

DYNAMICAL SIGNATURES FROM COMPETING, NONADIABATIC FRAGMENTATION PATHWAYS OF S-NITROSOTHIOPHENOL

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S-Nitrosothiols (RSNOs) are derived from the combination of sulfur and nitric oxide (NO) radicals in the Earth's atmosphere and fragment to products following photolysis. Extensive theoretical studies have focused on the thermodynamic and, to a lesser extent, photochemical properties of RSNOs. However, experimental studies of these compounds have been limited due to the inherent instability of RSNOs at room temperature. Using velocity map imaging (VMI), we explore the photodissociation dynamics of jet-cooled S-nitrosothiophenol (PhSNO) from 355 nm photolysis. We report the translational and internal energy distributions of the NO and thiophenoxy (PhS) co-fragments, which are determined by spatial detection of the ionized NO photofragments using 1+1 resonance-enhanced multiphoton ionization (REMPI). The velocity distributions indicate competing PhSNO nonadiabatic dissociation pathways, in which PhS is formed in the ground and first excited electronic states when probing high- and low-energy NO ($X^2\Pi_{1/2}, v'', J''$) rovibrational states, respectively. The results of multireference electronic structure calculations suggest that direct dissociation on the bright S_2 state results in PhS formed in its excited electronic state, whereas intersystem crossing into the triplet manifold leads to population of PhS in its electronic ground state. The dynamical signatures from the dissociation processes are imprinted on the fragments' quantum states and relative translation, which we explore in rigorous detail using state-resolved imaging and high-level theoretical calculations.