

Charge-Transfer Transitions in the Vacuum-Ultraviolet of Protein Circular Dichroism Spectra

Benjamin M. Bulheller, Jonathan D. Hirst

University of Nottingham

Circular dichroism (CD) is widely used in the structural characterization and secondary structure determination of proteins. Using the matrix method, protein CD can be calculated from first principles, with an accuracy which is almost quantitative for helical proteins. Thus, CD calculations and experimental data can be used in conjunction to aid structure analysis. The vacuum UV region (below 190 nm), where charge-transfer transitions have an influence on the CD spectra, can be accessed using synchrotron radiation circular dichroism (SRCD) spectroscopy. Recently, charge-transfer transitions in a conformationally diverse set of dipeptides have been characterized *ab initio* using complete active space self-consistent field calculations, and the relevant charge distributions have been parameterized for use in the matrix method for calculations of protein CD. We performed calculations of the vacuum UV CD spectra of 71 proteins, for which experimental SRCD spectra and X-ray crystal structures are available. The theoretical spectra are calculated considering charge-transfer and side chain transitions. This significantly improves the agreement with experiment.