Symmetry of Force Constants

- Suppose we have a set of symmetry-adapted coordinates (or displacement coordinates) we denote \( \{r\} \).

- Consider two coordinates \( r_{\alpha i} \) and \( r_{\beta j} \) which transform as basis functions for symmetry species \((\alpha i)\) and \((\beta j)\), respectively, and the energy derivative \( d^2E/dr_{\alpha i}dr_{\beta j} \).

- Since we know this derivative must be totally symmetric to be nonvanishing, let us use a projection operator to try to obtain a basis function for the totally symmetric irrep.

- The character for the totally symmetric irrep is one for all group elements, so the projection is just

\[
g^{-1} \sum_{G} G(r_{\alpha i} r_{\beta j})
\]
Symmetry of Force Constants

- Under an operation $G \in \mathcal{G}$ this coordinate product transforms as

$$g^{-1} \sum_{G} G(\alpha_i r_{\beta j}) = g^{-1} \sum_{G} G r_{\alpha i} G r_{\beta j} = g^{-1} \sum_{G} \sum_{k} \sum_{l} r_{\alpha k} r_{\beta l} D_{ki}^\alpha (G) D_{lj}^\beta (G).$$

- But the sum over $G$ here is just the GOT, giving

$$g^{-1} \sum_{G} G(\alpha_i r_{\beta j}) = g^{-1} \sum_{k} \sum_{l} \delta_{\alpha \beta} \delta_{ij} \delta_{kl} g n^{-1}_{\alpha} r_{\alpha k} r_{\beta l} = n^{-1}_{\alpha} \sum_{k} \delta_{\alpha \beta} \delta_{ij} r_{\alpha k} r_{\alpha k}.$$
or

\[ r_\alpha i r_\alpha i = n_\alpha^{-1} \sum_k r_\alpha k r_\alpha k, \]

where the value is actually independent of \( k \).
Higher Force Constants

• We can readily apply the same strategy to higher force constants, such as cubic or quartic terms.

• We have to deal with formulas such as

\[ g^{-1} \sum_{G} G(r_\alpha i r_\beta j r_\gamma k r_\delta l) \]

• There are no general formulas here, unfortunately: each situation has to be treated individually.

• Even for groups of low order this starts to be tedious by hand: for cases like \( T_d \) it’s easiest to write a small computer program.
Symmetry of Molecular Properties

- The same situation applies to the earlier perturbations we looked at.

- The polarizability can be treated in exactly the same way, for example, or hyperpolarizabilities by using more electric-field perturbations.

- Some general observations possible, such as centrosymmetric systems cannot have a dipole moment (since the latter is odd under inversion), or that all molecules must have a nonzero polarizability (because $x^2 + y^2 + z^2$, at the very least, must be totally symmetric).
Interaction with Radiation

- This can be done in a very rigorous way.
- We will simply look at the radiation as oscillating electric and magnetic fields.
- These fields can induce transitions between different quantum levels in the system.
- We will look first at the effect of dipole fields on nuclear motion (vibration and rotation), and then on the electronic motion.
- We could develop a response-type treatment but we will not explore that possibility here.
Spectroscopic Transitions

- Consider a system with two different quantum states $\Psi_i$ and $\Psi_f$. The electric field associated with incident radiation can induce a transition from $\Psi_i$ to $\Psi_f$ if the quantities

$$\int \Psi_i \tilde{\mu} \Psi_f d\tau,$$

where the integral is over all coordinates, are nonzero.

- The strength of the transition is proportional to the square of this transition moment.

- These quantum states can be rotational states, vibrational states, or electronic states.

- In any case, the transition is allowed if the transition moment is nonzero, otherwise it is forbidden.
Spectroscopic Transitions

- How much can we learn from symmetry?
- We can see immediately that unless $\Gamma(\Psi_i) \otimes \Gamma(\mu) \otimes \Gamma(\Psi_f)$ contains the totally symmetric irrep, the integral

$$\int \Psi_i \bar{\mu} \Psi_f d\tau$$

must vanish.
- An alternative viewpoint is that $\Gamma(\Psi_i) \otimes \Gamma(\Psi_f)$ contains $\Gamma(\mu)$. 
Vibrational Transitions

- Here the quantum states correspond to vibrational levels. Assume that the initial state is the ground vibrational state (no vibrational quanta and thus totally symmetric).

- Then a transition to an excited vibrational level $\Psi_f$ is forbidden unless $\Gamma(\Psi_f) \otimes \Gamma(\mu)$ contains the totally symmetric irrep.

- That is, the symmetry species of the excited state must transform in the same way as a component of the dipole moment.

- If the system is centrosymmetric, then the dipole transitions from the ground state lead to $u$ states.

- Sidebar: NH$_3$ vibrational transitions.
Harmonic Approximation

- If we make the approximation that all vibrational modes are harmonic, then the selection rules imply that only a single vibrational quantum in one mode can be excited or de-excited by radiation.

- In this case, the changing dipole moment induced by the electric field of the radiation is given entirely by the first derivative of a component of the molecular dipole moment with respect to the vibrational coordinate of the excited mode.

- This derivative is

\[
\frac{d\mu_i}{dQ_A} = \frac{d^2 E}{dQ_A df_i},
\]

from our expressions for the dipole moment. We see that this is nonvanishing if \( \Gamma(Q_A) \otimes \Gamma(f_i) \) contains the totally symmetric irrep, which is the same as the rule derived above.
Overtones and combinations arise from the breakdown of the harmonic approximation.
Raman Spectroscopy

- If vibrational transitions occur when a changing dipole moment is induced by a field, it is reasonable to ask whether a changing polarizability gives rise to vibrational transitions.

- These will have nonzero intensity if

\[ \int \Psi_i \alpha \Psi_f d\tau \neq 0. \]

- In the harmonic approximation, this requires that

\[ \frac{d\alpha_{ij}}{dQ_A} = \frac{d^3E}{dQ_A df_i df_j} \neq 0. \]

- Since these \textit{Raman transitions} couple \textit{g} states to the ground state in centrosymmetric systems, we observe that in this case transitions that are dipole-allowed will be Raman-forbidden.
• Sidebar: distinguishing cis- and trans-dichloroethylene.
Other Effects from the Radiation Field

- The radiation field includes higher-order electric multipole terms and magnetic terms.

- These effects (such as electric quadupole or magnetic dipole transitions) are extremely weak and are only rarely observed. The selection rules can be derived in complete analogy with the electric dipole transitions.

- The mixed electric/magnetic case is more interesting. This requires an excited state that can be reached both by electric and magnetic dipole transitions.

- But these are respectively polar and axial vectors, whose behaviour under improper rotations differs. Thus such transitions can be observed only if the symmetry comprises proper rotations alone. Such molecules are chiral, and this is the basis of their interaction with differently polarized light.
Rotational Spectra

- Here the incident electric field interacts with a dipole that changes with molecular orientation.

- Hence the molecule must have a permanent dipole moment for pure rotational transitions to occur.

- An applied static electric field can induce a dipole moment through the molecular polarizability. This is the Stark effect.

- The permanent dipole moment can have one, two or three components. This can be used to help identify the molecular symmetry.

- Sidebar: propadienone structure.