THE SPIN-VIBRONIC STRUCTURE OF $\tilde{X}\,^2E$ STATE OF METHOXY RADICAL IN THE C-H STRETCH REGION

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The presence of a conical intersection at the molecular geometry of three-fold symmetry has led to significant interest in studying the methoxy radical. Many studies in the past have analysed both spin-vibronic[1] and rotationally resolved spectra of the radical[2] . However, analysis of the spectra of the $\tilde{X}$ state of the CH_3O radical in the CH-stretch region has remained a challenge, as it has not only required a better potential energy surface (PES) than available, but also the development and improvement in efficiency of computational codes that solve spin-vibronic problems. In this talk, we present our efforts to understand and assign the spin-vibronic levels of the $\tilde{X}\,^2E$ state up to the 3000 cm^{-1} region. For this work, a PES has been calculated at the EOM-CCSDT/ANO1 level of theory. Subsequently this PES was fitted to a quartic power series expansion in all 9 vibrational normal coordinates (determined at the conical intersection) by the use of a machine-learning-based algorithm. After the addition of spin-orbit coupling to this PES, the spin-vibronic problem was solved using both Krylov-Schur and Lanczos algorithms using the SOCJT3 software [3] to converge eigenvalues and eigenvectors up to 3500 cm^{-1}. These eigenvectors were used, in conjunction with the dipole moment and its derivatives (calculated using finite differences at EOM-CCSDT/ANO1 level), to determine intensities for the spin-vibronic spectra. The calculated transition frequencies and intensities were used to assign the observed transitions of the spin-vibronic spectra of the radical [1,2,4] .

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