COLLISION-INDUCED SINGLET-TRIPLET CROSSING AND RECROSSING IN CH_2

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Transient absorption spectroscopy using a *c.w.* frequency-modulated titanium:sapphire laser has been used to measure the time-dependence of individual lines in the $\tilde{b} \leftarrow \tilde{a}$ spectrum of CH_2. The radical was formed by pulsed 308 nm excimer laser photolysis of dilute mixtures of ketene in argon at ambient temperature. For strong lines, we are able to follow more than three decades of decay. During the first few μsecs, the spectral line widths, shapes and decays vary systematically with the energy of the absorbing state. As the radicals undergo more collisions, the observed decay depends on chemical reaction with unphotolyzed precursor, collision-induced inter-system crossing to the triplet manifold, and vibrational relaxation in both the singlet and triplet manifolds. After translational and rotational thermalization, we find the absorptions for all measured levels exhibit bi-exponential decays. The initial decay rate reflects reactive loss, intersystem crossing, and an increasingly significant return flux from a growing population of vibrationally excited triplet. At longer times, the coupled singlet/triplet population decays with a slower, steady-state rate. In previous studies, only the initial decay could be observed, and it was interpreted as an irreversible process. Ortho and para CH_2 levels show systematic differences, probably due to the different patterns of mixed levels in the two nuclear spin modifications. We have modeled the reaction and relaxation in the system using a simplified master equation approach that provides insight into the processes occuring and the role of gateway rotational levels of mixed singlet-triplet character.