

HOONO ISOMERIZATION TO HONO INVOLVING CONICAL INTERSECTIONS

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The important atmospheric reactions $\text{HO} + \text{NO}$ and $\text{OH} + \text{NO}$ lead to formation and dissociation of the cis- and trans-isomers of the HOONO complex. In the present work, the global HONO potential energy surface (PES) is being studied by using high-level ab initio electronic structure methods. This PES and others in the same class have been studied previously by others. In the $\text{F} + \text{NO}$ reaction system, UCCSD(T) calculations showed that FONO isomerizes to FNO through a tight transition state involving a two-state avoided curve crossing. A similar mechanism has been invoked for HOONO, which is isoelectronic with FONO. CASSCF multi-configurational calculations on the $\text{CH}_2\text{O} + \text{NO}$ reaction located a conical intersection near where single-configurational DFT methods predict an intrinsic energy barrier; the barrier was suggested to be an artifact. In present work, the global HONO 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.
