More Stationary States on the SO_2-Formic Acid Potential Energy Surface

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Previous computational studies of the SO_2-formic acid system indicated the possible formation of two stable complexes, complex 1 containing a red-shifted (O-H···O) hydrogen bond, and complex 2 containing a blue-shifted (C-H···O) interaction. We now have identified several other minima on the SO_2-formic acid PES that involve rotamers of the formic acid OH group. When the formic acid carbonyl and OH group are in the less stable *anti* conformation, both (O-H···O) and (C-H···O) interactions are predicted to form, and both calculated X-H vibrational frequencies are red-shifted. In addition, several first-order saddle points were found. These include motions that convert an asymmetric complex into its mirror image by rotating SO_2 through a flat transition state, and motions in which formic acid rotates to a perpendicular orientation with C_s symmetry. Molecular dynamics studies were also undertaken to address the question of the relative importance of intramolecular vs. dissociation-recombination isomerization routes.