

FULLY STATE-RESOLVED PHOTODISSOCIATION OF FORMALDEHYDE: $\text{H}_2\text{CO} \rightarrow \text{H} + \text{HCO}$. K -CONSERVATION AND A RIGOROUS TEST OF STATISTICAL THEORIES

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The photodissociation dynamics of the reaction $\text{H}_2\text{CO} + h\nu \rightarrow \text{H} + \text{HCO}$ have been investigated in the range 60-400 cm^{-1} above the reaction threshold. Supersonically-cooled formaldehyde was excited into 15 specific J, K_a, K_c rotational states in two vibrational levels $2^1 4^1 6^1$ and $2^2 4^1$ in the $\tilde{A}(^1 A_2)$ state. The laser induced fluorescence spectra of the nascent HCO fragment provided detailed product state distributions (PSDs), resolved by N, K_a, K_c and J . When just the overall molecular rotation, N , is considered the PSDs are in remarkable agreement with calculations based on phase space theory (PST). However, when the projection of N onto the molecular frame (K_a, K_c) is included the distributions show consistent deviations from PST. In particular, there is a tendency to preserve the initial parent rotational motion about the a and b axes. The effect is that states with higher initial K_a in H_2CO produce higher final K_a in the HCO fragment. There is also a tendency for the upper/lower members of the asymmetry doublets in H_2CO to map onto the same upper/lower set of product state asymmetry doublets. Finally, there are oscillations in some of the detailed PSDs that remain unexplained.