

## ELECTRONIC AND INFRARED PHOTODISSOCIATION SPECTROSCOPY OF PROTOPORPHYRIN IN VACUO

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Porphyrins are ubiquitous macrocycles in biology, where they perform a variety of functions ranging from behaving as chromophores in proteins to molecular/electron shuttles. Porphyrins often incorporate a metal center and have substituents on the macrocycle periphery to allow this versatility. These species have been studied for decades, using many techniques primarily focused on solution and solid phase environments. While such techniques yield much useful information, the chemical environment and the temperatures involved in such studies usually lead to solvatochromic shifts, broadening of spectral lines, and spectral congestion. Even spectra obtained in cryogenic matrices exhibit shifts whose magnitude and even direction are hard to predict. As a consequence, the intrinsic photophysical properties of these molecules, i.e., in the absence of effects caused by chemical environments, have been elusive. We are able to circumvent these difficulties by studying cryogenically prepared, mass selected ions. Here we report the electronic and infrared spectra of metal free protoporphyrin mono- and dianions. We interpret the experimental data in the framework of quantum chemical calculations.