

AN AB INITIO STUDY AND INITIAL REFINEMENT OF THE ROVIBRONIC SPECTRUM OF SULFUR MONOXIDE ($^{32}\text{S}^{16}\text{O}$): DIABATIC VS. ADIABATIC REPRESENTATION AND THEIR EQUIVALENCE IN NUCLEAR MOTION CALCULATIONS

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An ab initio study of the rovibronic spectra of sulphur monoxide ($^{32}\text{S}^{16}\text{O}$) using internally contracted multireference configuration interaction (ic-MRCI) method using aug-cc-pV5Z basis sets is presented. It covers 13 electronic states $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^-$, $c^1\Sigma^-$, $A'^3\Sigma^+$, $A'^3\Delta$, $A^3\Pi$, $B^3\Sigma^-$, $C^3\Pi$, $d^1\Pi$, $e^1\Pi$, $C'^3\Pi$, and $(3)^1\Pi$ ranging up to 66800 cm^{-1} . The ab initio spectroscopic model includes 13 potential energy curves, 29 dipole and transition dipole moment curves, 25 spin-orbit curves, and 18 electronic angular momentum curves. A diabatic representation is built by removing the avoided crossings between the spatially degenerate pairs $C^3\Pi$ - $C'^3\Pi$ and $e^1\Pi$ - $(3)^1\Pi$ through a property-based diabatisation method. Non-adiabatic couplings and diabatic couplings for these avoided crossing systems are also presented. Finally, a rovibronic spectrum of SO is computed, where an initial refinement of the model to experimental data is shown - producing an initial semi-empirical line list for SO. All phases for our coupling curves are defined, and consistent, providing the first fully reproducible spectroscopic model of SO covering the wavelength range up to 147 nm.

We present a diabatisation procedure where the numerical equivalences between the diabatic and adiabatic representations are tested. We show that the commonly ignored first and second order non-adiabatic coupling terms are essential to the equivalence of the two representations, where we provide an analysis on the energy level convergences with basis size for Yttrium Oxide (YO) and a physical set of synthetic potential energy curves in the diabatic and adiabatic representations. The effect of this diabatisation on the accuracy of the final semi-empirical line list of SO is then discussed.