

## APPENDIX 1:

### GROUP THEORY

Group theory is the mathematics of symmetry. The significance of group theory for chemistry is that molecules can be categorized on the basis of their symmetry properties, which allow the prediction of many molecular properties. The process of placing a molecule into a symmetry category involves identifying all of the lines, points, and planes of symmetry that it possesses; the symmetry categories the molecules may be assigned to are known as point groups. All linear molecules have an infinite number of symmetry elements (consider the planes of symmetry that contain the molecular axis, for instance). However, it is easy to see that  $C_2H_2$  and  $C_2D_2$  have different symmetry properties than  $C_2HD$  because they possess a plane of symmetry through the center of the molecule perpendicular to the axis whereas  $C_2HD$  does not. Linear molecules such as  $C_2H_2$  and  $C_2D_2$  that have a point of symmetry at the midpoint of the molecule belong to the point group called  $D_{\infty h}$ . All other linear molecules, such as  $C_2HD$ , belong to the point group  $C_{\infty v}$ .

Molecular vibrations either conserve or break the various symmetry elements of the molecule. For instance, some vibrational modes conserve all of the symmetry elements of the molecule (the  $\nu_1$  and  $\nu_2$  vibrational modes of acetylene, for example). These vibrations are referred to as totally symmetric. More generally, the various vibrational modes of a molecule can be categorized in terms of their behavior with respect to the symmetry elements of the molecule. In fact, any motion of the molecule, including translations, rotations, and vibrations, can be categorized on this basis. The categories to which these motions are assigned are called “irreducible representations”, or “irreps” for short. The totally symmetric “irrep” is one example, which is designated by  $\Sigma^+$  for the  $C_{\infty v}$  point group and by  $\Sigma_g^+$  for the  $D_{\infty h}$  point group. However, the  $C_{\infty v}$  and  $D_{\infty h}$  point groups have an infinite number of possible irreps.

There are two major methods of determining which irreps the vibrational modes of a molecule correspond to. The first is to use some advanced group theory techniques to predict from the symmetry of the molecule alone how many vibrational modes will exist, their degeneracies, and what irreps they correspond to. If you know how to do this, great! You can crank out the mathematics for all three of the molecules in an hour or two. The other method is to do a normal mode analysis on the molecule which tells you what the vibrations look like. You can then examine how each vibrational mode behaves

with respect to the symmetry properties of the molecule and assign them to irreps on this basis. You will notice that all of this has been done for you earlier in the manual.

The most important application of group theory to this lab is that it allows you to determine which vibrational transitions are allowed or forbidden on the basis of symmetry. As discussed earlier, time-dependent quantum mechanics states that the transition probability between two quantum mechanical states can be described by an integral of the form

$$P_{i \rightarrow f} = \left| \int \psi_{\text{final}}^* \hat{\mu} \psi_{\text{initial}} \, d\mathbf{r} \right|^2$$

where  $\mu$  is the transition dipole operator. In general, computing this integral is difficult, but there are a few conditions under which the integral is identically zero, and hence the transition is forbidden. This is the origin of selection rules such as  $\Delta v = \pm 1$  for the harmonic oscillator. Another set of selection rules derives from group theory. Basically, you can see that if the product of the states and dipole operator above lead to an odd function, the integral will vanish. Similarly, when the initial and final vibrational modes belong to certain irreps, the integral goes to zero.

Group theory provides a quick method of determining whether a vibrational transition is allowed based on the symmetry of the molecule. This method rests on the notion of the direct product. Conceptually, you can think of the direct product as a process of multiplying irreps. When the direct product of the initial and final vibrational irreps is equal to (or contains) an irrep corresponding to a dipole transition (in the x, y, or z directions), the vibrational transition is symmetry allowed. For the  $C_{\infty v}$  point group the irreps for these transitions (the dipole operator) are  $\Sigma^+$  (for  $\mu_z$ ) and  $\Pi$  (for  $\mu_x, \mu_y$ ) and for the  $D_{\infty h}$  point group,  $\Sigma_u^+$  and  $\Pi_u$ . Keep in mind that the ground vibrational state always corresponds to the totally symmetric irrep (that is, if the atoms aren't moving, all symmetry elements are conserved).

So as an example, for the  $\nu_3$  mode of  $C_2H_2$ , the product of irreps for initial and final states is  $\Sigma_g^+ \times \Sigma_u^+ = \Sigma_u^+$ . This equals the symmetry of the dipole operator  $\mu_z$  and the transition is symmetry allowed. Alternatively, we can take products of the irreps for the three quantities in the integral above,  $\psi_{\text{init}}$ ,  $\mu$ , and  $\psi_{\text{final}}$ . If this product is symmetric, g, then the integral will not vanish and the transition is allowed. Again for  $\nu_3$  and using the  $\mu_z$  irrep,  $\Sigma_g^+ \times \Sigma_u^+ \times \Sigma_u^+ = \Sigma_g^+$ .

Thus, you can determine almost at a glance which fundamentals and “subtraction” bands are allowed for each molecule. To determine which combination bands are allowed, you need to know that the irrep corresponding to the excited state is the direct product of the irreps for the two vibrational modes involved. (How do these results

compare with the rule that vibrational transitions are allowed only if they involve an oscillating dipole moment? These group theory rules are the generalization of this rule. What are the advantages of the group theory formalism?)

Shoemaker provides a few rules for computing the relevant direct products. One other useful rule is that the direct product of any irrep with the totally symmetric irrep is itself. For convenience, you may wish to complete the “direct product tables” below.

$$\begin{aligned}
 g \times g &= u \times u = g & g \times u &= u \\
 \Sigma^{\pm} \times \Sigma^{\pm} &= \Sigma^{+} & \Sigma^{\pm} \times \Sigma^{\mp} &= \Sigma^{-} & \Sigma^{\pm} \times \Pi &= \Pi & \Sigma^{\pm} \times \Delta &= \Delta \\
 \Pi \times \Pi &= \Sigma^{+} + \Sigma^{-} + \Delta & \Delta \times \Delta &= \Sigma^{+} + \Sigma^{-} + \Gamma & \Pi \times \Delta &= \Pi + \Phi
 \end{aligned}$$

Direct product table for the  $D_{\infty h}$  point group

$D_{\infty h}$	$\Sigma_g^{+}$	$\Sigma_u^{+}$	$\Pi_g$	$\Pi_u$
$\Sigma_g^{+}$				
$\Sigma_u^{+}$				
$\Pi_g$				
$\Pi_u$				

Direct product table for the  $C_{\infty v}$  point group

$C_{\infty v}$	$\Sigma^{+}$	$\Pi$
$\Sigma^{+}$		
$\Pi$		