

## DOUBLE RESONANCE STUDIES OF COLLISIONAL ENERGY TRANSFER IN CH<sub>2</sub>

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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<sub>2</sub> is produced by 308 nm photolysis of CH<sub>2</sub>CO. 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<sub>2</sub> while the population of the same (in saturation recovery mode) or a different (in saturation transfer mode) singlet CH<sub>2</sub> 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<sub>2</sub>CO and He are  $1.6 \times 10^{-8}$  and  $2.1 \times 10^{-9}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, respectively. The saturation transfer kinetics is multi-exponential and depends on which pair of rotational states is saturated and probed.