MICROWAVE SPECTRUM AND THEORETICAL INVESTIGATION OF TRIFLUOROACETIC SULFURIC ANHYDRIDE

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Trifluoroacetic sulfuric anhydride, CF_3COOSO_2OH, has been produced under supersonic jet conditions from the reaction of sulfur trioxide and trifluoroacetic acid. The rotational spectra for both the parent and deuterated isotopologues have been recorded, but were notably weaker than similar spectra obtained for other carboxylic sulfuric anhydrides. The spectra were readily fit to a Watson A-reduced Hamiltonian with no evidence of internal rotation. M06-2X/6-311++G(3df,3pd) calculations indicate that the formation of CF_3COOSO_2OH proceeds through a $\pi_2 + \pi_2 + \sigma_2$ cycloaddition mechanism analogous to that previously established for other carboxylic sulfuric anhydrides. The barrier to formation for CF_3COOSO_2OH calculated at the CCSD(T)/CBS(D-T) level is slightly positive (0.7 kcal/mol), in contrast to the slightly negative value obtained for the formation of its acetic acid analog (acetic sulfuric anhydride). The possible role of internal rotation in the formation of both systems will be discussed.