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In this work, we take into account our recent studies on C$_3$ where we used perturbation-facilitated two-color resonant four-wave mixing spectroscopy to access the (dark) triplet manifold from the singlet ground state via “gate-way” levels (i.e. singlet-triplet mixed levels) [1] and the deperturbation investigation of the d$^3\Pi_g$, v= 6 level of the Swan band that unveiled the presence of the lowest quintet state ($^5\Pi_g$) of C$_2$[2].

We report on perturbation-facilitated optical-optical double-resonance experiments to access the first excited quintet state of C$_2$ via “gate-way states” in the perturbed d$^3\Pi_g$, v= 6. The newly found $^5\Pi_u$ state is characterized at rotational resolution by performing a least-squares fit of the observed transitions to a $^5\Pi_u$−$^5\Pi_g$ Hamiltonian. The work represents a rare case of a successful analysis of a quintet manifold of a molecule exhibiting a singlet ground state (1$^1\Sigma_g^+$).
