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

PETER R. FRANKE, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; JOHN F. STANTON, *Physical Chemistry, University of Florida, Gainesville, FL, USA*.

Recent advances in microwave spectroscopy, allowing for the measurement and fitting of thousands of spectral lines for a given chemical system, have prompted a need for high accuracy predictions of spectroscopic constants. The quartic Centrifugal Distortion (CD) constants are derived at fourth-order in Rayleigh-Schrödinger Vibrational Perturbation Theory (VPT4). Analytical expressions are presented. The constants are implemented in the CFOUR software package in both an explicit sum-over-states form and the analytical (i.e., algebraic) form. The expression for VPT4 quartic CD can be broken into ten distinct contributions, involving products of force constants, Coriolis constants, and coefficients in the expansion of the inverse moment of inertia tensor. It is considerably more complicated than the VPT2 vibration-rotation interaction constants and the VPT4 sextic CD constants. The quartic CD constants first appear at VPT2. The VPT4 level of approximation introduces corrections 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. The VPT4 quartic CD constants require a partial quartic force field, containing all force constants except those for which all indices are different (i.e., ϕ_{ijkl}). As this truncation of quartic force field is usually computed for VPT2 vibrational frequencies, it will be possible to obtain the CD constants alongside routine VPT2 frequencies with negligible added cost.