ANALYTICAL QUARTIC CENTRIFUGAL DISTORTION CONSTANTS BY FOURTH-ORDER RAYLEIGH SCHRÖDINGER VIBRATIONAL PERTURBATION THEORY

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With modern experimental techniques, rotational spectroscopy studies have succeeded at measuring the vibrational state dependence of the rovibrational constants of many asymmetric tops. However, theoretical predictions of vibrational dependence are currently only available for the rotational constants, via second-order Vibrational Perturbation Theory (VPT2). In this work, the quartic Centrifugal Distortion (CD) constants are derived at fourth-order (VPT4), allowing for prediction of their vibrational dependence. Analytical expressions are presented. The constants are implemented both in explicit sum-over-states form and the analytical (i.e., algebraic) form. The expression for VPT4 quartic CD involves the equilibrium rotational constants, force constants, Coriolis constants, and rotational derivatives. It is considerably more complicated than the VPT2 rotational constants or the VPT4 sextic CD constants. The VPT4 level of approximation introduces corrections to the VPT2 quartic CD constants that are linear in the vibrational quantum numbers. Approximately linear relationships have been identified in analyses of microwave spectra, which allow for direct comparison with the computed CD constants. Agreement is generally good for large molecules. Deficiencies for small, light molecules are addressed. Soon it will be possible to obtain VPT4 quartic CD constants alongside routine VPT2 vibrational frequency computations—with no added cost.