Chapter 5

DERIVATION OF SELECTION RULES*

5-1. DERIVATION OF SELECTION RULES FOR NONLINEAR MOLECULES OF THE MOST COMMON POINT GROUPS

The complete selection rules for nonlinear molecules of the point groups $T_d$, $D_{4h}$, $O_h$, $D_{3h}$, $C_{3v}$, and $C_{2v}$ are presented in this chapter. The selection rules govern which bands will appear in the infrared and Raman spectra. These selection rules will apply to any molecules with the above mentioned symmetries.

In Chapter 7, molecules in some of the above point groups will be analyzed by the normal coordinate treatment. For the derivation of selection rules we have employed the notation of Meister, Cleveland, and Murray.\(^{(1)}\)

5-2. THE $T_d$ POINT GROUP

The symmetry elements of the $T_d$ point group are illustrated in Fig. 5-1. The characters for the irreducible representations for $T_d$ are given in Table 5-1. Two main types of covering operations are possible, and these are called proper and improper rotations. A proper rotation is defined as a rotation through an angle $\pm \varphi$ about some axis of symmetry. An improper rotation is a rotation followed by a reflection in a plane perpendicular to the axis of rotation. Thus, a reflection may be considered an improper rotation through an angle of $0^\circ$. The center of symmetry (i) operation can be considered an $S_2$ operation and, thus, may also be considered an improper rotation. The difference between a proper and an improper rotation is shown in Fig. 5-2.

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Fig. 5-1. Symmetry elements for the \( T_d \) point group \((4C_3, 3C_2 \approx S_4, 6\sigma_d)\).

**Number of Fundamentals of Each Type**

The quantity \( \mathcal{E}(R) \) from Table 5-1 for \( \text{CCl}_4 \) is used to determine the number of fundamentals of each type\(^{(1,2)} \) where

\[
\mathcal{E}(R) = (\mu_R - 2)(1 + 2 \cos \varphi) \quad \text{for proper rotations}
\]

\[
= (\mu_R)(-1 + 2 \cos \varphi) \quad \text{for improper rotations}
\]

Here \( \varphi \) is the angle associated with the proper or improper movement and \( \mu_R \) is obtained from Table 5-1 and is the number of atoms left unchanged by the operation \( R \). The number of vibrations of each type depends on the number of atoms contained in the molecule\(^{(1,2)} \).