# Delayed Dissociation of Photoexcited Porphyrin Cations in a Storage Ring: Determination of Triplet Quantum Yields

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A technique is described wherein substituent-dependent excited-state properties of gas-phase porphyrins can be accurately quantified. Dissociation lifetimes of photoexcited porphyrin cations were measured in an electrostatic ion storage ring. From these data, upper limits for the triplet quantum yield of the following protonated porphyrins were obtained: protoporphyrin IX (0.63 ± 0.04), tetraphenylporphyrin (0.73 ± 0.03), tetra(*p*-methylphenyl)porphyrin (0.75 ± 0.03), and tetra(*p*-cyanophenyl)porphyrin (0.71 ± 0.03). The values compare well with those for porphyrins in solution.

## Introduction

Porphyrins are important in several areas of science, for example, in chemistry, geochemistry, and biology.[1] In particular, porphyrins play a significant role in many processes that involve the absorption of light, and as such, their excited-state properties are important. In one example pertinent to photobiology and photomedicine, it is well established that excited-state porphyrins can sensitize the production of singlet molecular oxygen.[2] The efficiency of this process depends on the porphyrin triplet state quantum yield, among other excited-state properties. Singlet oxygen is a reactive molecule that plays a significant role in mechanisms of oxidative degradation,[3] including those used to destroy a cancerous tumor in photodynamic therapy.[4] Therefore, experiments to characterize the excited-state behavior of porphyrins under a variety of conditions are seen to provide useful information.

Recently, we demonstrated that an electrostatic ion storage ring can be used to obtain information on triplet quantum yields of isolated porphyrin ions in vacuo after photoexcitation.[5] The instrument is unique in that it is possible to monitor transient ions with lifetimes as short as 10−100 $\mu$s, depending on the ion revolution time in the ring. In the experiments with porphyrins, two lifetimes were measured: (1) the lifetime with respect to the dissociation of vibrationally excited ions formed after internal conversion from the excited singlet state to the ground state ($S_1 \rightarrow S_0^* \rightarrow$ fragments) and (2) a longer lifetime due to the delay of dissociation by population of a triplet state ($S_1 \rightarrow T_1 \rightarrow S_0^* \rightarrow$ fragments). If fluorescence from the $S_1$ state is negligible, then the triplet quantum yield is obtained from the branching ratio between these two dissociation channels. Such measurements provide values that are characteristic of the isolated molecules free from solvent effects and with no molecular oxygen present to quench the excited states. These gas-phase experiments also preclude complications associated with porphyrin aggregation, which can occur in solution-phase experiments.[6−9] Finally, the experiment does not require a knowledge of triplet−triplet absorption coefficients. A limitation, however, is that the ionic systems should have dissociation lifetimes on the microsecond to millisecond time scales after photoexcitation.

In the current work, we have examined the photophysics of protonated protoporphyrin and three tetraarylporphyrin cations (Figure 1) upon 390 nm irradiation. To shed light on the possible dissociation channels, the ions were also subjected to collisions with helium in a separate experiment.

## Experimental Section

Two different experiments were carried out in our studies of porphyrin cations.

**Fragmentation Experiments.** The neutral, free-base porphyrins were dissolved in $CH_2Cl_2$/MeOH (1:1) and electrosprayed to produce the cations shown in Figure 1. The ions were accelerated to a kinetic energy of 50 keV (laboratory frame), and ions with the mass-to-charge ratio ($m/z$) of interest were selected by a magnet whose field strength could be varied. After collisions with helium, the product ions were analyzed with an electrostatic analyzer that scanned the kinetic energy of the fragment ions. A more detailed experimental description is given elsewhere.[10,11]

**Lifetime Measurements.** Lifetimes of photoexcited ions were measured with the electrostatic ion storage ring in Aarhus, ELISA (Figure 2).[12−14] Ions from an electrospray source were accumulated in a 22-pole ion trap in which they were thermalized by collisions with helium at room temperature. Ions were extracted from the trap after about 0.1 s, accelerated to a kinetic energy of 22 keV (laboratory frame), and those of interest selected with a bending magnet and injected into ELISA and stored. An ion bunch thus injected and stored contained about $10^4$ ions. Even though a multipole ion trap allows very gentle and efficient ion extraction, a small fraction of the ions were vibrationally excited in collisions with helium during extraction or in the region immediately after the trap. Metastable decay and collisions with residual gas in the ring led to the production

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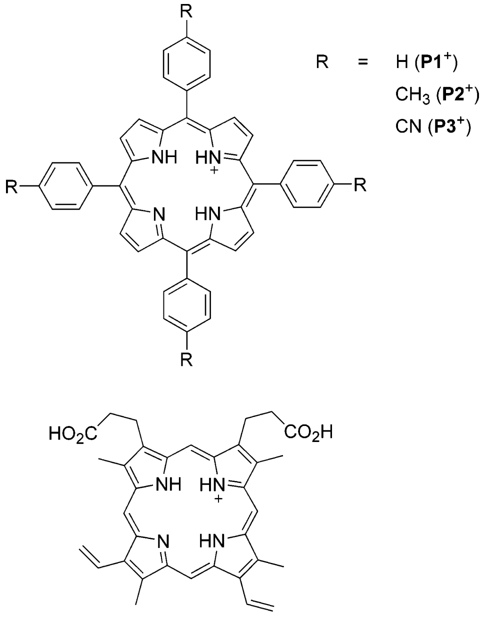

**pp**

**Figure 1.** Structures of the porphyrin cations under study.

of neutral fragments. Neutral fragments formed in the middle straight section of the ring on the side of the injection port and, subsequently ejected from the ring, were counted by a multichannel plate (MCP) detector (Figure 2).

After about 60 ms of storage time, the ions were irradiated with 390 nm light on the "back side" of the ring (Figure 2). A time delay of 60 ms ensured that all metastable ions produced in the injection process had decayed. The light source was a pulsed alexandrite laser (PAL101 from LightAge, Somerset, New Jersey). Its output was set to 780 nm, which was then frequency doubled to 390 nm. Experiments were performed with energies that were varied over the range of 0.1−1.3 mJ/pulse with an unfocused beam ~0.5 cm in diameter and a pulse width of about 30 ns (fwhm). The pulse repetition rate of the laser was 10 Hz, and each ion bunch was irradiated with only one laser pulse. Delayed dissociation of the photoexcited "hot" ions to form neutral fragments was again measured with the MCP detector. Because the first detection of fragments after laser irradiation is delayed by about half a revolution time in the ring, any rapid dissociation processes on the excited singlet state potential energy surface cannot be identified. Radiative de-excitation (i.e., fluorescence or phosphorescence) leads to "cold" ions that do not dissociate, and these processes are therefore not detected either.

## Results and Discussions

Fragmentation spectra obtained from high-energy collisions between protonated tetraarylporphyrin ions (P1$^+$, P2$^+$, and P3$^+$) and helium are shown in Figure 3. The principal dissociation channel is the loss of the aryl substituents from the porphyrin ring and the R group (CH$_3$ or CN) from the substituents of P2 and P3. These results compare well with photodissociation studies by Castoro et al.,[15] who showed that the photoexcitation of protonated tetrakis(4-pyridyl)porphyrin leads dominantly to the loss of C$_5$H$_4$N substituents from the porphyrin ring. In the case of pp (spectrum not shown), the loss of CH$_2$COOH ($\beta$ cleavage of the carboxymethyl group) is the lowest-energy channel.

Narrow peaks at half the mass-to-charge ratio of the parent ions are observed (denoted as $-$ e$^-$ in Figure 3) and are assigned to the doubly charged ions formed upon knocking out an electron in the collision. Assuming the ion interacts with a helium atom over a distance of about 10 Å, the interaction time is less than 10 fs (time of passage), which is shorter than the time of any vibrational period. Hence, the detachment process can be assumed to be vertical. Note that, from threshold measurements of Zubarev et al.,[16] ~12.8 eV is required to eject an electron from a gaseous porphyrin cation and it would thus take at least four 390 nm photons to photodetach an electron from the cation. Such a multiple-photon absorption process requires a high photon flux and is therefore not relevant in our ELISA experiment.

Unfortunately, we cannot determine which photofragments are formed in ELISA; only the yield of the resultant neutrals is measured. Thus, we assume that the fragments formed in the collision experiments are similar to those formed from statistical dissociation after photoexcitation.

In a separate experiment, the porphyrin cations were irradiated at 390 nm within the Soret band. The details of this transition have been described by Gouterman.[1] The decay kinetics of the ions after 390 nm photoexcitation were similar for all porphyrin cations studied, and a typical example is shown in Figure 4 for P2$^+$ decay. The spacing between the points is the ion revolution time (100 $\mu$s). In examining such decay data, it is important to recognize that the distribution of internal energy in the system will give a corresponding distribution in observed lifetimes. With this in mind, it is certainly clear that the data cannot be characterized by a single-exponential decay function. However, the data are reproduced reasonably well with a biexponential fitting function: $n(t) = \mathrm{d}N^*(t)/\mathrm{d}t = c_1k_1 \exp(-k_1t) + c_2k_2 \exp(-k_2t) +$ constant (Figure 4) where $N^*(t)$ is the number of excited ions at time $t$. The constant is the small background yield from collision-induced dissociation in the ring; this process takes place on a much longer time scale of seconds compared to the time scale of the decay of photoexcited ions.

To better understand events that give rise to fragments, the energy of the laser pulse was varied. With reference to the data in Figure 4, the first point in the time profile where the contribution from the long-lived decay component is negligible (i.e., signal recorded from dissociation 55 $\mu$s after photoexcitation) increases with pulse energy and asymptotically reaches a maximum (Figure 5). A fit to the low-energy points in Figure 5, where saturation does not appear to be a problem, indicates neither a linear nor a quadratic dependence on the energy $E$ (i.e., the data scale according to $E^{1.5}$). This suggests that, at these early times, ion fragmentation is a result of both one- and two-photon absorption. A similar treatment of the data that gives rise to the long-lived decay component indicates that, in this case, fragmentation may also have a contribution from two-photon absorption, though it is less important.

A biexponential fitting function was used to quantify all of the time-dependent decay profiles taken at different laser pulse energies, and the relative amounts of each of the two components were obtained. The fractions thus obtained for P2$^+$ are shown in Figure 6, where it is evident that the relative contribution of the short-lived component increases with an increase in pulse energy whereas the contribution of the long-lived component decreases. Extrapolation of the relative fraction of the long-lived component to zero pulse energy provides a branching ratio, $\gamma$, for these two components at the one-photon limit. For the data shown in Figure 6, the ratio determined is $0.79 \pm 0.03$.

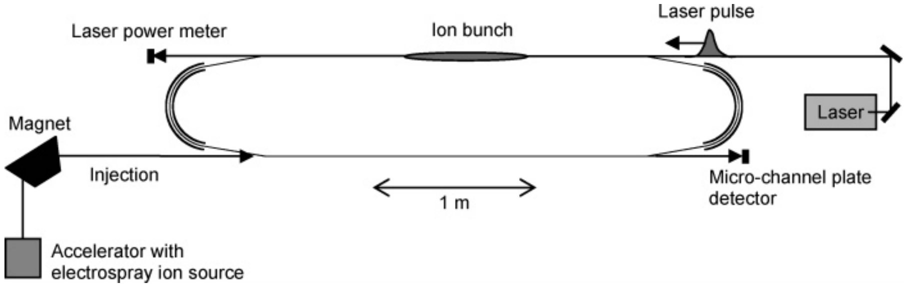

**Figure 2.** Schematic layout of the electrostatic storage ring ELISA showing ion injection and detection of neutrals by a microchannel plate detector on one side of the ring and a laser for excitation of the stored ions on the other side. A typical revolution time in the ring is 100 $\mu$s, and it therefore takes about 50 $\mu$s before the decay of ions photoexcited on one side of the ring is sampled on the other side.

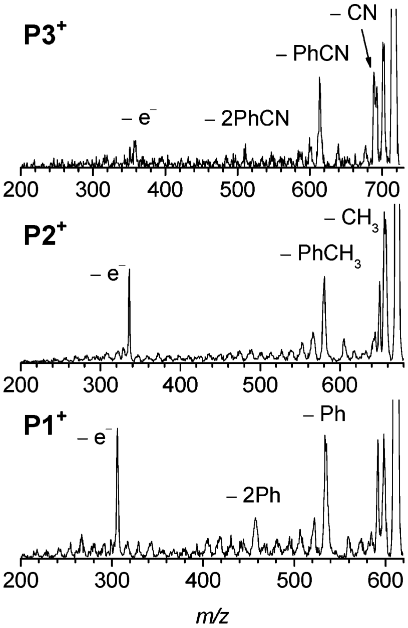

**Figure 3.** Fragmentation spectra for cations of P1, P2, and P3 after collisions with He. The translational energies in the center-of-mass frame are 325, 296, and 278 eV, respectively.

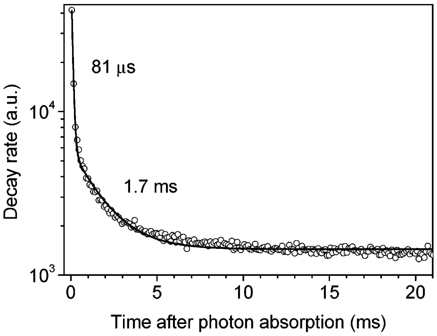

**Figure 4.** Decay profile for P2$^+$ after 390 nm irradiation (0.5 mJ/pulse). The ion revolution time is 100 $\mu$s, which is the spacing between the points. The solid line is a fit to the data assuming that two exponential functions characterize the decay. For these particular data, the respective time constants obtained were 81 $\mu$s and 1.7 ms.

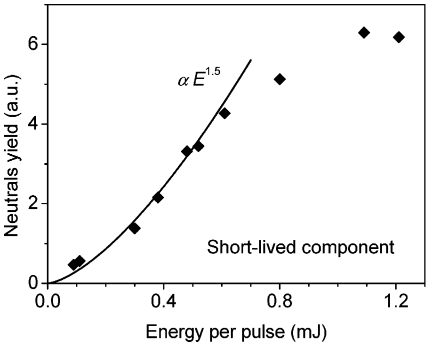

**Figure 5.** Yield of the first data point in the decay profile for P2$^+$ as a function of laser pulse energy $E$.

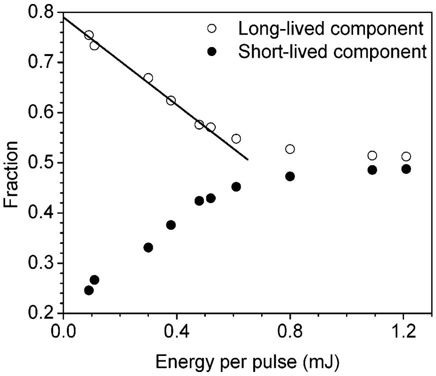

**Figure 6.** Relative amount of the long-lived and short-lived components for the decay of P2$^+$ as a function of the laser pulse energy. Extrapolation to zero energy gives a branching ratio at the one-photon limit of 0.79 ± 0.03 for this compound.

In the following text, we discuss our data in terms of the Jablonski diagram shown in Figure 7. Our interpretation is based on the thesis that, after excitation of the porphyrin to the $S_2$ state followed by internal conversion (IC) to $S_1$ within a few picoseconds,[17] dissociation occurs via two kinetically competitive channels. In one channel, IC followed by intramolecular vibrational redistribution, IVR, rapidly produces a vibrationally excited ion in the electronic ground state, $S_0$, in which the internal energy is distributed statistically among all degrees of freedom.[18] It is from this vibrationally excited state, $S_0$*, that dissociation occurs, and we infer that the fast component of our decay profiles corresponds to the lifetime of these hot ions. The process of intersystem crossing, ISC, from $S_1$ to the lower-lying triplet state, $T_1$, competes with $S_1 \rightarrow S_0^*$ internal conversion. In this case, the ions are "trapped" in the longer-lived $T_1$ state. Hence, there is a bottleneck in the production of $S_0$*, which in turn gives rise to the slow component in our dissociation decay profile. It is also kinetically possible that dissociation takes place from $T_1$ but with a lower rate than from the vibrationally excited ground state, $S_0$*. Although fluorescence from $S_1$ competes with both of these processes, it produces ground-state ions that are too cold to dissociate.

At high pulse energies, ions can absorb a second photon, either from $S_0$*, $S_1$, or $T_1$, to produce a state from which dissociation can occur more rapidly. These extra, energy-dependent rapid dissociation channels will then influence the number of ions that can "turn the bend" in ELISA and thus make it to the front side of the ring where neutrals are detected

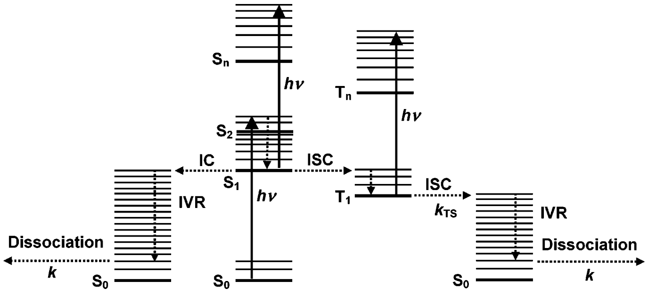

**Figure 7.** Jablonski diagram. IC = internal conversion, ISC = intersystem crossing, and IVR = intramolecular vibrational redistribution. The rate constant for statistical dissociation from the vibrationally excited electronic ground state is $k$. The rate constant for triplet-to-singlet intersystem crossing is $k_{TS}$. Initially, excitation occurs to S$_2$, but internal conversion to S$_1$ and IVR takes place within a few picoseconds. See the text for more details.

**TABLE 1: Statistical Dissociation Lifetimes $\tau$ (= 1/$k$), Triplet-State Lifetimes $\tau_{TS}$ (= 1/$k_{TS}$), and Triplet Quantum Yields $\Phi_T$ of Porphyrin Cations in Vacuo**

| | P1$^+$ | P2$^+$ | P3$^+$ | pp$^+$ |
|---|---|---|---|---|
| $\tau$/ms | 0.08 ± 0.02 | 0.09 ± 0.02 | 0.07 ± 0.02 | 0.06 ± 0.02 |
| $\tau_{TS}$/ms | 0.9 ± 0.2 | 1.8 ± 0.3 | 2.0 ± 0.3 | 1.8 ± 0.4 |
| $\Phi_T$ | 0.73 ± 0.03 | 0.75 ± 0.03 | 0.71 ± 0.03 | 0.63 ± 0.04 |

(Figure 2). The energy-dependent data shown in Figure 6 are consistent with this interpretation; the relative fraction of species that rapidly dissociate increases with energy at the expense of the more slowly dissociating species.

In the limit where the laser energy $E$ approaches zero (Figure 6), only one-photon absorption occurs, and we can estimate a branching ratio between the fast and slow components by linear extrapolation.[19] If we assume that at this low-energy limit the fraction of S$_0$* states that dissociate will be the same irrespective of whether they were produced from the S$_1$ or T$_1$ state then this branching ratio should reflect the yield of triplet state production in the ion. Triplet quantum yields, $\Phi_T$, thus obtained for all four porphyrin cations are shown in Table 1. These are simply the branching ratios $\gamma$ multiplied by $(1 - k_{TS}/k)$ to account for the fact that the time scales for dissociation and triplet-to-singlet intersystem crossing are not completely separated in time.

Our data indicate that, for these isolated porphyrin ions, $\Phi_T$ is large, about 0.7. This observation is consistent with measurements on analogous porphyrins in solution.[6,20−22] For example, $\Phi_T$ for the free-base tetraphenylporphine is reported to be 0.71 ± 0.03,[22−24] which is in good agreement with what we find for the protonated analogue (0.73 ± 0.03). Of course, when considering porphyrin ions in solution, it is not unreasonable to expect pronounced solvent effects on photophysical properties. In this regard, we note that although Gensch et al.[25] have shown that the protonation of the central ring in tetraphenylporphine has no influence on the triplet quantum yield relative to that of the neutral, Chirvony et al.[26] did see a significant lowering of the triplet yield upon double protonation of the porphyrin. Hence there are available data to justify a comparison between the behavior of singly protonated porphyrins and neutral porphyrins, but of course there may be cases where this is not valid.

It should be noted that our data provide upper limits for the triplet quantum yields because we have neglected any fluorescence that may occur after photon absorption. In solution, the fluorescence quantum yield, $\Phi_F$, of the free-base tetraphenylporphine is 0.09 following 648 nm excitation.[27] For tetraphenylporphine in the gas phase, $\Phi_F$ was also reported to be 0.1.[17] Changing substituents on the pendant phenyl ring generally has only a small effect on $\Phi_F$.[27−29] Double protonation of tetraphenylporphine results in $\Phi_F$ between 0.0005 and 0.15 depending on the solvent.[29] Thus, given the relative magnitudes of these fluorescence quantum yields, the fact that we neglect fluorescence in our study of these particular molecules is not likely to be a significant point.

Under the assumption that intersystem crossing from the T$_1$ state into the S$_0$ manifold is indeed the rate-limiting step in ion dissociation via this channel (i.e., $k \gg k_{TS}$ in Figure 7), the long-lived component of our decay profiles should reflect the lifetime of the porphyrin triplet state. As such, the data obtained indicate triplet lifetimes of ~1 ms or longer, which are quite reasonable for a gas-phase system in the absence of a quencher such as oxygen.

## Conclusions

We have determined upper limits for intrinsic triplet quantum yields of substituted porphyrins in the gas phase upon 390 nm photoexcitation. The experimental technique described herein demonstrates how one can obtain useful information about the excited-state behavior of ionic porphyrins in the gas phase that, in turn, can complement the information obtained from solution-phase systems.

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(18) The internal energy of the P2$^+$ ions prior to photon absorption is 1.2 eV assuming an initial temperature of 300 K, and after absorption it is 4.4 eV (microcanonical temperature of 604 K). This is based on PM3 calculated vibrational frequencies using the Gaussian 98 program package (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M.

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(19) A linear extrapolation is a reasonable approximation. The fraction of the long-lifetime component, $\gamma$, depends on the pulse energy $E$ in the following way, $\gamma = \{\Phi_T(1 - b\sigma E)\}/\{1 - (1 - \Phi_T)^2 a\sigma E\}$, where $\sigma$ is the cross section for absorption from the room-temperature electronic ground state $S_0$. The parameters $a$ and $b$ correct for absorption by the "hot" electronic ground state (after one-photon absorption) and the triplet state, respectively. For the systems under study, $\Phi_T$ is large. Thus, the denominator in the above expression approaches 1 to give an almost linear dependence on $E$.

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