VIBRATIONAL PREDISSOCIATION OF THE METHANOL DIMER

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Examples of vibrational predissociation of hydrogen bonded (H-bonded) complexes in solution are rare while the gas phase counterpart is relatively well-understood today. Recent infrared pump probe studies of H-bonded alcohol oligomers in CCl_4 solution revealed that excitation of the OH (D) stretch of the H-bonded alcohol molecules leads to fast vibrational energy relaxation (VER) and concomitant H-bond breaking. The timescales of the relaxation and H-bond breaking events are on the order of 1 ps, which is faster than the VER timescale of a non-H-bonded monomer. To account for above experimental findings, it was suggested that the excited oligomers predissociate via a direct energy transfer from the OH (D) stretch to the H-bond degrees of freedom, which immediately breaks the H-bond. However, subsequent theoretical studies have failed to corroborate the proposed mechanism. Here we consider the vibrational predissociation of the H-bonded methanol dimer. Our reduced dimensional model for the methanol dimer includes three degrees of freedom, the H-bond donor OH stretch, the H-bond donor OH torsion and the H-bond stretch. The potential energy surface is computed using electronic structure program. Gas phase predissociation rates are obtained using both simple Fermi's Golden Rule approach and more rigorous close-coupling calculations. Our results demonstrate that a direct energy transfer from the OH stretch to the H-bond stretch is extremely slow. However, predissociation pathways involving highly excited torsional states are much more efficient, with timecales on the order of 100 ps. In solution, the solvent molecules could potentially facilitate the predissociation process of the methanol dimer either by modifying the potential energy surface or by taking up excess energy. Current work attempts to include the methanol-solvent interaction in a system-bath coupling sense. This will hopefully provide some insights into the previous experimental work.