

## GATEWAY MEDIATED INTERSYSTEM CROSSING IN C<sub>2</sub>H<sub>2</sub>

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Laser Excited Metastable (LEM) spectra of C<sub>2</sub>H<sub>2</sub> indicate that a single vibrational level of the T<sub>3</sub> surface couples the 3ν<sub>3</sub> level of the S<sub>1</sub> surface to a dense manifold of T<sub>1</sub> and T<sub>2</sub> states. In the proposed coupling mechanism, Gateway Mediated Intersystem Crossing (GMISC), the spin-orbit matrix element between the 3ν<sub>3</sub> S<sub>1</sub> state and one near-degenerate vibrational level of the T<sub>3</sub> state is much larger than the direct interaction between 3ν<sub>3</sub> S<sub>1</sub> and any other T<sub>1</sub> or T<sub>2</sub> level. This is due to a near degeneracy between the S<sub>1</sub> and T<sub>3</sub> vibrational states and a nearby S<sub>1</sub>-T<sub>3</sub> surface crossing. The S<sub>1</sub> state interacts with the background triplet states indirectly through T<sub>3</sub> via T<sub>3</sub> ~ T<sub>2,1</sub> matrix elements. Evidence for this mechanism includes a shift between the LIF and LEM spectra, an interference effect near J = 5 in the LEM spectrum, and the strength of the LEM signal for the 3ν<sub>3</sub> band relative to other bands in the  $\tilde{A}$ - $\tilde{X}$  band system. Other experiments in which S<sub>1</sub> ~ (T<sub>3,2,1</sub>, S<sub>0</sub>) interactions were observed will be discussed in the context of the GMISC model.