

PHOTODISSOCIATION DYNAMICS OF CH₂OO ON MULTIPLE POTENTIAL ENERGY SURFACES: EXPERIMENT AND THEORY

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Criegee intermediates are zwitterionic carbonyl oxide species that result from alkene ozonolysis in the Earth's troposphere. UV excitation of the simplest Criegee intermediate, CH₂OO, across most of the broad span of the (B ¹A') - (X ¹A') spectrum results in prompt dissociation to two energetically accessible asymptotes: O (¹D) + H₂CO (X ¹A₁) and O (³P) + H₂CO (a ³A''). Dissociation proceeds on multiple singlet potential energy surfaces that are coupled by two regions of conical intersection (CoIn). Velocity map imaging studies reveal a bimodal total kinetic energy (TKER) distribution for the O (¹D) + H₂CO (X ¹A₁) products. The unexpected low TKER component corresponds to highly internally excited H₂CO (X ¹A₁) products. Full dimensional trajectory calculations suggest that the bimodal TKER distribution of the O (¹D) + H₂CO (X ¹A₁) products originates from two different dynamical pathways: a primary pathway evolving through one CoIn region to products and a smaller component sampling both CoIn regions during the dissociation process. Those that access both CoIn regions likely give rise to the more highly internally excited H₂CO (X ¹A₁) products. The remaining trajectories dissociate to O (³P) + H₂CO (a ³A'') products after traversing through both CoIn regions. No trajectories follow the more thermodynamically favorable spin-forbidden pathway to O (³P) + H₂CO (X ¹A₁) products. This complementary experimental and theoretical investigation provides insight into the photodissociation of CH₂OO via multiple dissociation pathways through two regions of CoIn that control the branching and energy distributions of products