Will Water Act as a Photo-catalyst for Cluster Phase Chemical Reactions? Vibrational Overtone Induced Dehydration Reaction of Methanediol

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The possibility of water catalysis in the vibrational overtone induced dehydration reaction of methanediol is investigated using *ab initio* dynamical simulations of small methanediol-water clusters. Quantum chemistry calculations employing clusters with one or two water molecules reveal that the barrier to dehydration is lowered by over 20 kcal/mol because of hydrogen-bonding at the transition state. Nevertheless, the simulations of the reaction dynamics following *OH*-stretch excitation show little catalytic effect of water and, in some cases, even show an anticatalytic effect. The quantum yield for the dehydration reaction exhibits a delayed threshold effect where reaction does not occur until the photon energy is far above the barrier energy. Unlike thermally induced reactions, it is argued that competition between reaction and the irreversible dissipation of photon energy may be expected to raise the dynamical threshold for the reaction above the transition state energy. It is concluded that the quantum chemistry calculations of barrier lowering are not sufficient to infer water catalysis in photochemical reactions, which instead require dynamical modeling.