Statistical Modeling through Iterative Techniques: Evaluating the Impact of Intersystem Crossing and Multiple Entrance Complexes on Oxygen Atom Transfer Reactions

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A fundamental understanding of how chemical processes affect the properties of plasmas at high temperatures and pressures is critical to Air Force and Space Force goals in areas of communication, sensing, combustion, navigation, and catalysis. Using a variable ion source temperature adjustable selected ion flow tube (VISTA-SIFT), we are able to measure the kinetics of many oxygen transfer reactions, which are featured prominently in these areas of interest. Fe^+, V^+, Co^+, and $Ti^+ + N_2O$ systems all had apparent kinetic effects resulting from multiple entrance complexes and an intersystem crossing (ISC). Through statistical modeling, we treat the ISC as a unimolecular process similar to an isomerization between two wells, as a function of both energy and angular momentum using RRKM, and at a very constrained geometry along the crossing seam between two surfaces. In the majority of reactions studied, intersystem crossing and multiple entrance complexes play the primary role in controlling reactivity. We hope that future work can provide a practical and approachable method to treat these kinetic features in a wide range of reaction systems.