GATEWAY MEDIATED INTERSYSTEM CROSSING IN C_2H_2

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Laser Excited Metastable (LEM) spectra of C_2H_2 indicate that a single vibrational level of the T_3 surface couples the $3\nu_3$ level of the S_1 surface to a dense manifold of T_1 and T_2 states. In the proposed coupling mechanism, Gateway Mediated Intersystem Crossing (GMISC), the spin-orbit matrix element between the $3\nu_3$ S_1 state and one near-degenerate vibrational level of the T_3 state is much larger than the direct interaction between $3\nu_3$ S_1 and any other T_1 or T_2 level. This is due to a near degeneracy between the S_1 and T_3 vibrational states and a nearby S_1-T_3 surface crossing. The S_1 state interacts with the background triplet states indirectly through T_3 via $T_3 \sim T_{2,1}$ 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 $3\nu_3$ band relative to other bands in the $\tilde{A}$-$\tilde{X}$ band system. Other experiments in which $S_1 \sim (T_{3,2,1}, S_0)$ interactions were observed will be discussed in the context of the GMISC model.