HOONO ISOMERIZATION TO $HONO_2$ INVOLVING CONICAL INTERSECTIONS

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The important atmospheric reactions HO_2 + NO and OH + NO_2 lead to formation and dissociation of the cis- and trans- isomers of the HOONO complex. In the present work, the global HNO_3 potential energy surface (PES) is being studied by using high-level ab initio electronic structure methods. This PES[a] and others in the same class have been studied previously by others. In the F + NO_2 reaction system, UCCSD(T) calculations showed that FONO isomerizes to FNO_2 through a tight transition state involving a two-state avoided curve crossing[b]. A similar mechanism has been invoked for HOONO, which is isoelectronic with FONO. CASSCF multi-configurational calculations on the CH_3O + NO_2 reaction located a conical intersection near where single-configurational DFT methods predict an intrinsic energy barrier; the barrier was suggested to be an artifact[c]. In present work, the global HNO_3 PES is being investigated by both the UCCSD(T) and CASSCF methods in order to study the influence of low-lying excited electronic states on the ground state PES and reaction dynamics.

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