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 $d\,^3\Pi_g, v=4$ 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 $d\,^3\Pi_g, v=6$ state of the dicarbon and lead to the discovery of the first high-spin state of C_2. The energetically lowest quintet ($^5\Pi_g$) 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 $\tilde{X}\ ^1\Sigma_g^+$ 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 $d\,^3\Pi_g, v=6$. 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 ($^1\Sigma_g^+$).

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[a] P. Bornhauser, G. Knopp, T. Gerber, and P.P. Radi, Journal of Molecular Spectroscopy 262, 69 (2010).
[b] P. Bornhauser, Y. Sych, G. Knopp, T. Gerber, and P.P. Radi, J. Chem. Phys. 134, 044302 (2011).
[c] A. Fowler, Monthly Notices of the Royal Astronomical Society 70, 484 (1910).
[d] Y. Sych, P. Bornhauser, G. Knopp, Y. Liu, T. Gerber, R. Marquardt, and P.P. Radi, J. Chem. Phys. 139, 154203 (2013).