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Ultrafast Electronic Relaxation of Excited State of Biomimetic Metalloporphyrins in the Gas Phase

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1. Introduction

Biomimetic molecules are systems that provide a direct and simpler reproduction of a molecular process essential to the living world, i.e. they mimic a function or a structure of a biomolecular edifice. The idea is to isolate this process and allow a selective study of a specific function by physicochemical methods, in a reductionist way. In that respect, gas phase studies of biomolecules are ideal, since they allow the application of a variety of highly sensitive and selective tools to the study of these model systems: mass spectrometry, photoelectron spectroscopy, for example, provided that the molecular system has been vaporised. In addition, the system is studied in absence of solvent, which greatly simplifies the interpretation of the fundamental effects and consequently allows to infer the effects of the medium since, in the gas phase solvents can be introduced in a gradual manner via clusters. Also gas phase measurements allow a direct comparison with results from quantum chemistry calculations. Great progresses have been fuelled in this direction by the developments of mass spectrometry. The studies in the gas phase have been mostly dedicated to the elucidation of the basic structure of the building blocks of proteins, i.e. small peptides (Simons, 2004).

In turn, other biological functions have been less studied by the gas phase biomimetic approach. Hematoproteins hosting hemoporphyrins (the heme, see fig 1) are ideal systems to examine in this way, since they are at the heart of the oxygen and small molecules transport within blood and that their active site is localised very precisely on the metal atom embedded in their central porphyrin. Thus, if one studies the active porphyrinic site of myoglobin at short time scales (in the subpicosecond time domain), the interaction with the environing protein (globin myoglobin) can be minimised.

In hemoproteins, the attachment of oxygen to the iron of the heme is a complex process involving a potential barrier. This barrier results from the crossing of two surfaces of

different electronic and spin configuration of the metal atom (Harvey, 2000). Also, the metal-ligand bond is very sensitive and affected by charge flow in either direction, metal to porphyrin or the reverse, due to their similar ionisation energies. As an example, oxygen is bound to FeII but not to FeIII hemoproteins. Therefore, the study of the reverse process to ligandation, the dissociation of the ligand from the metal centre, is in practice only performed via electronic excitation through allowed electronic transitions of the heme porphyrin, providing sufficient energy to break the metal ligand bond. In these conditions, to be effected, this dissociation must involve first a reorganisation of the electron distribution between the porphyrin and the metal atom, Fe, i.e. an electronic relaxation. The electronic relaxation by itself does not necessitate a protein to be characterized, nor a ligand on the active metalloporphyrin. It is thus of great importance to investigate the electronic relaxation in protein-free metalloporphyrins and to track charge transfer states as intermediates in the dissociation of ligated porphyrins. The complete relaxation process and dissociation is extremely rapid from the Q band excited low spin Myoglobin-CO in the liquid phase; it is deemed to lead in less then 150 fs to the ground state high spin Myoglobin (Fuss et al., 2004).

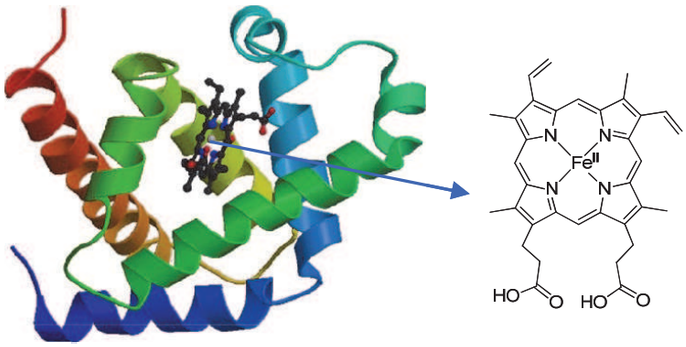


Fig. 1. Schematic picture of myoblobin and the active site, protoporphyrin IX (right).

Electron transfer and proton transfer are the most common mechanisms at the heart of many biochemical reactions. Zwitterions corresponding to the charge separation within a single molecule are commonly observed, as in soluble aminoacids (glycine $NH_3^+CH_2COO^-$) and small protein strands, while phosphate ionic groups are ubiquitous in biochemical structures. On the other hand, excited state charge transfer (CT) processes are just as important. If one considers photosynthesis, there is a chain of excited CT transfers initiated within the chlorophylls in the reaction centres. This mechanism is far more complex to disentangle, due to its multiple pathways and brevity. In addition, charges flow, in this process between different subunits of the reaction centre. On the other hand, charge transfer processes in *excited states* can drive other processes, such as electronic relaxation. They are also difficult to characterise experimentally (Shafizadeh et al., 2009) and by quantum chemistry. In model nickel porphyrins, recent TDDFT calculations have shown the existence of a diversity of charge transfer states (CT), either porphyrin to metal or the reverse. In this nickel porphyrin (Patchkovskii et al., 2004), the lowest CT state is of the porphyrin to metal transfer type and can retain transient electronic excitation. On the experimental side, great endeavour has been put in solutions of hemoproteins and porphyrins to characterise by spectroscopic methods these CT states (Rodriguez et al., 1989). These studies show in general that the charge transfer is only partial and is a convenient way to picture the charge flow in these systems.

Here, the ultrafast relaxation in metalloporphyrins is analysed in order to characterise the driving forces connecting the excited states of hemoporphyrins. It is showed that the mechanism is triggered by an ultrafast initial electron transfer from the porphyrin to the central metal by a comparative study of many systems. We have thus studied metalloporphyrins of increasing complexity from model tetraphenyl porphyrins hosting several transition metals, as biological systems host various metals within their central core, Fe, Cu, Co, Mg (Milgrom, 1997). Based on this relaxation mechanism, we describe that of more complex biomimetic ones: Fe protoporphyrin IX (heme) and vitamin B12.

2. Photophysics of porphyrin systems

The continuous absorption spectra of heme and other metalloporphyrins observed in solutions are dominated by the intense B (Soret) and Q absorption bands involving excitation of the porphyrin cycle of the heme in a $^1(\pi, \pi^*)$ transition (Gouterman, 1978). Aside these strong bands, at the edge of infra red, there are other less prominent bands of interest. These have been assigned by spectroscopic investigations and Stark spectroscopy to include porphyrin-to-metal charge transfer states CT and (d,d) electronic transitions (Eaton et al., 1978; Franzen et al., 1999).

The transients after a short pulse excitation have been abundantly (Steer and Tripathy, 2007) studied in solutions by transient absorption methods. However, the dynamics of relaxation of hemoporphyrins and other metalloporphyrins is complex and is not yet completely understood. The relaxation of simpler metalloporphyrins has been also studied extensively, by transient absorption measurements as models, especially the decay of nickel porphyrins. The relaxation of the S_1 state was characterized as a rapid transfer of excitation (τ>350 fs) from the ring excited state $^1(\pi, \pi^*)$ to a (d,d*) metal excited state. It was also observed that the (d,d*) state further relaxed to the ground state within 20 ps, probably due to the interaction with the solvent. On the other hand, there are few studies observing the decay of the S_2 excited state. For NiTPP excited in S_2, it has been inferred by the observation of broad transient spectra, that decay from S_2 to S_1 is the initial step to relaxation populating the (d,d*) states at times below 700 fs (Rodriguez and Holten, 1989).

We reexamine here these conclusions and find a different interpretation, owing to the precision (energetic, temporal) offered by gas phase measurements and the absence of vibrational relaxation. On the other hand, Fe Protoporphyrin IX or heme, has been shown to follows a different relaxation pathways: Ishizaka et al. (Ishizaka et al., 2009) have studied the dynamics of relaxation of excited oxymyoglobin Mb $O_2(Fe^{II})$ and met-myoglobin, met Mb (Fe^{III}) in solution. The authors, find that the fast relaxation is due to a rapid (femtosecond time scale) charge transfer from the porphyrin to the vacant d orbital of the iron and the oxygen orbital is not involved in these transitions. These results suggest that the charge transfer from the porphyrin to the metal is the key event in excited state relaxation of the heme in MbO2.

In the present work, the relaxation dynamics of metalloporphyrin-based systems have been investigated by time dependent pump-probe spectroscopy, in the gas phase. The gas phase allows to measure the intrinsic properties of the active site, especially it separates the electronic and vibrational contributions in the relaxation process, and the absence of medium eliminates the vibrational cooling. This relaxation is found in transient absorption measurements as an additional transient, not present here. Time dependent spectroscopy can probe very fast relaxation processes immediately after excitation with a resolution

determined only by the autocorrelation time of the pump and probe pulses. Electronic relaxation, resulting from non adiabatic couplings between the electronic states involved, is effected via a wavepacket motion after the ultrafast excitation (Mestdagh et al., 2000). The wavepacket goes through the funnels of the conical intersections into the surfaces of lower electronic states. The characterization of this wavepacket movement can give information on the dynamics of the excited system under study. This is achieved in pump probe time dependent experiments.

2.1 Femtosecond pump-probe experiments

The principle of the experiment is shown schematically in Fig 2. The initial state (S_2) is populated by a 400 nm pulse laser (pump laser) and is ionised by a second laser pulse (probe laser). The delay between the pump and probe pulses is varied in a stepwise manner and t=0 is defined by the temporal coincidence of both pulses. Ionisation forms a molecular ion and an electron. In our setup, it is possible to detect either the ion or the electron. Detecting the ion leads to information on masses and fragments. Detecting the electron leads to information on the kinetic energy of the ejected electrons, reflecting the evolution of electronically excited intermediate states. In a simplified view of the conservation of momentum (vibrational) between the evolving state and the ion, the energy of ionisation is only dependent upon the electronic energy of the states probed. Thus as electronic energy is transformed into vibrational energy, the energy of ionisation increases (then, the photoelectron energy decreases, see figure 6 a). Thus, varying the time delay between pump and probe lasers, one can follow the evolution of the initial state, through various electronic states via their photoelectron energy (electron detection) or their ionisation efficiency (ion detection).

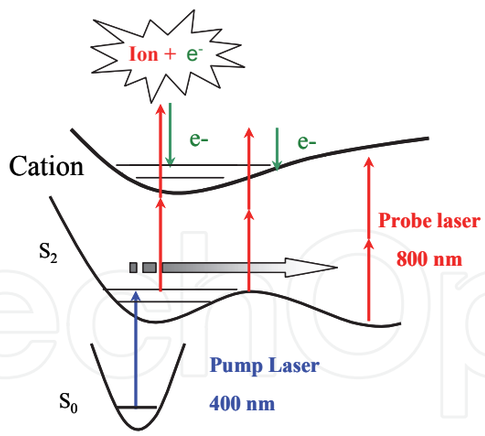


Fig. 2. Principle of a pump-probe experiment with ion or electron detection.

The experimental apparatus is a pulsed supersonic molecular beam coupled with a velocity map imaging device along the design of (Eppink and Parker, 1997) and a standard time-of-flight mass spectrometer (TOF-MS). A schematic overview of experimental setup is shown in figure 3.

A carrier gas (helium) expanded supersonically through a pulse valve entrains the vapour of the molecule under study. The resulting molecular beam is collimated by a single skimmer before entering the interaction region. In this region, the neutral molecular beam is

irradiated with the pump and probe lasers. In accordance with typical absorption spectra of porphyrin systems, the second harmonic of the Ti:sapphire femtosecond laser at 400 nm (70 fs), was used as the pump pulse. The evolution of porphyrin excited in the Soret band (S_2) is followed by a second femtosecond laser, the probe laser. The probe laser at 800 nm passes through an optical delay line. This probe laser ionizes the excited system during its evolution. Thus, the generated ions and electrons can be followed temporally by varying the delay between the pump and probe lasers.

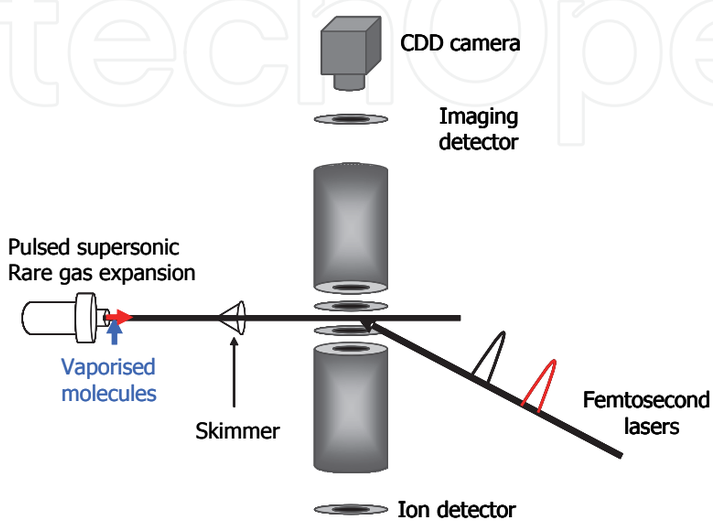


Fig. 3. Experimental setup.

2.2 Evaporation methods

The difficulty in performing the spectroscopy in the gas phase of molecules of biological interest is the vaporization of these systems. Most biomolecules are non volatile at room temperature and thermally unstable at vaporization. In order to minimize the fragmentation and maximize the number density of the species, different methods have been devised, minimising the heating or the duration of the heating. Traditional methods, such as electrospray, widely used in mass spectroscopy cannot be employed here since they produce mostly multiply charged or protonated molecules. For spectroscopic investigations of cold neutral systems, we used here two different methods: thermodesorption and laser vaporization coupled with a supersonic expansion. We will see that among the different molecules studied, some families are very stable towards heating, thus they can be simply heated until a sufficiently high vapour pressure is reached for the experiment, without any decomposition. On the other hand, more fragile systems, such as hemin or heme or vitamin B_{12} are totally fragmented in the heating process and required more delicate vaporization methods. For these molecules, we have implemented a new evaporation system based on laser desorption.

2.2.1 Thermodesorption

The molecules under study (commercial products from Aldrich) are mixed with graphite powder and pressed in a hydraulic press under ~ 5 Ton to form a cylindrical pellet. The pellet is heated in an oven and the temperature is typically held at about 500 K. Graphite has

been used as a matrix material for studying fragile molecules, since it is unreactive and protects the heated compounds from oxidation. It is a good heat conductor, and does not vaporize until 1000°C. Immediately after evaporation, the molecule vapour is picked-up by a supersonic expansion of helium or argon. The supersonic expansion allows the immediate cooling of the molecular systems after vaporization.
The main advantages of this method are (i) it is very simple to use and (ii) the molecular beam is stable. This method has been applied to the vaporisation of a series of metallo-tetraphenylporphyrins and octaethylporphyrins. These two families of porphyrins are very robust and do not need excessive heating (~250°C).

2.2.2 Laser desorption

While thermodesorption method is efficient for introducing robust species into a molecular beam, it can not be used for the study of thermally unstable molecules, as is the case of most bio-molecules. In order to avoid thermal degradation of fragile systems, a very rapid heating is performed by means of laser desorption method. A short, pulsed laser, irradiation allows a very fast evaporation before the thermal degradation of molecules of interest. Furthermore, since most of laser energy is absorbed by graphite matrix rather than biomolecules, the photochemical degradation of molecules can be minimized (Piuzzi et al., 2000). To do this, a mixed graphite-molecule pellet is rotated at the tip of the nozzle of a pulsed valve. It is laser heated by a frequency doubled of a pulsed ns Nd:YAG laser, at 532 nm. The YAG spot is adjusted to match the orifice of the supersonic beam and changed in position, to take into account the consumption of the active material. The time delays for the valve opening and the firing of the desorption laser are controlled within a 10 μs range with a sub-microsecond precision, which allow a rapid cooling of evaporated molecules.
This evaporation method permits measurements for a large class of biomolecules, which cannot be studied by thermodesorption method. We shall compare here mass spectra of a thermally unstable bio-molecule, hemin, obtained by these two different vaporization methods, in Fig 4.
Hemin is the salt form of the heme group with a Cl axial ligand. This complex molecule is very fragile and its fragmentation pattern depends on the vaporization method. Figure 4 shows the comparison between the two mass spectra of hemin ionized by 400+800 nm laser pulses, obtained by using the thermo-desorption fig 4a or by laser desorption, fig 4b. In the spectrum obtained by thermodesorption, the parent ion is absent, when comparing with the mass spectrum obtained by laser ablation in figure 4b. This latter spectrum shows two main peaks at 651 and 616 amu, corresponding to the parent ion hemin $[Fe\ PP\text{-}Cl]^+$ and the fragment $[Fe\ PP]^+$. The next two intense peaks are respectively at 571 and 557 amu, corresponding to [Fe PP *minus* COOH]$^+$ and [Fe PP minus CH_2COOH]$^+$. The next four peaks are respectively at 512, 498, 484 and 472 uam. The peak at 512 corresponds to [Fe PP *minus* $CH_2(COOH)_2$]$^+$ and the difference of mass between these four peaks is *14 -15* amu corresponding to plucking the side -CH_2 or -CH_3 groups, off the (porphyrin) macrocycle. The fragmentation pattern observed in figure 4b is similar to the fragmentation reported by (Jones et al. 1994), using laser desorption. The peaks at lighter masses than 600 amu are broad and symmetric, while the peaks at 651 and 616 amu are narrow and asymmetric. The shape of the peaks around 651 and 616 amu is well reproduced by the isotopic distribution of the carbon, iron and chlorine atoms convoluted with the instrumental function corresponding to a mass resolution of 500. The observed difference in width between fragments is due to multiphoton photofragmentation processes, between the light fragments

and the intact [Fe PP-Cl] and [Fe PP]. In difference, since hemin is the parent molecule, still intact after evaporation, the fact that the shape of the peak of the [Fe PP] fragment is the same as that of hemin, is a strong indication that the Cl loss does not proceed through the ionization but is a result of the vaporization.

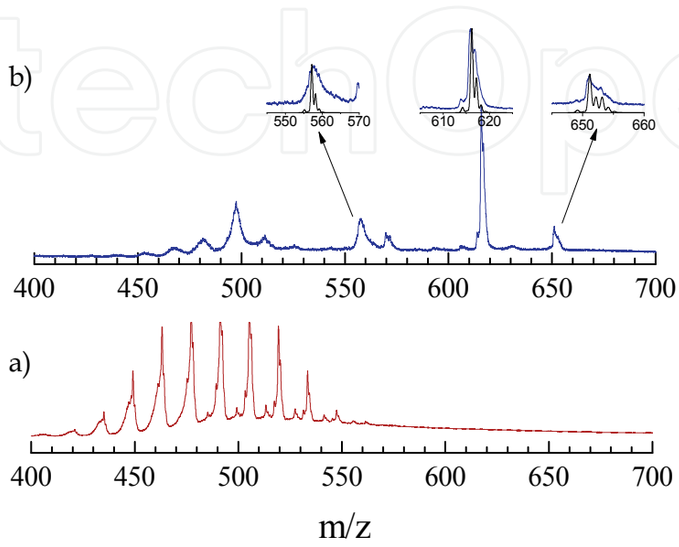


Fig. 4. Time of Flight mass spectra of hemin [Fe^{III} PP-Cl] following 400/800 nm photoionization integrated over all pump/probe delays. (a) [Fe^{III} PP-Cl] is evaporated using the thermodesorption technique (b) [Fe^{III} PP-Cl] is evaporated using the laser desorption technique. In the insert a simulation of the contours of the peaks at 651; 616 and 557 amu is obtained with the isotopic distribution of carbon iron and chlorine convoluted with the instrumental function corresponding to a mass resolution of 500.

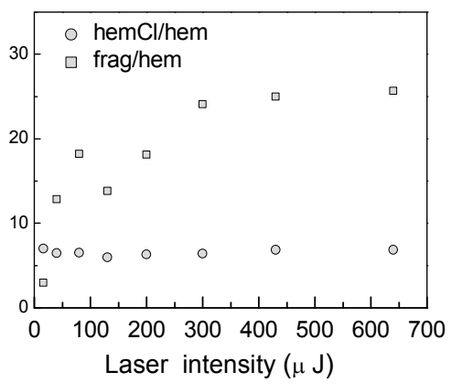


Fig. 5. Ratio of intensities of [Fe^{III} PP-Cl]$^+$ to [Fe^{II} PP]$^+$. The circles, ○, represent the ratio of the area under the [Fe^{III} PP-Cl]$^+$ mass peak to the area under the [Fe^{II} PP]$^+$ peak . The squares, □, represent the ratio of the area under the fragments of [Fe PP]$^+$ to the area of the [Fe PP]$^+$ peak. The x axis is the laser energy in μJ.

To verify this, we have varied the intensity of one colour ionization with 400 nm pulses. Fig 5 shows the ratio of the area under the hemin peak to the area under the [Fe PP] peak. This ratio is almost constant within experimental fluctuations, while varying the intensity of the ionisation laser over the broad range 16 μJ - 650 μJ. This can be ascribed to the ionisation of [Fe PP-Cl] and [Fe PP] with the same efficiency by three 400 nm photons. In difference, the ratio of the areas under other fragments (masses between 420 amu and 589 amu) peaks to the area of hemin, constantly increases while the laser intensity is increased; for the highest laser energies, this ratio goes to saturation.
We conclude that [Fe PP-Cl] and [Fe PP] are formed within the vaporization process. In difference, the peaks located between 600 amu and 420 amu increase strongly with the intensity of the ionising femtosecond laser. This observation, together with their large width below 600 amu, larger than the simulated isotopic distribution in figure 4b, indicates that these peaks result from ionic fragmentation by the absorption of multiple 400 nm photons in hemin. In such case, metastable ions are formed that decompose during their flight through the ionisation region providing a trailing edge in their time of flight.
It can be seen here that in the presence of thermally fragile bonds, the most efficient method to form neutral molecules in the gas phase is laser desorption. This method can be considered as relatively mild since it permits to observe the parent ion and fewer fragments as compared to the thermodesorption. However, the molecular beam is less stable, due to fluctuations of the laser intensity in the evaporation process, and the unavoidable inhomogeneities of graphite pellet.

3. Ultrafast relaxation of metalloporphyrins: from model molecules to biomimetic systems

A systematic study of the decay of an ensemble of model metalloporphyrins serves to delineate the electronic relaxation mechanism that will be applied to biomimetic porphyrin-like molecules.

3.1 Porphyrin models

Tetraphenyl- and octaethyl- porphyrin are among the most thermal and chemical stable porphyrin families. We characterised with these molecules the decay mechanism applied to the more complex parent biomolecules, which contain also a porphyrin cycle or its derivative. The study of such model systems thus provides a basis for interpretation of the evolution in the more complex real systems.
The relaxation dynamics of this family has been widely investigated in solution by different techniques such as transient absorption (Drain et al., 1998; Rodriguez et al., 1991[a]) up-conversion fluorescence spectroscopy (Gurzadyan et al., 1998) or resonant Raman spectroscopy (Petrich and Martin, 1989; Kumble et al., 1995). In the gas phase, very few works have been done on the spectroscopy of porphyrins. As an example, (Even et al., 1982), investigated the fluorescence excitation and they estimated the lifetime of the S_2 excited state in the picosecond time domain.

3.1.1 S_2-S_1 Internal conversion in zinc tetraphenyl porphyrin

We shall describe here a systematic study of the time evolution of electronically excited transition metal porphyrins. A central point is that we differentiate the case of filled shell, $3d^{10}$ metalloporphyrin, ZnTPP and porphyrins containing open d shell metals, in order to

interpret the effect of empty d orbital on the electronic relaxation of excited state metalloporphyrins.

The time-resolved photoelectron and photoion spectra have been investigated for ZnTPP (Sorgues et al., 2006). The photoelectron spectrum integrated over all angles and pump/probe delay is displayed in Fig. 6a. The photoelectron signals as a function of the delay between the pump and probe pulses are presented in Fig. 6b and Fig. 6c for low energy (0.2 eV) and high energy (0.8 eV) electrons, respectively. The photoelectrons of different kinetic energy presented different relaxation behaviours. For high photoelectron energies, the decay can be described by a short time constant of about 600 fs. On the other hand, at low electron energies, the photoelectron can be analyzed by two time constants, a short rise time with the same time constant (600 fs) followed by a plateau.

The photoelectron spectra reflect the dynamics of the transient excited state before ionization. This measurement provides additional information compared to the photoion signal that integrates this information. For example, we can differentiate photoelectrons resulting from different electronic excited states, thus their evolution can be followed separately, which is not the case in using the ion detection.

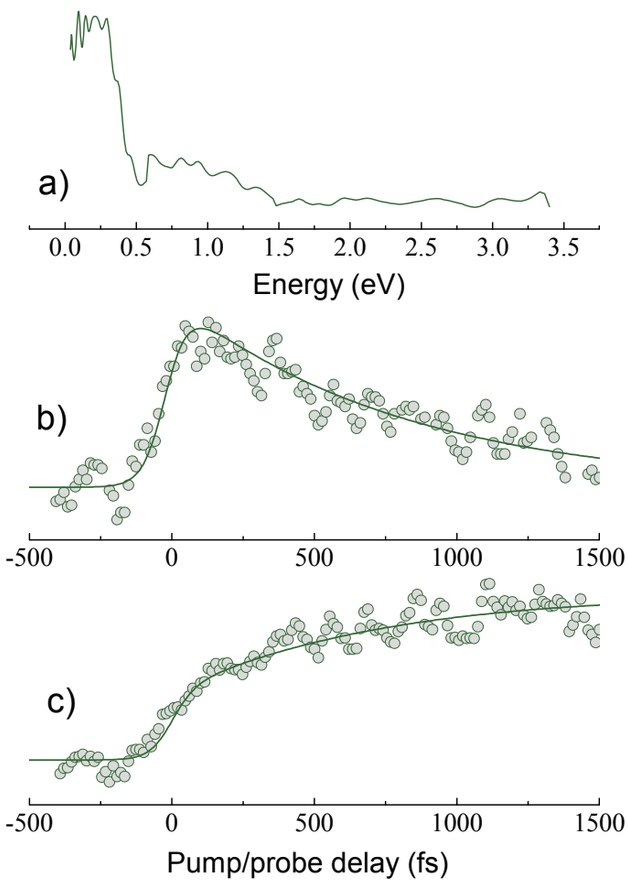


Fig. 6. a) Time integrated electron kinetic energy release (KER) spectrum of ZnTPP obtained under (400/266 nm) pump/probe conditions. Time evolution of the electron KER spectrum of ZnTPP b) at E=0.56 – 1.5 eV and c) at E=0.04-0.53 eV.

The relaxation of the S_2 excited state of ZnTPP can be interpreted in Fig. 7. The first decay of higher kinetic energy photolectrons corresponds to the ionization of resonantly S_2 excited state with a 600 fs lifetime. This decay corresponds to a rapid internal conversion from the S_2 to the S_1 excited state. At lower kinetic energy, the photoelectron time resolved profiles picture the evolution of the S_1 excited state. This decay shows a rapid growth with the same time constant as the decay of S_2, suggesting that S_1 state is directly populated from the S_2 state. This result indicates that S_2-S_1 internal conversion is the main relaxation pathway of S_2 excited state of ZnTPP, which is in agreement with solution measurements of the low fluorescence quantum yield of S_2 excited state of porphyrins. The kinetics and plateau reached for the S_1 state matches the kinetics observed in solution, with S_1 fluorescent with a nanosecond lifetime (Liu et al., 2006). The above deactivation scheme is pictured in figure 7 with the 600 fs time constant internal conversion connecting S_2 and S_1.

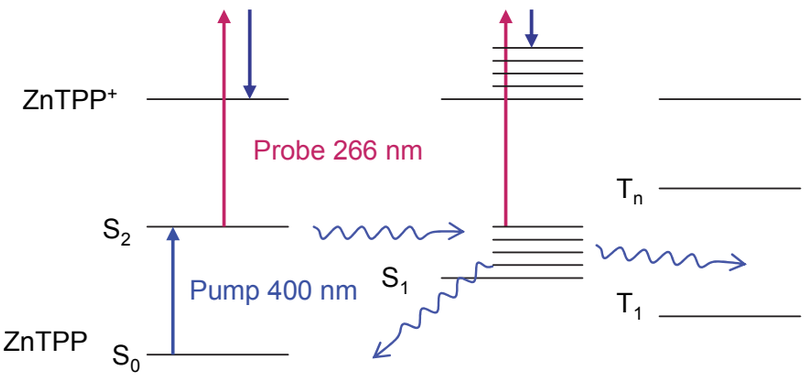


Fig. 7. Relaxation pathways of ZnTPP excited in the S_2 state.

To further assess the information provided by the photoelectron detection, the time resolved parent ion $[ZnTPP]^+$ signal is displayed in Fig. 8a. This decay can be simulated by two time constants, the first initial process of 600 fs, followed by a long-lived plateau, but here the rise of the S_1 state population is lost. This decay is the sum of the decay of the population of S_2 and the rise of S_1, the ionisation cross section of the latter one being lesser. These results show that the photoelectron and photoion detections are two complementary techniques to probe the dynamics of excited electronic states.

3.1.2 Decay of S_2 in transition metal porphyrins

We now examine the electronic relaxation of the S_2 state of a series of 3d-unfilled metal porphyrins (Sorgues et al. 2006). The time resolved ion signal of two porphyrins, CuOEP and NiOEP are presented in Fig. 8b and Fig. 8c, where the detection mass was centered at the parent ion mass. A similar relaxation profile was found for all the porphyrins hosting a d^5 to d^9 transition metal. The temporal evolution of these porphyrins consists of two exponential decay components. The results for the ensemble of metalloporphyrins studied are summarized in Table 1. As we can see in Table 1, a dramatic change has been observed for the lifetimes of porphyrins of 3d-unfilled metal as compared to ZnTPP. In fact, all the lifetimes of the S_2 excited states of these porphyrins are shorter by an order of magnitude. The first relaxation step occurs within the first 100 fs, while the second long-lived plateau of ZnTPP is replaced by a picosecond decay component. This observation indicates that these porphyrins of open d shell metals exhibit a different relaxation pathway from that of ZnTPP.

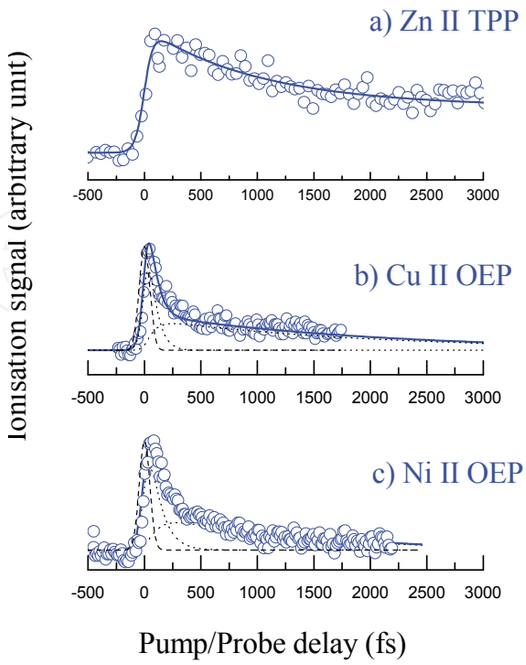


Fig. 8. Ion signals of (a) $[ZnTPP]^+$, (b) $[CuOEP]^+$ and (c) $[NiOEP]^+$ as a function of time delay between the pump (400 nm) and the probe (800 nm)

Metalloporphyrin	Configuration of the Metal	Lifetime of initial state S_2	Lifetime of relaxed state	σ_2/σ_1
Zn TPP	d10	600±50 fs	3 ns	1.0±0.1
FeIII OEP	d5	50±20 fs	2000±200 fs	0.33±0.05
RuII OEP	d6	80±20 fs	1200±100 fs	0.33±0.05
RuII TPP	d6	70±20 fs	1200±100 fs	0.33±0.05
CoII TPP	d7	80±20 fs	500±100 fs	0.11±0.05
NiII TPP	d8	50±20 fs	375±50 fs	0.20±0.02
NiII OEP	d8	100±20 fs	1200±100 fs	0.25±0.02
CuII TPP	d9	65±20 fs	2000±200 fs	0.075±0.025
CuII OEP	d9	65±20 fs	2000±200 fs	0.25±0.02

Table 1. Decay lifetime of the S2 excited state of different metalloporphyrins: M-TPP or M-OPE.

3.1.3 The porphyrin-to-metal charge transfer model as driving mechanism for the relaxation of S_2

The nature of the ultrafast dynamics of these porphyrins containing 3d-unfilled metal is detailed in Fig. 9. As we showed in previous paragraph, the first 600 fs relaxation step of ZnTPP was attributed to the S_2-S_1 internal conversion. This channel can be excluded in the case of porphyrins of transition metals since this relaxation mechanism is centered on the porphyrin, its decay rate would depend only on the porphyrin macrocycle and not on the

nature of the central metal. Indeed when comparing the evolution of an octaethyl and tetraphenyl transition metal porphyrin one finds no difference. Since there is such a difference between non transition metal (Zn) and transition metal porphyrins, the mechanism must be ascribed to the coupling of the porphyrin with the metal.

The S_2 excited state is relaxed to a ring to metal charge transfer state, as we show now, owing to the presence of available empty d orbital of transition metal. This is the result of the following discussion. Once S_2 is excited, its population can, in principle, cascade through several electronic states lying between S_2 and the ground state via one of the following mechanisms:

i. Relaxation to the S_1 state.
ii. Relaxation to a charge (ē) transfer state, metal-to-porphyrin.
iii. Transfer of the excitation from the ring $^1(\pi,\pi*)$ to a metal ($d,d*$) excited state .
iv. Relaxation to a triplet state located on the porphyrin $^3(\pi,\pi*)$.
v. Relaxation to a ring-to-metal charge (ē) transfer state.

Channel i) was excluded above since the associated decay rate would depend only on the porphyrin modes and not on the nature of the central metal, Zn or transition metal. In this case the decay times would be similar for Zn and transition metals but they are found to be strikingly shorter for transition metals. In addition, photoelectron spectra of relaxed Zn porphyrin and transition metal porphyrins greatly differ, indicating a different relaxed excited state. The detected signal (ionisation efficiency) of the relaxed state, as a consequence, also differs as shown in Table 1.

Channel ii) is improbable since it does not occur for ZnTPP where Zn could transfer an electron to the porphyrin cycle. Also, strictly the same evolution is observed for Fe^{II} or Fe^{III} protoporphyrins (see below). If a metal-to-porphyrin mechanism was involved, the withdrawal of an electron from Fe^{III} would be extremely improbable.

Channel iii) seems inefficient since it involves a double change in the electron configuration. Also it can be viewed as an excitation transfer from the porphyrin cycle to the metal through a Förster type mechanism (Förster, 1948). This dipole-dipole interaction process is highly improbable due to the bad overlap between the ππ* excitation on the porphyrin and the dd* forbidden transition of the metal.

Channel iv) where the presence of a metal flips the spin of the macrocycle electrons in a time less than 100 fs, seems highly improbable. However final triplet states after a longer evolution are likely triplet states as in copper prorphyrins.

Hence, by exclusion of the channels involving the porphyrin i), the (d,d*) states of the metal iii), and the metal to porphyrin states ii), the most probable relaxation pathway from the S_2 excited state is the formation of a ring to metal charge transfer state v). In this case, the metal must have a vacant *d* orbital with suitable energy, in order to accept the charge. This the case for transition metals up to copper, as pictured in figure 9. It is interesting to note that the addition of an electron acceptor group on the prophyrin ring is likely to channel electrons away from it. Rodriguez et al. (Rodriguez et al., 1991[b]) have observed the quenching of the fluorescence, hence the rapid decay of the S_1 state of the free base porphyrin substituted with a quinone group, which they correlate with a charge transfer from the porphyrinic cycle to the quinone. In addition, charge transfer is facile between the porphyrin and the metal and due to their respective low ionisation potential and high electron affinity. This porphyrin-to-metal CT mechanism is further supported by calculations on Ni porphyrin (NiTPP) (Patchkovski et al., 2004) where many low lying CT states are found, the lowest being of porphyrin-to-metal character.

3.1.4 Further evolution of the charge transfer state

This rapid charge transfer (partial or complete) induces a direct mechanism through a conical intersection, because only a rapid wavepacket motion can connect the potential energy surfaces of S_2 and the charge transfer surface within this 100 fs time domain. This charge transfer is followed by retrodonation to the porphyrins from one low lying d orbital to the empty π orbital on the prophyrin, thus preparing a (d,d*) state localized on the metal (Fig.9). The further relaxation of (d,d*) state occurs in the 10 ps range which is relatively long lived in our detection conditions. In conclusion, the porphyrin-to-metal CT state is only a transient state that plays an important mediating role in the overall relaxation of these metalloporphyrins. On the other hand, if faster relaxation processes come at play, this relaxation mechanism can be superseded.

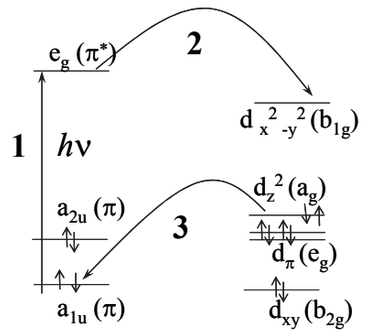


Fig. 9. Mechanism of the relaxation pathway of the S_2 excited state of transition metals with empty d orbitals.

3.2 Hemin: iron protoporphyrin IX

We have shown in the previous paragraph that the time evolution of model porphyrins follows an initial charge transfer mechanism. Here, with the preceding model, the time evolution of gas phase excited of iron III protoporphyrin chloride, (hemin, $Fe^{III}PPCl$), and iron II protoporphyrin (heme $Fe^{II}PP$), is analysed in the same terms and compared to the results of the zinc protoporphyrin. This latter system, owing to the lack of free d orbitals on the metal site is unable to accept an electron at this location, as for the model ZnTPP.

The parent ion of hemin can only be observed in using laser desorption. In particular, our evaporation method allowed (serendipitously) detecting simultaneously $Fe^{II}PP$ and $Fe^{III}PPCl$, in a single experiment (Ha-Thi et al., 2010) .

The time resolved ion signals of hemin $Fe^{III}PPCl$ and heme $Fe^{II}PP$ are represented in Fig. 10a and Fig. 10b, respectively. The time evolution of these two molecules is very similar and can be analyzed by a three step sequential deactivation process after excitation. The ultrafast initial decay on the order of 50 fs is followed by a second relaxation process of 250 fs.

According to the relaxation mechanism derived for the transition metal porphyrin models, a first transient is formed, a CT state, within 50 fs. The model mechanism applies well here since both hemin and heme undergo the same transient behaviour, i.e. through the same porphyrin to metal transfer. The second decay component, 250 fs can be undoubtedly attributed to the relaxation of this charge transfer state leading to the formation of a dd*

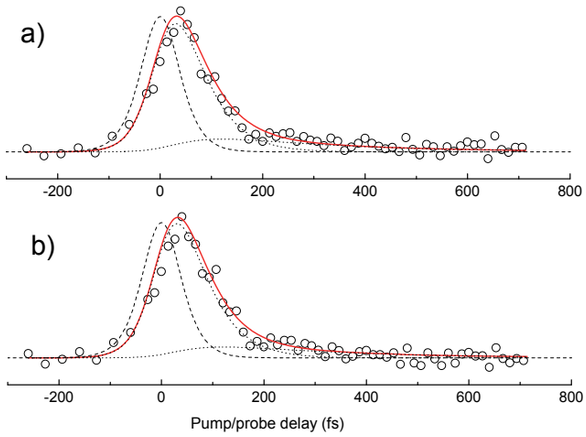


Fig. 10. Time evolution of hemin [Fe PP Cl], [Fe PP], while scanning the pump/probe delay (400/800 nm) (a) recorded at the mass of parent molecules $[Fe\ PP\ Cl]^+$. (b) The observation is set at the mass of $[Fe\ PP]^{+\cdot}$ The experimental points are fitted by the solid line following a three level model. The contribution of each component is represented by dotted curves; the dashed curve indicates the cross correlation of the pump and probe pulse

excited state by a retrodonation of a metal electron of lower energy to the ring (see figure 9). In solutions, (Ishizaka et al., 2009), studying the myoglobin systems (FeMb), have concluded from the transient absorption spectra of $Fe^{II}MbO2$ and $Fe^{III}metMb$, that the product detected at 600-700 nm, is similar to the absorption band of the porphyrin cation. This is in accordance with a porphyrin-to-metal charge transfer into the available empty d orbital of iron, since only the $porphyrin^+$ ring has oscillator strength. Similarly, these authors observed a relaxation lifetime of 250 fs for this charge transfer state.

The main difference in hemin with the previous model system is a new decay channel introduced by the porphyrin structure of hemin and heme: the competition that comes into play for the decay of the excited state S_2. It is seen, by studying ZnPP, that efficient S_2-S_1 internal conversion takes place and is extremely rapid (65 fs). The fact that the internal conversion and the deactivation via the charge transfer mechanism have a very similar relaxation rate means that the 65 fs decay of S_2 in hemin and heme is probably a convolution of these two processes all leading to CT. However, the important information is the outcome of this relaxation since in a one electron picture, as showed in figure 9, the excited S_1 state is also of π^* nature leading to the CT state, the route to the CT state being in this case less direct from S_2.

In conclusion, the charge transfer from the porphyrin to the vacant d orbital at the transition metal site, is the key event in the relaxation for both compounds. This relaxation is very fast and is not affected by the presence of the chlorine atom, which remains spectator in the relaxation and is not dissociated from the heme group.

3.3 Vitamin B_{12}

Here, we discuss the gas phase ultrafast electronic relaxation in another system, vitamin B_{12}, cyanocobalamine (figure 11) in light of the preceding mechanism. Vitamin B_{12} is an essential human nutrient and plays a key role in the living cell, affecting DNA synthesis and regulation. In these processes the CN ligand to cobalt is exchanged for a methyl or hydroxyl group. The investigation of the photodissociation and the related electronic relaxation is examined here with the background of the previously mentioned systems.

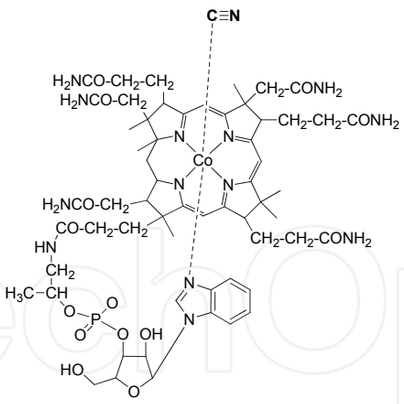


Fig. 11.Vitamine B_{12} $C_{63}H_{88}$ Co $N_{14}O_{14}P$.

The behaviour of the excited states of cyanocobalamine has been investigated in solution (Harris et al., 2007; Shiang et al., 2006). Recently we have reported, the first observation of the time evolution of vitamin B_{12} in the gas phase (Shafizadeh et al., 2008). Vitamin B_{12} is formed by a cobalt III atom coordinated in the pocket of a corrin. The corrin system is similar to the porphyrin ring except for one missing bridging methane (CH_2) and its partial saturation. The cobalt ion of the vitamin B_{12} is in a six-coordinate state, with four nitrogen atoms of the corrin ring and the two axial ligands, a cyano (-CN) and a dimethylimidazole.
The time evolution signal of vitamin B_{12} obtained following an excitation at 400 nm, is represented in Fig. 12a, detecting the parent ion. The vitamin B_{12} signal is characterized by an ultrarapid 100 ± 30 fs decay, followed by a longer component, of picosecond time duration. This behaviour is viewed in comparison with the above mentioned CoTPP Fig 12b (see paragraph 3.1.2…) which shows a very similar decay profile.

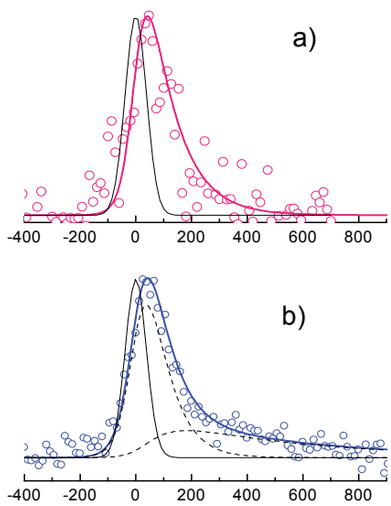


Fig. 12. Time evolution of vitamin B_{12} (a), while scanning the pump/probe delay (400/800 nm) compare to the time evolution of CoTPP (b). The experimental points are fitted by the solid line following a three level model. The contribution of each component is represented by dotted curves; the dashed curve indicates the cross correlation of the pump and probe pulse.

As analysed for model metalloporphyrins, the initial decay of B_{12} excited at 400 nm is assigned here to the relaxation to a porphyrin-to-metal charge transfer state, from a state that is likely S_2. However, the initial excited state is less well defined as in the case of more symmetric porphyrin molecules, like CoTPP. The subsequent picosecond decay can be interpreted in the same scheme as a retro-donation to the porphyrin, from a low d orbital of the metal. This second decay can be comparable with transient absorption measurements in condensed phase by Shiang et al. (Shiang et al., 2006).
Concerning the metal-ligand bond, excitation of CN-ligated cobalt does not lead to the dissociation of Co-CN bonding in the vitamin B_{12}, consistently with the high affinity of the CN to the Co^+ metal ion.

4. Conclusions

A new experimental approach for the exploration of the electronic relaxation of fragile excited biomimetic molecules allows studying these systems in the gas phase without degradation.
Here, the ultrafast relaxation of the second electronically excited state of metalloporphyrins of $\pi\pi^*$ nature is analysed. It is showed that the mechanism is triggered by an ultrafast initial electron transfer from the porphyrin to the central metal by a comparative study of many systems. Metalloporhyrins of increasing complexity have been studied from model tetraphenyl porphyrins hosting several transition metals, to more complex biomimetic ones: Fe protoporphyrin IX (heme) and vitamin B_{12}. The initial step of relaxation leads to an ultra fast porphyrin to metal charge transfer. This CT seems to be the doorway to the relaxation process of these compounds. In all systems studied here, the charge transfer direction is always from the porphyrin ring to metal. Once the CT state is reached, the time evolution varies from one species to other. In the case of nickel tetraphenyl porphyrins, the (d,d) state is reached. In the case of iron porphyrins the CT relaxes to the ground state as is the case for myoglobin (Kholodenko et al., 2000). The similarity between the solution and gas phase shows that the electronic relaxation properties of the heme group reflect that of hemoproteins and can serve as a biomimetic model.
This gas phase study paves the way for a series of investigations on ligated systems and possibly linked to small proteins. In this respect we have initiated the study in the gas phase of 'picket fence' porphyrins, i.e. models for the heme protein environment with simpler proteins, in order to study their time resolved photodissociation, the departure of the labile ligand.

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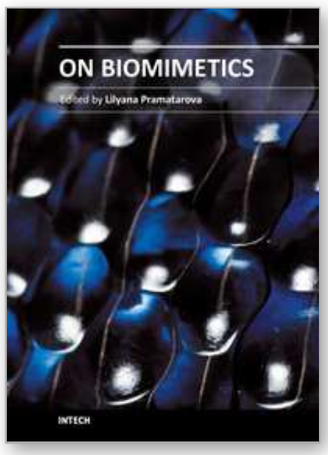
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Bio-mimicry is fundamental idea â€˜How to mimic the Natureâ€™ by various methodologies as well as new ideas or suggestions on the creation of novel materials and functions. This book comprises seven sections on various perspectives of bio-mimicry in our life; Section 1 gives an overview of modeling of biomimetic materials; Section 2 presents a processing and design of biomaterials; Section 3 presents various aspects of design and application of biomimetic polymers and composites are discussed; Section 4 presents a general characterization of biomaterials; Section 5 proposes new examples for biomimetic systems; Section 6 summarizes chapters, concerning cells behavior through mimicry; Section 7 presents various applications of biomimetic materials are presented. Aimed at physicists, chemists and biologists interested in biomineralization, biochemistry, kinetics, solution chemistry. This book is also relevant to engineers and doctors interested in research and construction of biomimetic systems.

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