PERTURBATION FACILITATED OPTICAL OPTICAL DOUBLE RESONANCE INVESTIGATION OF THE QUINTET MANIFOLD OF C$_2$ BY APPLYING TWO-COLOR FOUR-WAVE MIXING

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The potential of four-wave mixing spectroscopy for deperturbation studies has been demonstrated by an analysis of the spin-orbit and $L$-uncoupling interaction between the $d^3\Pi_u, v = 4$ and the $b^3\Sigma_g^-, v = 16$ states of C$_2$.$^a$ The double-resonance method provides unambiguous assignments of perturbed transitions by intermediate level labeling. Furthermore, the sensitivity of the method unveiled extra transitions that originate from the perturbing $b^3\Sigma_g^-, v = 16$ state. A following study$^b$ has successfully applied the method to deperturb the $d^3\Pi_u, v = 6$ state of the dicarbon and lead to the discovery of the first high-spin state of C$_2$. The energetically lowest quintet ($^5\Pi_u$) has been characterized by applying a conventional Hamiltonian. The detailed study unraveled major issues of the so-called high-pressure band of C$_2$ which were initially observed back in 1910$^c$ and later observed in numerous experimental environments.

In this work we take into account our recent studies on tri-carbon$^d$ where we used perturbation-facilitated two-color resonant four-wave mixing spectroscopy to access the (dark) triplet manifold of C$_3$ from the singlet $X^1\Sigma_g^+$ ground state via “gate-way” levels (i.e. singlet-triplet mixed levels). In a similar way, we performed for this study perturbation-facilitated optical-optical double-resonance experiments to access the first excited quintet state of C$_2$ via “gate-way states” in the perturbed $d^3\Pi_u, v = 6$. 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 ($^1\Sigma_g^+$).

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