

REVERSIBILITY OF INTERSYSTEM CROSSING IN THE $\tilde{a}^1A_1(000)$ and $\tilde{a}^1A_1(010)$ STATES OF METHYLENE, CH_2

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The lowest energy singlet (\tilde{a}^1A_1) and triplet (\tilde{X}^3B_1) electronic states of methylene, CH_2 , are only separated by 3150 cm^{-1} , but differ greatly in chemical reactivity. Overall methylene reaction rates and chemical behavior are therefore strongly dependent on collisionally-mediated singlet-triplet interconversion. Collisions with inert partners tend to depopulate the excited singlet state and populate vibrationally excited triplet levels in CH_2 . This process is generally considered as irreversible for large molecules, however, this is not the case for small molecules such as CH_2 . An investigation of the decay kinetics of CH_2 in the presence of argon and various amounts of oxygen has been carried out using transient frequency modulation (FM) absorption spectroscopy, to monitor *ortho* and *para* rotational levels in both the $\tilde{a}^1A_1(000)$ and $\tilde{a}^1A_1(010)$ states. In the $\tilde{a}^1A_1(000)$ state, all observed rotational levels follow double exponential decay kinetics, a direct consequence of reversible intersystem crossing. The relative amplitude of the slower decay component is an indicator of how quickly the reverse crossing from excited triplet levels becomes significant during the reaction and relaxation of singlet methylene. The *para* rotational levels show more obvious signs of reversibility than *ortho* rotational levels. Adding oxygen enhances the visibility of reversibility for both *ortho* and *para* levels. However, in the $\tilde{a}^1A_1(010)$ state where the FM signal is 5-10 times smaller than the $\tilde{a}^1A_1(000)$ state, there is no evidence of double exponential decay kinetics.

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 and DE-SC0012704 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

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