Quantifying transition dipole strengths to identify molecular structures

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Vibrational and electronic transition dipole strengths are often good probes of molecular structures, especially in excitonically coupled systems of chromophores. One cannot determine transition dipole strengths using linear spectroscopy unless the concentration is known, which in many cases it is not. In this paper, we report a simple method for measuring transition dipole moments from linear absorption and 2D IR spectra that does not require knowledge of concentrations. Our method is tested on several model compounds and applied to the amide I′ band of a polypeptide in its random coil and α-helical conformation as modulated by the solution temperature. It is often difficult to confidently assign polypeptide and protein secondary structures to random coil or α-helix by linear spectroscopy alone, because they absorb in the same frequency range. We find that the transition dipole strength of the random coil state is 0.12 ± 0.013 D^2, which is similar to a single peptide unit, indicating that the vibrational mode of random coil is localized on a single peptide unit. In an α-helix, the lower bound of transition dipole strength is 0.26 ± 0.03 D^2. When taking into account the angle of the amide I′ transition dipole vector with respect to the helix axis, our measurements indicate that the amide I′ vibrational mode is delocalized across a minimum of 3.5 residues in an α-helix. Thus, one can confidently assign secondary structure based on exciton delocalization through its effect on the transition dipole strength. Our method will be especially useful for kinetically evolving systems, systems with overlapping molecular conformations, and other situations in which concentrations are difficult to determine. [1]

References