PREDICTING CORIOLIS VIBRATION-ROTATION COUPLING COEFFICIENTS FOR ANALYSIS OF ROTATIONAL SPECTRA, PART 1: THEORY AND IMPLEMENTATION

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The fitting and assignment of the rotational spectra of Coriolis-coupled distorted rotors is considerably more difficult than for isolated distorted rotors due to the sensitivity of a non-linear least-squares fit to the initial parameters and the lack of *a priori* predictions of the Coriolis coupling coefficients for all but the simplest couplings. Herein, we present our efforts to automatically generate computational predictions of Coriolis coupling coefficients (G_α, $F_{\beta\gamma}$, and their corresponding centrifugal distortion terms) using the outputs of Gaussian or CFOUR programs. The theory for deriving vibration-rotation couplings (through Van Vleck-style perturbation of the vibration-rotation Hamiltonian) and the formulas necessary for calculating a variety of coupling coefficients (G_α, $F_{\beta\gamma}$ for $\sum_i |\Delta v_i| \leq 3$ and G_α^J, G_α^K, $F_{\beta\gamma}^J$, $F_{\beta\gamma}^K$ for $\sum_i |\Delta v_i| = 2$) have been known for some time, yet only predictions of G_α for $\sum_i |\Delta v_i| = 2$ have been used. Our implementation for predicting coupling coefficients of low order in rotation (G_α and $F_{\beta\gamma}$) is straightforward. We found for terms of higher order (G_α^J, G_α^K, $F_{\beta\gamma}^J$, $F_{\beta\gamma}^K$), however, that it is necessary to carry out reductions of the respective formulas. We therefore adapted the methodology used for reducing the centrifugal distortion to obtain predictions of the coupling coefficients that can be used for *a priori* prediction and for post-fitting comparison directly to those determined experimentally.