DYNAMICAL FINGERPRINTING IN FORMALDEHYDE DISSOCIATION

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Photolysis of formaldehyde to H + HCO, may occur on both the electronic ground state (S_0) and the first excited triplet state (T_1). A dynamical signature distinguishing the products of these two chemical channels has been previously established.[a]

This criterion is now used to qualitatively investigate the branching ratios for these pathways at excitation energies immediately below the T_1 potential energy barrier, and exceeding it. Comparisons are also made to the yield of the molecular product, CO, which is only generated on the S_0 surface. Near the threshold for T_1 participation, continual activity of both the S_0 and T_1 channels has been seen, with dominance fluctuating depending on the formaldehyde rovibrational state prepared.[b] This fluctuation is confirmed in the region of the T_1 threshold, with the triplet channel dominating the majority of states. The fluctuations diminish as the energy of the system increases away from the barrier of the triplet surface.

It is also demonstrated that both pathways significantly populate the first vibrationally excited state of the HCO product once the energetic threshold is reached. Reaction on the singlet surface, however, is seen to gives rise to slightly higher vibrational excitation.

[a] H. M. Yin, S. H. Kable, X. Zhang and J. M. Bowman *Science* **311**, 1443, 2006.

[b] L. R. Valachovic *et al J. Chem. Phys.* **112**(6), 2752, Feb 2000.