

INTERPRETATION OF MOLECULAR SPECTRA USING VIBRATIONAL PERTURBATION THEORY

ANNE B. McCOY, MARK A. BOYER, *Department of Chemistry, University of Washington, Seattle, WA, USA.*

We recently developed an implementation of vibrational perturbation theory (VPT) based on the approach described by Sakurai in which the perturbation theory calculations are performed numerically using linear algebra approaches. This has been incorporated in the PyVibPT n codes. Advantages that are realized by this approach include flexibility with respect to the coordinates used to expand the Hamiltonian and in the identification of possible resonance interactions. Specifically, in PyVibPT n resonances are identified based on the size of corrections to the wave function from higher-order terms in the Hamiltonian. This approach has the advantage over the Martin test, which focuses on corrections to the energies from the first order corrections to the Hamiltonian, in that our approach treats the first and second order corrections to the Hamiltonian in a more balanced manner. It also allows us to identify resonance interactions that have large effects on the intensities or other properties, while having only small impacts on the energies.

This implementation of VPT has been used in several studies of vibrational spectra. These include an analysis of the IR-cryo-SEVI spectra of vyonoxide in collaboration with the Neumark group. In this study, the vyonoxide ion is excited to states with one quantum of excitation in the CO or CH stretching vibration prior to electron photodetachment. We also describe how VPT was used to reassess the assignment of the vibrational spectrum of $\text{H}^+(\text{C}_2\text{H}_4)$. Additionally, we use VPT to obtain insights into the origins of IR intensity for transitions by decomposing the transition moment into contributions from higher order terms in the expansions of the potential and dipole moment surfaces.