

CORRELATED STATE DISTRIBUTIONS FOR H₂ AND CO FROM FORMALDEHYDE PHOTODISSOCIATION USING DC SLICE IMAGING: THE "ROAMING H-ATOM MECHANISM"

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We present a detailed experimental investigation of formaldehyde dissociation to H₂ and CO following excitation to a series of vibrational bands in S₁. The CO was detected by (2+1) REMPI at various rotational states of CO (J = 5-45) and the CO velocity distributions were measured using state-resolved DC Slice Imaging. These high-resolution measurements revealed the internal state distribution in the correlated H₂ cofragments. The results show that rotationally hot CO (J = 45) is produced in conjunction with vibrationally "cold" H₂ fragments ($\nu = 0-3$): these products are formed through the celebrated skewed transition state. After excitation of formaldehyde above the threshold for the radical channel (H₂CO → H + HCO) we find formation of rotationally cold CO (J = 5-15) correlated to highly vibrationally excited H₂ ($\nu = 5-7$). These products are formed through a novel roaming mechanism that involves intramolecular H-abstraction (D. Townsend et. al. *Science* **306**, 1158 (2004)), and avoids the region of the transition state entirely. The current measurements give us detailed insight into the energy dependence of the branching to these different reaction mechanisms.