

Collisional Quenching of OH Radicals: Dynamical Outcomes

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Abstract

The nascent OH $X^2\Pi$ product state distributions arising from collisional quenching of electronically excited OH $A^2\Sigma^+$ by several molecular partners have been determined using a pump-probe technique. For H_2 and N_2 collision partners, the majority of OH $X^2\Pi$ products are observed in their lowest vibrational level, $v''=0$, with significantly less population in $v''=1$. The OH ($v''=0$) products are generated with a substantial degree of rotational excitation, peaking around $N''=15$ with H_2 as the collision partner and $N''=18$ with N_2 . Complementary measurements of the branching fraction into OH $^2\Pi$ product states demonstrate that reaction is the dominant decay pathway for quenching of OH $A^2\Sigma^+$ by H_2 , while nonreactive quenching is the dominant pathway for N_2 . These observations are discussed in the context of theoretical calculations that examine the topography of the conical intersections which couple the electronically excited and ground state potential energy surfaces. The experimental observables are interpreted as dynamical signatures of nonadiabatic passage through the conical intersection regions responsible for quenching in both systems.