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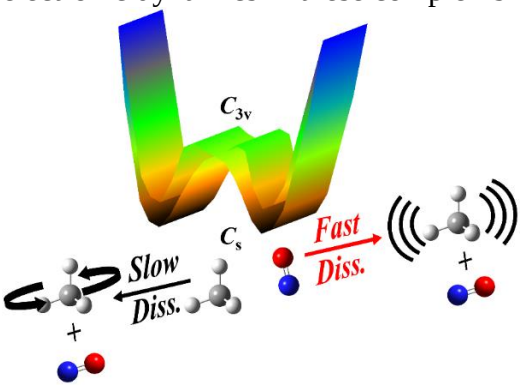
Quantum-State Control on Multidimensional Potential Energy Surfaces: Driving Chemical Outcomes with Spectroscopic Accuracy

ABSTRACT:

In bimolecular collisions of atmospherically-relevant molecules such as open-shell radicals and alkanes, relative molecular configurations can significantly change reactive and non-reactive outcomes. To probe this isomer-dependence, experiments are needed that can quantify both the initial molecular configuration and internal energy of the collision partners with spectroscopic accuracy. Recent work by our group demonstrated that upon infrared (IR) excitation, the dynamics of the nitric oxide-methane collision complex (NO-CH_4) are dependent on the initial monomer configurations, as small changes in configuration substantially affect the energies, electronic couplings, and predissociation pathways due to the Jahn-Teller effect. In this talk, we compare the spectroscopic signatures and dynamical outcomes from IR activation of NO-CH_4 and NO-C_2H_6 (ethane). IR action spectroscopy with 1+1 resonance-enhanced multiphoton ionization of NO products was employed to characterize the fundamental CH stretch transitions of NO-CH_4 and NO-C_2H_6, as well as to initiate the non-reactive decay mechanisms of the collision complexes. Furthermore, velocity map imaging (VMI) was utilized to explore the dynamics prior to and following IR excitation, imprinted on the NO photoproducts. Substantial differences in the ion image anisotropies and velocity distributions indicate separate IR-initiated dissociation mechanisms for NO-CH_4 and NO-C_2H_6 along pseudo Jahn-Teller surfaces. An isomer-dependent framework is used to unravel the coupled vibrational and electronic dynamics in these complex bimolecular reactions.



Research in the Kidwell group applies laser-based techniques to explore reactive processes at a fundamental level in order to address atmospheric and physical chemistry problems. Specifically, we study the photochemistry and bimolecular reactivity of neutral molecules, reactive intermediates, and molecular clusters using laser spectroscopy and imaging methods accompanied by high-level theory and reaction modeling. Our experimental measurements provide important benchmarks for theoretical studies in order to determine detailed mechanisms, which are necessary for predictive atmospheric chemistry modeling.