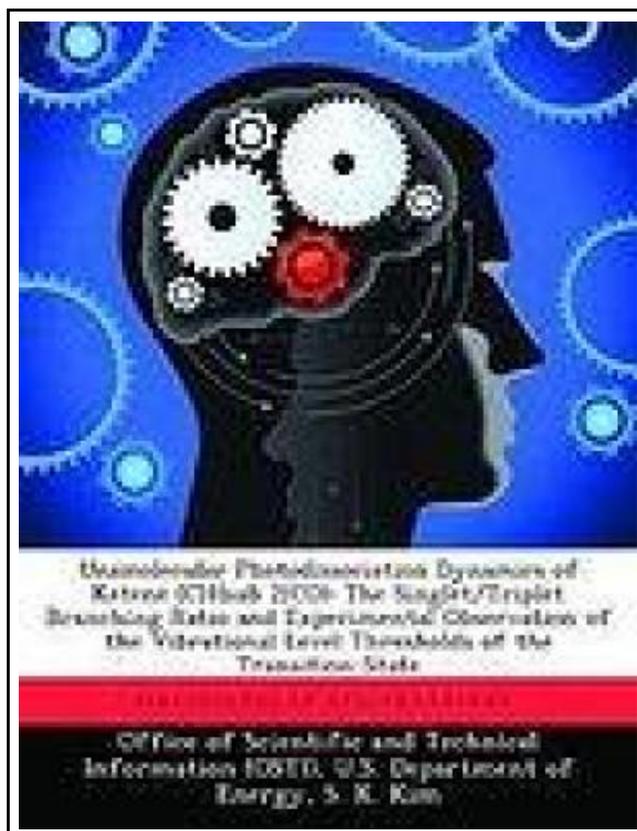


## Unimolecular Photodissociation Dynamics of Ketene (CHCO): The Singlet/Triplet Branching Ratio and Experimental Observation of the Vibrational Level Thresholds of the Transition-State



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*(Prof. Demond McClure)*

## UNIMOLECULAR PHOTODISSOCIATION DYNAMICS OF KETENE (CHCO): THE SINGLET/TRIPLET BRANCHING RATIO AND EXPERIMENTAL OBSERVATION OF THE VIBRATIONAL LEVEL THRESHOLDS OF THE TRANSITION-STATE



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Biblioscholar Jan 2013, 2013. Taschenbuch. Book Condition: Neu. 246x189x13 mm. This item is printed on demand - Print on Demand Neuware - The rotational distributions of CO products from the dissociation of ketene at photolysis energies 10 cm<sup>1</sup> below, 56, 110, 200, 325, 425, 1,107, 1,435, 1,720, and 2,500 cm<sup>1</sup> above the singlet threshold, are measured in a supersonic free jet of ketene. The CO( $v = 0$ ) rotational distributions at 56, 110, 200, 325, and 425 cm<sup>1</sup> are bimodal. The peaks at low  $J$ 's, which are due to CO from the singlet channel, show that the product rotational distribution of CO product from ketene dissociation on the singlet surface is well described by phase space theory (PST). For CO( $v = 0$ ) rotational distributions at higher excess energies, the singlet and triplet contributions are not clearly resolved, and the singlet/triplet branching ratios are estimated by assuming that PST accurately predicts the CO rotational distribution from the singlet channel and that the distribution from the triplet channel changes little from that at 10 cm<sup>1</sup> below the singlet threshold. At 2,500 cm<sup>1</sup> excess energy, the CO( $v = 1$ ) rotational distribution is obtained, and the ratio of CO( $v = 1$ ) to CO( $v = 0$ ) products for the singlet channel is close to the variational RRKM calculation, 0.038, and the separate statistical ensembles (SSE) prediction, 0.041, but much greater than the PST prediction, 0.016. Rate constants for the dissociation of ketene (CHCO) and deuterated ketene (CDCO) have been measured at the threshold for the production of the CH(D) and CO. Sharp peaks observed in photofragment excitation (PHOFEX) spectra probing CO ( $v = 0, J = 2$ ) product are identified with the C-C-O bending mode of the transition state. RRKM calculations are carried out for two limiting cases for the dynamics of K-mixing in highly vibrationally...

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