PATTERNS OF BROKEN PATTERNS

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Spectroscopy − it is all about patterns. Some patterns look so indescribably complicated that, unlike pornography, you *do not* know one when you see one. It is tempting to say that, at high vibrational excitation, interactions among normal mode basis states are so strong and widespread that all patterns are obliterated. But this is not true. When normal mode frequencies are in near integer multiple ratios, polyads emerge. A polyad is a robust pattern often comprising many vibrational eigenstates. Each such pattern might span many hundreds of cm^{-1}, and it is inevitable that several unrelated polyad patterns overlap. When polyads overlap, it might seem impossible to disentangle them. However, the key to disentanglement is that polyads come in families in which successive generations are related by harmonic oscillator matrix element selection and *scaling rules*. Families of polyads are described by families of scaling-based effective Hamiltonian matrices, $\mathbf{H}^{\mathrm{eff}}$. No matter how complex and overlapped, the polyad $\mathbf{H}^{\mathrm{eff}}$ serves as a magic decoder for picking out the polyad pattern. Sometimes the polyad patterns are systematically broken (a meta-pattern), owing to proximity to an isomerization barrier, as occurs in highly excited bending levels of the S_1 state of HCCH, which encode the trans-cis minimum energy isomerization path. Quantum Chemists often dismiss $\mathbf{H}^{\mathrm{eff}}$ models, precisely because they are models that do not express the full dimensionality of the complete Hamiltonian. But an $\mathbf{H}^{\mathrm{eff}}$ explains rather than describes. Shunning $\mathbf{H}^{\mathrm{eff}}$s is like throwing out the baby with the bath water. Don't do it!