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

D. Townsend[1,2], S. A. Lahankar[3], S. K. Lee[1,2,3], S. D. Chambreau[3], A. G. Suits[1,2,3]*,
X. Zhang[4], J. Rheinecker[4] , L. B. Harding[5] and J. M. Bowman[4]*

[1]Department of Chemistry, Stony Brook University, Stony Brook, NY 11794
[2]Chemistry Department, Brookhaven National Laboratory, Upton NY 11973
[3]Department of Chemistry, Wayne State University, Detroit MI 48202
[4]Department of Chemistry and Cherry L. Emerson Center for Scientific Computation,Emory University, Atlanta, GA, 30322
[5]Chemistry Division, Argonne National Laboratory, Argonne IL 60439
*asuits@wayne.edu; jimbowma@emory.edu

We present a combined experimental and theoretical investigation offormaldehyde (H_2CO) dissociation to H2 and CO at energies just above the threshold forcompeting H elimination. High-resolution state-resolved imaging measurements of the CO velocity distributions reveal two dissociation pathways. The first proceeds through awell-established transition state to produce rotationally excited CO and vibrationally cold H2. The second second dissociation pathway yields rotationally cold CO in conjunctionwith highly vibrationally excited H 2. Quasi-classical trajectory calculations performed ona global potential energy surface for H 2CO suggest that this second channel represents anintramolecular 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.