

PERTURBATIONS I HAVE KNOWN AND LOVED

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A spectroscopic perturbation is a disruption of a ${}^1\Sigma - {}^1\Sigma$ -like *regular pattern* that can embody level-shifts, extra lines, and intensity anomalies. Once upon a time, when a band was labeled “perturbed,” it was considered worthless because it could at best yield molecular constants unsuited for archival tables. Nevertheless, a few brave spectroscopists, notably Albin Lagerqvist and Richard Barrow, collected perturbations because they knew that the *pattern of multiple perturbations* formed an intricate puzzle that would eventually reveal the presence and electronic symmetry of otherwise unobservable electronic states. There are many kinds of *patterns of broken patterns*. In my PhD thesis I showed how to determine absolute vibrational assignments for the perturber from *patterns among the observed values of perturbation matrix elements*. When a ${}^3\Pi$ state is perturbed, its six (Ω , parity) components capture a *pattern of level shifts and intensity anomalies* that reveals more about the nature of the perturber than a simple perturbation of the single component of a ${}^1\Sigma$ state. In perturbation-facilitated OODR, a perturbed singlet level acts as a spectroscopic doorway through which the entire triplet manifold may be systematically explored. For polyatomic molecule vibrations, a vibrational polyad (a group of mutually perturbing vibrational levels, among which the perturbation matrix elements are expected to follow harmonic oscillator scaling rules) can contain more components than a ${}^3\Pi$ state and *intrapolyad patterns* can be exquisitely sensitive not merely to the nature of an interloper within the polyad but also to the eigenvector character of the vibronic state from which the polyad is viewed. Variation of scaled polyad interaction parameters from one polyad to the next, *a pattern of patterns*, can signal proximity to an isomerization barrier. Everything in Rydberg-land seems to scale as n^{*-3} , yet a trespassing valence state causes all scaling and propensity rules go out the window.