

PRF #: 56174-ND6

Project Title: Electronic Laser Photodissociation Spectroscopy of Gas-Phase Metalloporphyrins and Metalloporphyrin-Aromatic Molecule Complexes

PI Name, Affiliation: Dr Caroline Dessent, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

The project involves the study of the electronic spectroscopy and photochemistry of isolated, gaseous metalloporphyrins (MPs) and their aromatic molecule complexes. These studies are being performed for the first time in a novel custom-adapted laser-interfaced commercial mass spectrometer (LIMS), where the porphyrins are produced as gaseous ions via electrospray ionization, mass-selected and then subjected to laser photoexcitation in an ion trap. Excellent progress has been made on the project over the year, including the measurement of gas-phase electronic spectra of several MPs and their aromatic complexes within our LIMS, accompanying mass spectrometry measurements and computational chemistry calculations to support the interpretation of the experimental results.

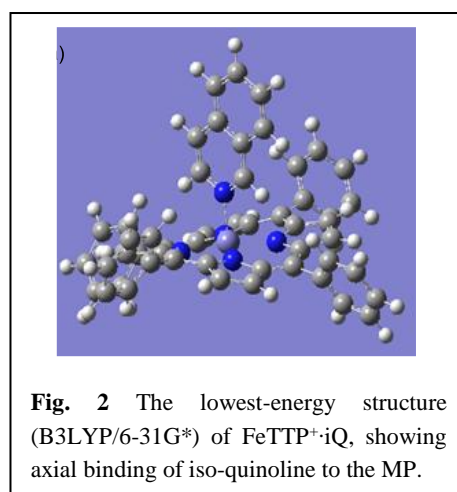
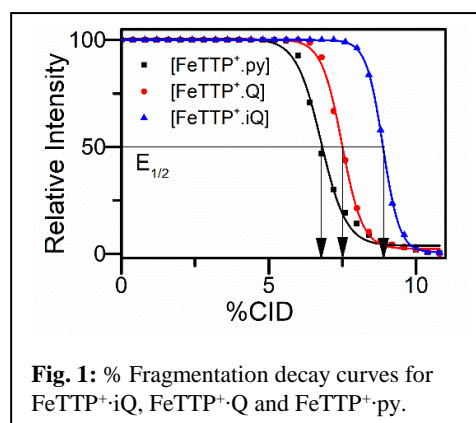
In our initial work on the project,¹ we successfully measured the gaseous electronic spectra and photofragmentation pathways of i) the non-metallated prototype porphyrin system, TPP·H⁺, ii) hemin⁺ (FeTTP⁺), iii) a vanadium oxide TPP system (VOTPP), iv) NiTTP, and v) very preliminary results of the porphyrin-aromatic molecule complex, [FeTTP⁺·pyridine].¹ Our initial focus over the second year of the project was to perform collision-induced dissociation measurements of MP-molecule complexes to allow us to measure the relative binding energies of the aromatic molecules to the MP, and use these to test our computational methods. Measurements have been performed using collision-induced dissociation (CID), as well as high energy collisional dissociation (HCD). Fig. 1 shows the results of a series of HCD collisional dissociation measurements conducted on complexes with FeTTP⁺. These measurements clearly show that the binding energies (which are proportional to the CID energy) increase on going from pyridine to isoquinoline.

Although our measured binding energies (Fig.1) are in good agreement with the predictions of low-level calculations from Stoyanov et al.,² we have so far been unable to replicate this trend in higher-level DFT (B3LYP/6-31G*) calculations. DFT calculations for these clusters are challenging due to the size of the systems, but it is imperative that we are able to do successful DFT calculations as a basis to interpreting our spectroscopic results. The structure shown in Fig. 2 provides a clue as to why the popular B3LYP functional may not be working well for these systems. Inspection of the structures shows that they involve considerable dispersion interactions. To address this, we are now using the Truhlar suite of functions (i.e. M06 2X), known to do an excellent job of calculating dispersion interactions,³ to recalculate the structures and binding energies. (This is time-consuming as M06 2X calculations require significantly more time than B3LYP ones.)

Over this year, we have re-acquired the gas-phase photodissociation spectra of the following MPs and clusters, as we discovered that the preliminary spectra acquired earlier in the project suffered from significant multiphoton effects, leading to spectral broadening and some spectral inconsistencies under repeat runs. We now have high-quality spectra for:

- i) FeTTP⁺ monomer (2.0-3.8 eV)
- ii) FeTTP⁺·pyridine (2.0-3.8 eV)
- iii) FeTTP⁺·iso-pyridine (2.5-3.8 eV)

The new spectra are suitable for publication once we resolve the best DFT functional for these systems, which will then be employed to calculate the TDDFT excited-state spectra for the systems, and allow a full interpretation of the experimental results.



Alongside these studies, we have also conducted work to characterize the spectroscopic properties of another class of N-aromatic molecules, which we are now investigating in their complexes to MPs, namely flavin or pteridine molecules. As the intrinsic gas-phase spectra of this class of molecules was very poorly characterized, we needed to start this section of the project by performing spectroscopic studies of the isolated molecules prior to measuring the cluster spectra. This has proved to be a highly successful piece of work, with two publications resulting from it:

i) Protonated Alloxazine:

A full photodissociation study was performed, allowing us to measure the intrinsic gaseous electronic spectra of protonated alloxazine (Fig. 3), and probe the nature of how protonation affected the electronic structure of alloxazine's MOs.⁴ This will provide a basis for interpreting the interactions of alloxazine with a positively charged MP such as FeTTP⁺.

ii) Deprotonated Alloxazine and Lumichrome:

Both of the anionic forms of these molecules were studied via laser photodissociation spectroscopy. Our aim was to perform basic measurements on a deprotonated N-aromatic for potential binding to neutral MPs, such as neutral Zn and Ni MPs. The spectroscopic study yielded very novel results, which will be likely to have impact outside of the immediate project area, relating to the electron capture properties of Flavin molecules. In particular, the study revealed that a transient negative ion resonance was identified close to the detachment energy of both alloxazine and lumichrome. While electron capture through this resonance led to break up of the molecular framework for alloxazine, the molecule remained intact for lumichrome. We were able to trace this effect to the involvement of the methyl groups on the lumichrome molecule, which is able to couple to the excess electron and hence shorten transient negative ion lifetime.

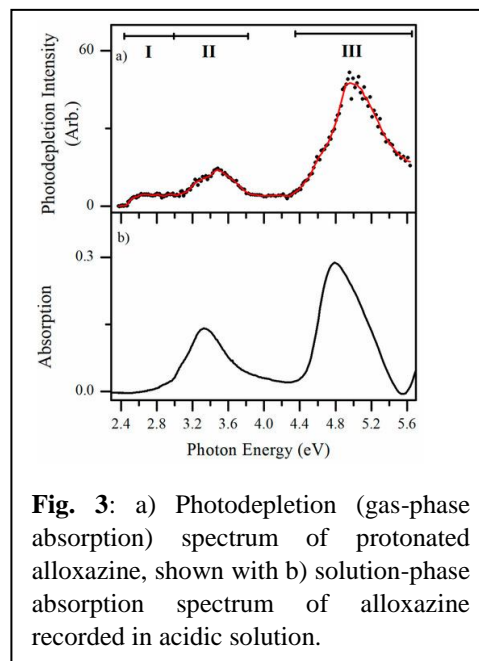


Fig. 3: a) Photodepletion (gas-phase absorption) spectrum of protonated alloxazine, shown with b) solution-phase absorption spectrum of alloxazine recorded in acidic solution.

Career Impact: The award of funding from the ACS-PRF for this project had a significant impact on my career, as it provided me with research funds over a period when I had no other funding. This allowed me to maintain research activity in my research group, through the student support it provided. Furthermore, the two publications which have been forthcoming from the project are important outputs from my research group, with publication [4] being likely to be particularly significant. For the students who have worked on the project, it provided sole support for Mathew Hawkrige to complete an MSc by Research,¹ as well as providing Edward Mathews with essential support to allow him to acquire the Flavin spectra which have subsequently be published in publications [4] and [5] and form part of his recently submitted PhD thesis. Finally, the award has provided support for 6 months for another student, Kelechi Oleanya, who is now leading the MP-complex work. This will provide her with material for her PhD thesis. Importantly, the funding has provided essential financial support for Kelechi, a Nigerian student, who has largely self-funded her PhD, but without the ACS-PRF support, she would have been unable to continue with her PhD.

References

1. Mathew Hawkrige, Electronic Laser Photodissociation Spectroscopy of Gas-Phase Metalloporphyrins and Metalloporphyrin-Aromatic Molecule Complexes, MSc Res. Thesis, (2018): <http://etheses.whiterose.ac.uk/20332/>
2. S. R Stoyanov, C. X Yin, M.R Gray, J. M Stryker, S. Gusarov and A. Kovalenko, J. Phys. Chem., 2010, 114, 2180–2188.
3. M. Walker, A.J.A. Harvey, A. Sen, C.E.H. Dessent, J. Phys. Chem. A, 117, 12590, 2013.
4. Observation of Near-Threshold Resonances in the Flavin Chromophore Anions Alloxazine and Lumichrome, E. Mathews and C. E. H. Dessent, J. Phys. Chem. Lett. 9, 6124, 2018.
5. Protomer-Dependent Electronic Spectroscopy and Photochemistry of the Model Flavin Chromophore Alloxazine, E. Mathews, R. Cercola and C. E. H. Dessent, Molecules, 23, 2036, 2018.