AB INITIO LINE LISTS FOR FOUR ISOTOPOLOGUES OF TRIPLET ($\tilde{X}^3B_1$) METHYLENE

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Complete line lists for four isotopologues of methylene (CH_2, CHD, CD_2, and $^{13}CH_2$) in its triplet electronic state ($\tilde{X}^3B_1$) have been variationally computed using accurate *ab initio* potential energy and dipole moment surfaces (PES and DMS). In the triplet state, methylene exhibits a large-amplitude bending vibration and can reach a quasilinear configuration due to its low barrier ($\sim$2000 cm^{-1}), making necessary to use a suitable nuclear-motion Hamiltonian[1]. For the first time, the predicted *ab initio* height of the barrier to linearity (1924.6 cm^{-1}) agrees well with that obtained from an empirical PES published almost 40 years ago (1931$\pm$30 cm^{-1})[2]. The available experimental band origins for the three isotopologues (CH_2, CD_2, and $^{13}CH_2$) are reproduced with errors less than 0.1 cm^{-1} while the total root mean square deviation with the empirical transitions including those for CHD is of 0.112 cm^{-1}.

Due to the very pronounced centrifugal distortion, the rovibrational energy levels strongly overlap, even at rather small rotational quantum numbers, which renders meaningless the use of standard polyad models. In that case, the effect of the rovibrational interactions cannot be ignored, even for the ground vibrational state (000) with $K_a \geq 5$ and global variational calculations where all couplings are inherently taken into account are preferred. Comparison of our *ab initio* line positions and intensities with previous experimental works will be given. This work has been submitted for publication[3].

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[1] M. Rey, D. Viglaska, O. Egorov, A. V. Nikitin, (2023, submitted).

[2] doi:10.1063/1.450944, P. R. Bunker, P. Jensen, W. P. Kraemer, R. Beardsworth, *J. Chem. Phys.*, **85**, 3724, (1986).

[3] O. Egorov, M. Rey, D. Viglaska, A. V. Nikitin, (2023, submitted).

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