INVISIBLE ELECTRONIC STATES AND THEIR DYNAMICS REVEALED BY PERTURBATIONS

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Sooner or later everyone working in the field of spectroscopy encounters perturbations. These can range in size from a small shift of a single rotational level to total destruction of the vibrational and rotational patterns of an electronic state. To some workers perturbations are a source of terror, but to others they are the most fascinating features of molecular spectra, because they give information about molecular dynamics, and about states that would otherwise be invisible as a result of unfavorable selection rules. An example of the latter is the essentially complete characterization of the $\tilde{b}^3A_2$ state of SO_2 from the vibronic perturbations it causes in the $\tilde{a}^3B_1$ state. The S_1-trans state of acetylene is a beautiful example of dynamics in action. The level patterns of the three bending vibrations change dramatically with increasing vibrational excitation as a result of the vibrational angular momentum and the approach to the isomerization barrier. Several vibrational levels of the S_1-cis isomer, previously thought to be unobservable, can now be assigned. They obtain their intensity through interactions with nearby levels of the trans isomer.