CONFORMATIONS OF METAL CATION TRYPTOPHAN COMPLEXES VIA IRMPD WITH THE FREE ELECTRON LASER

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Metal cations can bind to tryptophan in various chelating conformations including zwitterionic (salt-bridge) and charge-solvated conformations. Infrared (IR) spectroscopic information obtained by IRMPD was used to determine the conformations of Trp complexes of all of the alkali cations, as well as silver cation. Structure analysis of the gas-phase complexes used the infrared multiple photon dissociation (IRMPD) spectrum (600 to 1800 cm^{-1}) obtained by irradiation of the trapped cation complexes by the FELIX free electron laser and Fourier-transform ion cyclotron resonance (FT-ICR) ion detection. Using comparisons with DFT predictions, characteristic diagnostic IR peaks were identified for the zwitterionic conformation and both of the likely charge-solvated conformations. The results strongly ruled out more than a few percent of zwitterion structures. For the small, tightly bound ions Li^+ and Ag^+, the spectra indicated predominantly N/O/Ring chelated charge-solvated complexes, whereas for the larger metal ions an increasing fraction of the alternative O/Ring chelation was observed. The trend of increasing O/Ring chelation in comparison with N/O/Ring chelation with increasing metal ion size and decreasing binding strength is entirely consistent with the calculated stabilities. These systems can be useful analogs for understanding modes of chelation of metal ions by polypeptides.