

Electron detachment of super-excited porphyrin anions in an electrostatic ion storage ring

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Abstract. To study the photoexcitation and subsequent reactions of large molecular ions, anions of 5,10,15,20-tetraphenyl-21H,23H-porphine, which is a typical metal-free porphyrin, were produced and stored in an electrostatic ion storage ring at the Tokyo Metropolitan University. The circulating ions were merged using a pulsed laser, resulting in the production of super-excited anions, which eventually yielded neutral species. The decay profile deviated considerably from t^{-1} behavior, depending on the laser fluence and excitation wavelength.

PACS. 33.80.Eh Autoionization, photoionization, and photodetachment – 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states

1 Introduction

Porphyrins are undoubtedly one of the most important organic molecules in various fields of science, partly because of the interest in their biological activities and the ability to control their molecular properties using systematic substitution or polymerization. To date, most experimental studies have been conducted in solution or the solid phase, and few gas-phase studies have been performed [1], especially for ions isolated in vacuo [2].

Despite the experimental difficulty, which is mainly due to the limited target density, the ion data obtained in vacuo provide important information because the data are characteristic of isolated porphyrins, and are free from solvent effects, contamination, or the complications associated with porphyrin aggregation that may occur in solution [3]. The first electrostatic ion storage ring made in Aarhus proved to be a powerful tool for studying heavy ions [4]. Subsequently, several electrostatic rings have been constructed or are under construction.

The ring constructed at Tokyo Metropolitan University, the TMU E-ring, is dedicated to reaction and spectroscopic studies of cold ions [5]. The configuration of the ion optics is essentially the same as at the ring at the High Energy Accelerator Research Organization [6], and all the electrodes can be cooled with liquid nitrogen to circulate cold ions. A laser desorption (LD) ion source attached to the ring can be used to produce positive and negative porphyrin ions. In this study, anions

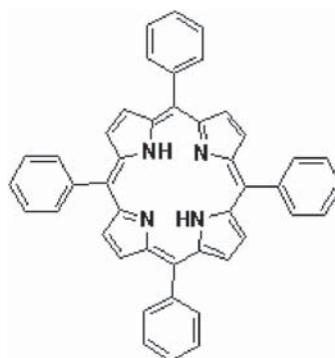


Fig. 1. Molecular structure of H₂TPP.

were stored in the TMU E-ring, and laser-merging experiments were conducted to examine the delayed process of electron detachment, or dissociation, of a typical metal-free porphyrin molecule, 5,10,15,20-tetraphenyl-21H,23H-porphine (hereafter H₂TPP). The molecular structure of H₂TPP, C₄₄H₃₀N₄, is shown in Figure 1.

2 Experiments

A schematic drawing of the ring and ion injection system is presented in Figure 2. The LD ion source comprising electrodes for ion extraction and a rotating sample holder was set in a chamber under a high voltage (–14 kV), and was connected to the TMU E-ring by an accelerating tube and ion transport system. H₂TPP powder was dissolved in CHCl₃, and the solution was put in the sample holder. An

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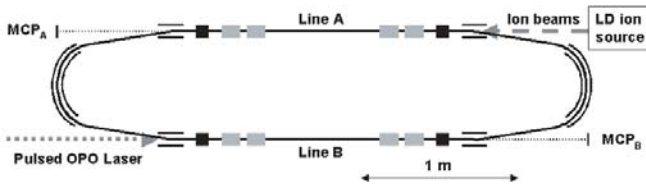


Fig. 2. Schematic view of the TMU E-ring and relevant instruments.

H₂TPP cast film prepared in this way was desorbed by the fourth harmonic output of an Nd:YAG laser. The anions were extracted on applying a pulsed high voltage (8 μ s, -1 kV) after 5 μ s irradiation. The 5 μ s delay propelled the energetic ions away from the acceleration area. Since the voltage in the ion source chamber was -14 kV, the anions were accelerated to a total kinetic energy of 15 keV. Then, the anions passed through an adjustable aperture, typically 2 mm in diameter, and were injected into and stored in the ring. Unlike other electrostatic rings, the TMU E-ring does not have a mass analyzer in the beam injection system. Therefore, various ions were stored in the ring simultaneously. For some purposes this is advantageous, although in this study, coexisting ionic species, such as fragments or clusters, were not wanted. To eject such undesirable ions, the anions with different circulating frequencies from H₂TPP were dumped using a pulsed electric field synchronized with H₂TPP. The details of this ion beam “purification” procedure will be given in a subsequent publication [7].

The pressure in the ion source was about 1×10^{-6} Pa during operation, whereas the pressure in the ring was kept at $3\text{--}4 \times 10^{-9}$ Pa by virtue of the three-stage differential pumping system. Under typical operating conditions, the number of ions in the bunch initially stored in the ring was on the order of 10^4 .

After storage for 60 ms, when the bunched structure of the beam was lost completely (i.e., when a DC beam was circulating), a pulsed optical parametric oscillator (OPO) laser pumped using an Nd:YAG laser was merged in straight sections known as “Line B”. Neutral species generated during circulation, which likely arose via electron detachment, were detected with microchannel plates (MCPs) at the ends of two straight sections of the ring. Hereafter, the detectors at the ends of the lines A and B are called MCP_A and MCP_B, respectively.

MCP_B could detect both prompt and delayed processes, whereas MCP_A only measured the delayed process, since ions had to survive for at least a half revolution in the ring to reach MCP_A. Conversely, the signals from MCP_A were free from scattered laser light, whereas care had to be taken when MCP_B was used. In fact, the merged laser beam was tilted slightly when MCP_B was applied, and the laser fluence was adjusted carefully to eliminate any background signal. In this study, the delayed processes were studied mainly using MCP_A to measure the neutral yield enhanced by laser merging as a function of the wavelength and fluence of the OPO laser.

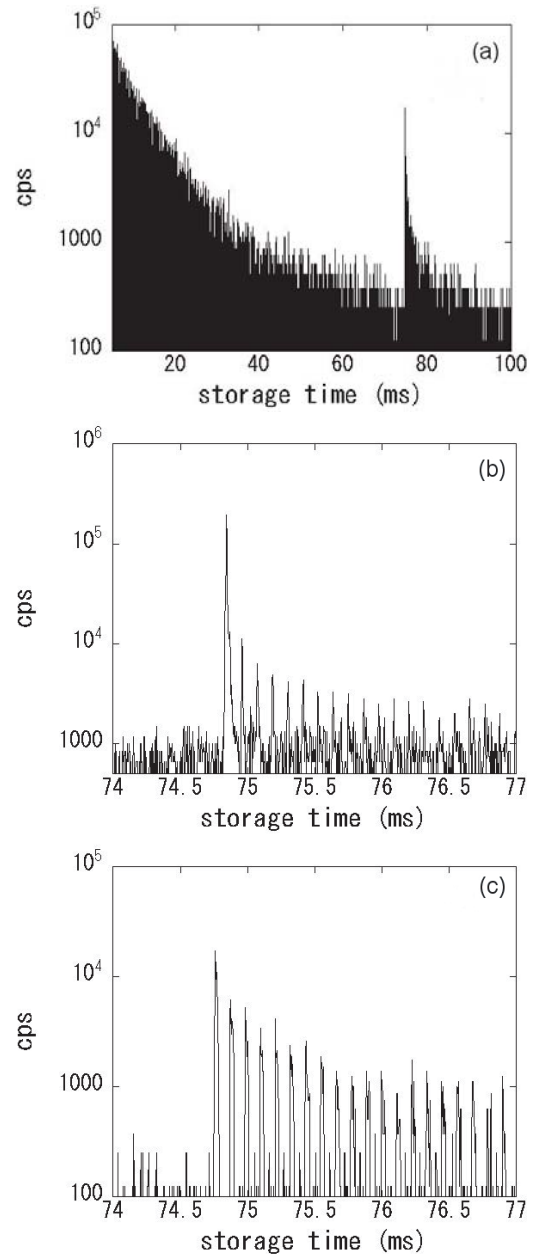


Fig. 3. The neutral yield as a function of the ion storage time. (a) For storage up to 100 ms, detected using MCP_B; the plot from 74 to 77 ms on an expanded scale detected using (b) MCP_B and (c) MCP_A.

3 Results and discussion

The signals of the neutral species detected using MCP_B for storage times for up to 100 ms, with laser merging at a storage time of 75 ms, are shown in Figure 3a. Three processes are responsible for the formation of neutrals. The signals detected just after injection are attributed mainly to auto-electron detachment or the delayed dissociation of “hot” anions. The rapid decay of these signals is due to the preferential reduction of the hot anions, which results in cooling of the beam. Eventually, the relative importance of a minor process forming neutrals increases; this process,

collision-induced detachment (or dissociation) with residual gases, is the dominant source of neutrals after storage for 60 ms. The storage lifetime of H_2TPP anions was about 7 s under the optimum conditions. The third source is laser-induced electron detachment. As shown in Figure 3a, the yield of neutral particles increased dramatically with the laser irradiation at 75 ms. Since the electron affinity of H_2TPP is less than one-photon energy of the laser used in this study, electron detachment using one-photon absorption is possible energetically. The laser fluence was kept below the saturation level, so that the depletion of the yield of neutrals after laser irradiation was not marked, unlike the laser merging experiments using adenosine 5'-monophosphate reported by the ELISA group [8].

Closer inspection of the laser-induced process enables the resolution of the weaker peaks emerging every 113 μs after the main peak, as shown in the figure on an expanded scale (Fig. 3b). These are due to neutral particles detected several revolutions after irradiation. The delayed components are more than one order of magnitude smaller than the prompt component. The prompt component is reasonably assigned to direct photodetachment, whereas the delayed signals are due to electron detachment or the dissociation of super-excited anions, which have sufficient internal energy for decomposition. Considering the timing uncertainty arising from the merging beam configuration, the delayed process may also contribute to the first “prompt” peak, whereas the subsequent signals are due solely to the delayed process.

To study the delayed process in more detail, MCP_A was used to detect neutral signals. A typical result is shown in Figure 3c, in which the peak width of the laser-induced signals is about 30 μs , which is consistent with the fact that the straight section for laser merging is about 30% of the ring circumference.

It is generally agreed that delayed processes are statistical; that is, detachment (or dissociation) takes place after the excitation energy is redistributed to all the vibrational modes. Therefore, the neutral yield should be governed by the total excess energy of anions, namely, the sum of the initial internal energy (before photoexcitation), E_0 , and the absorbed photon energy, $n h\nu$, where n is the number of photons absorbed by the anion. Since H_2TPP is a large molecule, E_0 is very large, even when the autodetachment rate is very small. In other words, the energy spread of $E_0 + n h\nu$ is quite large. As reported by the ELISA group, a broad distribution of the initial internal energy results in the decay process being fitted to a t^{-1} function [9–11]. This means that the decay rate itself is a function of the laser fluence, since the number of absorbed photons changes, whereas the slope in the log-log plot is independent of the fluence.

The log-log plots of the areal intensity of each peak against the time after irradiation with the 600 nm laser, obtained for various laser fluences, are shown in Figure 4a. At 16.8 mJ/cm^2 , the data can be fitted with a straight line, indicating that the power law is also valid. However, the slope deviates considerably from -1 , depending systematically on the laser fluence. That is, lowering the fluence

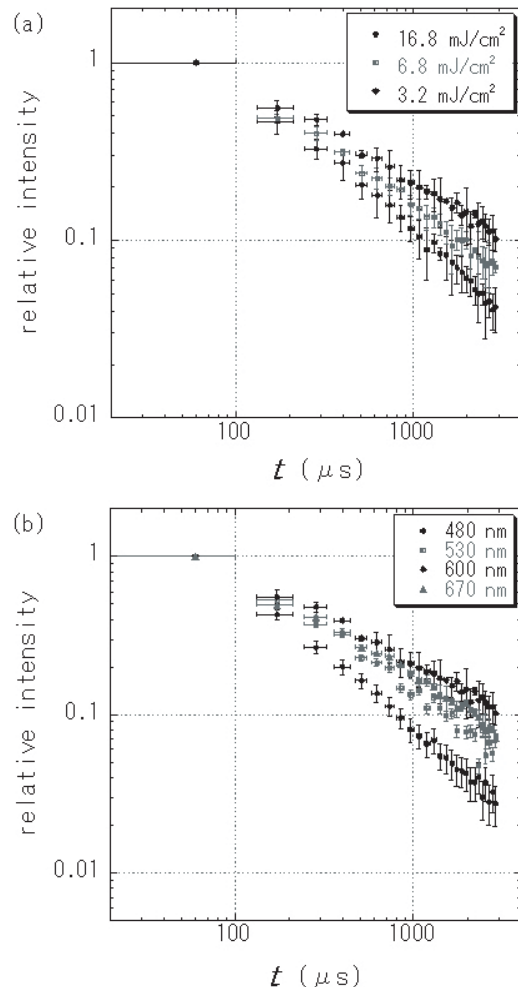


Fig. 4. Log-log plots of the relative neutral yield, normalized using the first peak, versus the time after excitation. (a) The laser fluence was varied while the wavelength was fixed at 600 nm. (b) The excitation wavelength was varied while the laser fluence was fixed at 3.2 mJ/cm^2 . The horizontal error bars are estimates of the reaction time after laser merging, and the vertical error bars indicate the square root of the number of accumulated events.

produces a gentle slope, which is about -0.5 at a low fluence. This indicates that the super-excited anions do not populate various internal energies uniformly, at least if the contribution of multiphoton excitation is small.

The decay also depends on the excitation wavelength, as shown in Figure 4b. At 480 nm, the slope is close to -1 , while at longer wavelengths, the plots deviate from t^{-1} behavior. The trend is less systematic, although it shows strong absorption at 480 nm.

If the target ions were not very hot, the decay profile of the delayed process induced by photoexcitation would not be characterized by t^{-1} dependence. In fact, the delayed processes induced by the photoexcitation of porphyrin and fullerene ions prepared using an electrospray source do not show the t^{-1} decay [2, 12]. In this case, however, the initial decay of the ions extracted from the LD source can be fitted to t^{-1} decay (not shown), indicating that the ions

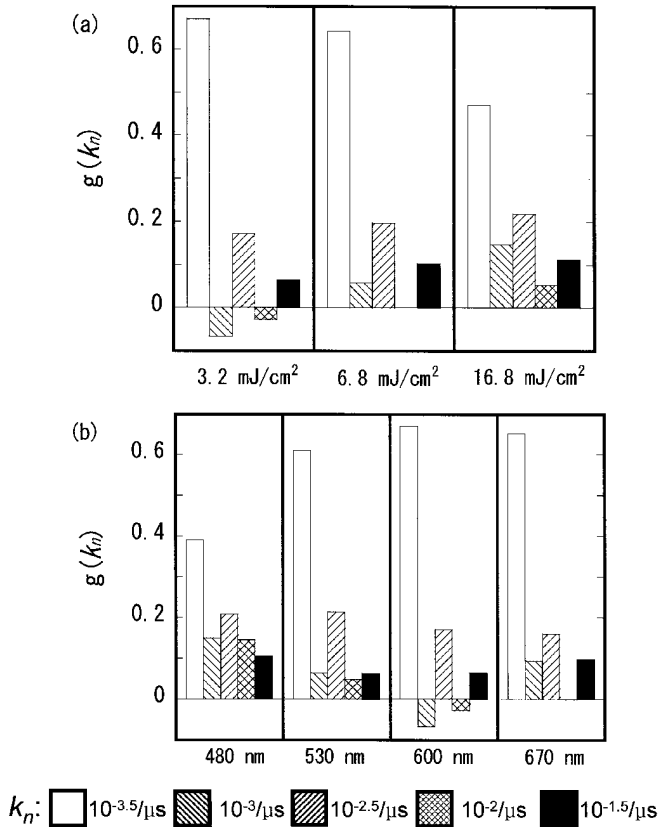


Fig. 5. The estimated populations of photoexcited H₂TPP anions with decay rate constants of $10^{-3.5}$, 10^{-3} , $10^{-2.5}$, 10^{-2} , and $10^{-1.5} \mu\text{s}^{-1}$. The negative values for a population are due to the sparsity of the energy level, which is an artificial limitation. (a) The distribution functions obtained with various laser fluences, estimated from Figure 4a. (b) The distribution functions obtained with various wavelengths, estimated from Figure 4b.

are hot, and the storage time was not sufficiently long for radiative cooling.

It will be helpful to determine how the super-excited states populate the accessible energy range. Provided that the neutral yield, $I(t)$, is given by the sum of decay components, the observed decay can be fitted by the function:

$$I(t) \propto \int k(E)g(E)e^{-k(E)t}dE, \quad (1)$$

where $g(E)$ is a distribution function and $k(E)$ is the rate constant. In this study, the continuous variable k is replaced by five k_n s, since the number of data points is limited. That is, the decay was fitted by the function:

$$\sum_{n=1}^5 k_n g(k_n) e^{-k_n t}, \quad (2)$$

where $g(k_n)$ is a distribution function and k_n is the rate constant given in μs^{-1} . The validity of this approximation is shown by fitting the decay obtained at 480 nm, which shows dependence close to t^{-1} . The distributions of $g(k_n)$

obtained for various laser fluences and wavelengths are shown in Figures 5a and 5b, respectively.

Although the distributions of $g(k_n)$ are somewhat scattered, at least they are not populated equally. As Figure 5a shows, the longer lifetime component is enhanced at lower fluences. The wavelength dependence of $g(k_n)$ is also shown in Figure 5b. At 480 nm excitation, the dependence of $g(k_n)$ on k_n is relatively weak, which is consistent with the prediction based on the broad distribution of energy. In contrast, the results obtained for other wavelengths show a marked preference for smaller k , which corresponds to a small excess energy of the anions.

In conclusion, the results indicate that the energy distributions of “hot” ions produced by the photoexcitation of “hot” or intact ions produced in a hot source under equilibrium conditions are distinguishable. To elucidate the relative importance of the photon energy and initial energy in the decay process, laser merging experiments involving longer storage times are now under way.

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