Use of Vibrational Perturbation Theory in the Analysis of Vibrational and Rotational Spectroscopy

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The calculation of vibrational frequencies by means of vibrational perturbation theory applied to the Watson Hamiltonian (Watsonian) is briefly reviewed. Uses and abuses of second-order vibrational perturbation theory (VPT2) are illustrated, as well as various ways to identify and treat "dangerous" (Fermi) resonances, both real and "artificial". VPT for the Watson Hamiltonian has recently been extended to fourth order; analytic expressions are given for the second anharmonicity constants (y_{ijk}) for the first time. This work complements earlier high-order numerical perturbation theory by Sibert and co-workers, and has also been extended to the mixed vibration-rotation problem. Various applications of VPT4 are shown, and compared to VPT2. Recommendations and practical considerations for using the VPT-based treatment of the Watsonian are also highlighted.