HOW DO HYDROGEN BONDS BREAK IN SMALL ALCOHOL OLIGOMERS ?

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Hydrogen bonding liquids play vital roles in condensed phase chemical processes. It is well-known that in the gas phase alcohol clusters undergo vibrational predissociation after hydroxyl (OH) stretch excitation. Recent infrared pump probe studies on alcohol oligomers in CCl_4 solution suggest that similiar processes might occur in the condensed phase too. Following OH stretch excitation, ultrafast hydrogen bond breaking events have been observed on the timescale of 1 ps, the mechanism of which is still unclear. To answer the titular question, we consider vibrational predissociation of the hydrogen bonded methanol dimer. We construct a 5-dimensional model for the dimer including the hydrogen bond stretch, the donor OH stretch, the donor OH bend, and both the OH and methyl rotation about the CO axis of the donor. The potential energy surface is computed ab initio. A vibrational self-consistent field representation is adopted to calculate predissociation rates with the Fermi's Golden Rule approach. In addition, close-coupling calculations are performed yielding results in good agreement with the Fermi's Golden Rule approach. The predissociation rates strongly depend on the hydrogen bond strength. For our model methanol dimer, the timescale is on the order of 100ps. When the potential energy surface is scaled to correspond to the hydrogen bond strength of the methanol oligomers, a timescale on the order of 1ps is obtained. It has been suggested in the literature that predissociation occurs as a result of energy deposited in the OH stretch flowing directly into the hydrogen bond stretch. However, our results clearly demostrate that the predissociation occurs via highly excited OH rotational states. From our results, a simple nonadiabatic curve crossing picture for the predissociation process emerges, which provides a usefull framework for future study of solvent assisted vibrational predissociation.