

APPLICATIONS OF TRANSIENT FM DOPPLER SPECTROSCOPY IN UNIMOLECULAR REACTIONS

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Frequency-modulated transient absorption spectroscopy is applied to measurements of Doppler-broadened line shapes of unimolecular reaction products. The combination of high spectral resolution, good time resolution, and good sensitivity allows accurate measurements at sample densities typical of photoinduced processes in slit jet expansions. The velocity distributions of selected rotational states of CH_2 are determined from the photoinitiated dissociation of ketene, CH_2CO . Energy and momentum conservation allows transformation of the velocity distributions to a distribution of internal energies of the undetected coincident reaction product. The correlated state distributions of CO for specific CH_2 states are contrasted with global CO state distributions, and various statistical models that have been applied to the unimolecular dissociation of ketene.