Spectroscopy and dynamics of isolated porphyrin molecules

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Introduction
Traditionally, the field of reaction dynamics has been dominated by studies of molecular systems containing a small number of atoms. However, it has recently been demonstrated that the same experimental and theoretical techniques can be applied to build an understanding of more complex systems in nature. In this case, the strategy has involved the isolation of building blocks for biological molecules in the gas phase or within a theoretical model for the electronic structure. Notable studies in the literature have included carbohydrates\(^1\), amino acids\(^2\), small peptides\(^3\) and nucleobases\(^4\). In each case, the absence of solvent or a host has given insight into the intrinsic properties of the molecular subunit, and in turn, an interpretation of the chemical properties of the parent biomolecule.

Recent experiments in our group have used meso-tetraphenylporphyrin \((H_2TPP)\) as a model system to study the structure and dynamics of isolated porphyrins in the gas phase. The conformational landscape for this particular porphyrin molecule has a large number of energy minima. These include two conformers of lowest energy (separated by only 0.06 eV\(^5\)) containing, respectively, a planar and ruffled structure for the tetrapyrrole ring. The seeding of \(H_2TPP\) into a supersonic expansion of an inert-carrier gas into a vacuum apparatus results in cooling of internal vibrational modes in the molecules and, consequently, the individual conformational states can be trapped behind the potential barriers on the energy surface. Our objective is to use spectroscopic methods to select a particular conformational state of the porphyrin. This will then be followed by a detailed study of the molecular dynamics for the photoinduced reaction.

Results and discussion
The large organic molecules are seeded into an inert-carrier gas by evaporation from an oven located in the expansion region of a supersonic jet. The mass spectrum of \(H_2TPP\) shown in fig. 1 was obtained by laser ionization (using a nanosecond-pulsed Nd:YAG laser pumped dye laser) followed by time-of-flight detection of the ion-signal intensity using a standard Wiley-McClaren mass spectrometer. The full mass spectrum revealed that fairly little fragmentation of the porphyrin occurs under isolated conditions. The spectrum shown in fig. 2 was obtained by ionization of \(H_2TPP\) using two different pulsed-laser wavelengths with gated detection of the signal corresponding to the parent molecule. A tunable laser was used to stimulate the electronic transition between the \(S_0\) and \(S_1\) states (with a visible wavelength represented by the value on the horizontal axis) and this was followed by UV-ionization using a fixed wavelength of 266 nm. Both of these wavelengths were generated by separate nanosecond-pulsed Nd:YAG laser pumped dye lasers. The broad peaks indicate a considerable congestion of different vibration transitions between the ground, \(S_0\), and excited, \(S_1\), states. A pulsed valve designed to generate a colder molecular beam has now been constructed and it is anticipated that the lower temperature of the \(H_2TPP\) will reveal vibrational structure in the R2PI spectrum corresponding to the \(S_1\) state.

We have already identified that the lifetime of the \(S_1\) state depends on the wavelength used to excite the porphyrin molecule. In fig. 3, the intensity of the R2PI signal for the \(H_2TPP\) mass peak is shown as a function of the time delay between the visible and ultra-violet laser pulses. This data was recorded at fixed values for the visible-laser

Figure 1. Photoionization time-of-flight mass spectrum of meso-tetraphenylporphyrin.

Figure 2. Resonance-enhanced two-photon ionization spectrum of meso-tetraphenyl porphyrin.
wavelength of 560 and 640 nm respectively. The signal intensity at negative values of the time delay corresponds to the arrival of the UV photon ahead of the visible photon (and the R2PI signal is zero in the region, as might be expected). The width of the each laser pulse is only 7ns and, therefore, the tail in the intensity profile at positive wavelengths reflects the lifetime of the excited state for each of the different wavelengths. At the shorter value of 560 nm, the lifetime of the excited state is quite short (~10 ns). In contrast, at the longer wavelength of 640 nm, the initial rapid decline of the signal intensity is followed by a long tail in the time profile reflecting the presence of two decay pathways with time constants of ~10 ns and >1 µs respectively. The longer time constant seems to indicate that the evolution of the excited state involves intersystem crossing and formation of a triplet-state of porphyrin at this wavelength.

Conclusion
Presently, we are directing our efforts towards building a new pulsed valve to obtain jet-cooled biomolecules with lower vibrational temperatures. This is a crucial stage in the development of our experiments designed to investigate the photoinduced reaction of single-conformational states of porphyrins. The preliminary data presented in this paper demonstrates the potential of molecular beam methods for the study of biological molecules and the gas-phase measurements of the excited-state lifetime provide an insight into the initial evolution of the electronic states involved in the photoreactions of porphyrins. We intend to continue our work to obtain a detailed understanding of the radiative and non-radiative decay pathways.

References