1.25: Summary of applying group theory to molecular motions

1. Atomic or molecular translations transform in the same way as the x, y, z (or T_x, T_y, T_z) functions listed in the character tables.
2. Molecular rotations transform in the same way as the R_x, R_y, R_z functions listed in the character tables.
3. The irreducible representations spanned by the motions of a polyatomic molecule may be determined using the $3N$ Cartesian basis, made up of x, y, z axes on each atom. The characters of the matrix representatives are best determined using a table as follows:

$$\begin{array}{ll} \text{Operation:} & \text{List the symmetry operations in the point group} \\ \Gamma_{\text{Cart}} & \text{List the characters for } x+y+z \text{ (from the character table) for each operation} \\ N_{\text{unshifted}} & \text{List the number of atoms in the molecule that are unshifted by each symmetry operation} \\ \Gamma_{3N} & \text{Take the product of the previous two rows to give the characters for } \Gamma_{3N} \end{array} \tag{1.25.1}$$

4. The irreducible representations spanned by the molecular vibrations are determined by first subtracting the characters for rotations and translations from the characters for Γ_{3N} to give the characters for Γ_{vib} and then using the reduction formula or inspection of the character table to identify the irreducible representations contributing to Γ_{vib}.
5. The molecular displacements for the vibrations of each symmetry may be determined by using projection operators on the $3N$ Cartesian basis vectors to generate SALCs.
6. Alternatively, a basis of internal coordinates (bond lengths and angles) may be used to investigate stretching and bending vibrations. Determine the characters, identify the irreducible representations, and construct SALCs.

Contributors and Attributions

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