

Excitonic Splitting und Vibronic Coupling in Hydrogen Bonded Dimers

The investigation of excitonic coupling of molecular dimers has a long history in chemical physics. We investigate the $S_1 \leftarrow S_0$ / $S_2 \leftarrow S_0$ excitations of the supersonic jet-cooled 2-aminopyridine (2AP) self-dimer, (2AP)₂, and of the 2-pyridone self-dimer, (2PY)₂. The vibronic spectra of the ¹²C- and ¹³C-isotopomers were measured by two-color resonant two-photon ionization and UV/UV-depletion spectroscopies. In both systems, the $S_2 \leftarrow S_0$ excitation is allowed, but the $S_1 \leftarrow S_0$ transition is forbidden. A single ¹²C/¹³C isotopic substitution breaks the symmetry of the dimer, so that the ¹³C isotopologues exhibit both S_1 and S_2 electronic origins, which are split by the excitonic interaction. The excitation transfer rate can be directly deduced from the size of the splitting. In traditional linear vibronic coupling treatments, the coupling is mediated by monomer intramolecular vibrational modes and couplings to intermolecular vibrations are not considered. For (2AP)₂, major vibronic coupling contributions arise from the monomer $6a'$ vibration. Effects of the intermolecular modes are also large and an approximate treatment will be discussed.