The Roaming Atom: Straying from the Reaction Path in Formaldehyde Decomposition

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We present a combined experimental and theoretical investigation of formaldehyde (H₂CO) dissociation to H₂ and CO at energies just above the threshold for competing H elimination. High-resolution state-resolved imaging measurements of the CO velocity distributions reveal two dissociation pathways. The first proceeds through a well-established transition state to produce rotationally excited CO and vibrationally cold H₂. The second second dissociation pathway yields rotationally cold CO in conjunction with highly vibrationally excited H₂. Quasi-classical trajectory calculations performed on a global potential energy surface for H₂CO suggest that this second channel represents an intramolecular hydrogen abstraction mechanism: one hydrogen atom explores large regions of the potential energy surface before bonding with the second H atom, by-passing the saddle point entirely.