PREDICTING CORIOLIS VIBRATION-ROTATION COUPLING COEFFICIENTS FOR ANALYSIS OF ROTATIONAL SPECTRA, PART 2: DISCUSSION AND COMPARISON TO EXPERIMENT

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We have developed a method for automatically generating predictions of Coriolis vibration-rotation coupling coefficients from Gaussian or CFOUR programs using previously known formulas, allowing us to make predictions for coupling coefficients G_α and $F_{\beta\gamma}$ for $\sum_i |\Delta v_i| \leq 3$ and G_α^J, G_α^K, $F_{\beta\gamma}^J$, $F_{\beta\gamma}^K$ for $\sum_i |\Delta v_i| = 2$. Herein, we compare the results of these predictions to experimentally determined coupled-state fits that have been published. For example, the predictions of the lower order constants (G_α and $F_{\beta\gamma}$) are in qualitative agreement (within 10%) of the recently published fits of benzonitrile, phenyl isocyanide, and phenyl acetylene. In the course of implementing the predictions for the higher order coupling coefficients (G_α^J, G_α^K, $F_{\beta\gamma}^J$, $F_{\beta\gamma}^K$), we found it necessary to apply reductions to the formulas to facilitate direct comparison to experiment (akin to that done for A-reduced or S-reduced centrifugal distortion constants). Since both the centrifugal distortions and the coupling coefficients require reductions in the Coriolis coupled distorted rotors fit, the question arises whether the choice in the reduction for the centrifugal distortions impacts the choice in the reduction for the coupling coefficients. Thus, in addition to comparing our predictions to experimentally determined values, we explore the implications of the choice for the reductions of the centrifugal distortion constants and of the coupling coefficients.