DOUBLE RESONANCE STUDIES OF COLLISIONAL ENERGY TRANSFER IN CH_2

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We have studied rotational energy transfer by optical-optical double resonance methods in order to understand the close connection between rotational energy transfer and the mixed-state mechanism of intersystem crossing. Singlet CH_2 is produced by 308 nm photolysis of CH_2CO. After thermalization of the rotational and translational distribution, a bleaching tunable dye laser pulse depletes the population of a selected rotational level of singlet CH_2 while the population of the same (in saturation recovery mode) or a different (in saturation transfer mode) singlet CH_2 rotational level is monitored with FM absorption spectroscopy on a different vibrational band of the $\tilde{b} - \tilde{a}$ system. The bleaching laser is blocked and unblocked to record a reference and a bleached transient waveform. The difference of the two signals as a fraction of the reference signal is the saturation recovery signal, which is found to follow a single exponential decay to a final value closed to half of the initial thermal Boltzmann fraction of the population in the bleached level. The rate coefficients for saturation recovery by collision with CH_2CO and He are 1.6×10^{-8} and 2.1×10^{-9} cm^3 $molec^{-1}$ s^{-1}, respectively. The saturation transfer kinetics is multi-exponential and depends on which pair of rotational states is saturated and probed.