PROTOMERS OF FLAVIN RADICAL ANIONS PROBED WITH PD ACTION SPECTROSCOPY

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Protonation or deprotonation sites mediate many cases of biological photochemistry. For example, flavin ions have several photobiological functions such as initiating DNA repair (occurring in some bacteria and frogs for example) and are central to quantum mechanical compass used by birds for navigation. These pathways involve various stages of flavin protonation and deprotonation, isomers and redox states. Furthermore, intermediate flavin radicals (which are formed in the biological photoredox pathways) have several possible protonation isomers (protomers) that are challenging to characterize due to their reactive nature and the additional challenge of separating isomeric species. Using photodissociation (PD) action spectroscopy coupled with mass spectrometry, reactive species (such as flavin radical ions) can be isolated in a vacuum and characterized based on their spectroscopic properties without reacting away. By photodissociating flavin adenine dinucleotide dianion (FAD) in an ion trap, multiple flavin radical anion fragments are formed. Photoproduct flavin ions in three redox states can each be separately re-isolated in the ion trap, in turn, and assigned by photodissociation action spectroscopy. Franck Condon simulations confirm that noncanonical protomers of these flavin radical ion are formed by direct photodissociation of larger flavins. These results reveal the structure of radical-anion products and provide assigned gas-phase spectra for reference and with these in hand, can provide new insights into the complex redox chemistry of FAD in biochemical systems.