LASER-INITIATED SHUTTLING OF A WATER MOLECULE BETWEEN H-BONDING SITES

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Stimulated emission pumping-hole filling spectroscopy has been used to shuttle a single water molecule back and forth between two well-separated hydrogen bonding sites on *trans*-formanilide (TFA). The solvent-shuttling reaction can be driven by selective excitation of either isomer (C=O or NH bound) with different SEP excitation wavelengths. The energy thresholds for C=O bound $\rightarrow$ NH and NH $\rightarrow$ C=O bound isomerization are both about 1000 cm^{-1}, close to half the total binding energy of water to TFA (1990 cm^{-1}). The two thresholds are combined to determine the relative energies of the two minima. The minimum-energy pathway for the reaction has been calculated using the nudged elastic band method. This pathway involves an in-plane motion of the water molecule, with a transition state in which the water accepts a weak hydrogen bond from the C-H group of the aldehyde carbon. Not far above this pathway, many other pathways open up, including pathways that bring the water molecule up over the top of the aromatic ring and amide group.