ASSIGNING COMPLEX VIBRATION-TUNNELING SPECTRA USING FRANCK-CONDON FINGERPRINTS

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We propose Franck-Condon fingerprinting as a method to assign complex vibration-tunneling spectra. The $\tilde{B}$ electronic excited state of Thiophosgene ($SCCl_2$) is our prototype case. Assignment of its spectrum has proven to be difficult because large tunneling splittings and near-degenerate vibrational frequencies. The dispersed fluorescence spectrum of each unkown vibration-tunneling state reveals its wavefunction character onto the known $SCCl_2$ vibrational progressions in the ground states. This Franck-Condon fingerprint allows us to assign several vibration-tunneling states of $SCCl_2$ in the $\tilde{B}$ electronic excited state. These assigned transitions could be fitted by an effective vibration-tunneling Hamiltonian within measurement uncertainty.