Since Ag(II) porphyrins are not phosphorescent, either a low-lying 2T_d - 4T_d level or a (d, π^*) charge transfer state as

postulated by Antipas *et al.* [22] must intervene between the ${}^2T_1 \rightarrow {}^4T_1$ and 2S_0 . This low-lying state is also seen in the nickel porphyrin complexes and has already been discussed. Tsvirko and his colleagues [2] have also postulated the existence of a low-lying charge transfer state to explain the quenching of S_2 fluorescence in the Eu(III) tetra-*para*-tolyporphyrin complex.

An alternative explanation could be that the 4T_1 state is never populated and the decay could be ${}^2S_1 \rightarrow {}^2T_1$ (less than 6 ps) and ${}^2T_1 \rightarrow {}^2(d, \pi^*)$ (which would have a 12 ps time constant) and finally ${}^2(d, \pi^*) \rightarrow {}^2S_0$ with a time constant of more than 1 ns [23].

Within isoelectronic series there appears to be a heavy metal effect on intersystem crossing (compare palladium and platinum and silver and copper), but the greatest influence on intersystem crossing is the existence of unpaired electrons in the complex. Charge transfer states of the metal electronic states with the π system of the porphyrins may be important pathways of decay of the excited state where the energy levels of the charge transfer states are accessible.

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