Appendix B

The Nature of Photon-Induced Electronic Transitions

When a photon is absorbed by a molecule and causes an electronic transition to occur, the *electronic* energy of the molecule changes from $E_0(\mathbf{R})$, its ground-state value before absorption, to $E_x(\mathbf{R})$, its excited-state value. The energy of the photon of frequency $h\nu$ must match $E_x(\mathbf{R}) - E_0(\mathbf{R}) = h\nu$. For any given frequency ν, this condition will generally not be met at *all* molecular geometries $\{\mathbf{R}\}$; only at particular geometries $\{\mathbf{R}_c\}$ will $h\nu = E_x - E_0$.

There is much more to understanding photon absorption than is contained in the above relation. Often the electronic absorption spectrum of a molecule (even one which subsequently undergoes a photoreaction) displays sharp vibrational structure, especially when the molecule is in the gas phase or in an inert matrix such as frozen argon or nitrogen. This vibrational structure arises because the ground and excited electronic states of the molecule have quantized vibrational energy levels $\{\epsilon_\nu^0\}$ and $\{\epsilon_{\nu'}^x\}$, respectively. Even when the excited state has vibrational levels that are broadened by dissociation (i.e., they are not actually bound), vibrational structure can persist in the absorption spectrum if the width of the state ($\hbar$ divided by the dissociation lifetime) remains less than the spacing between the levels.

When vibrational structure is seen, the energy of the photon must also obey the equation $h\nu = \epsilon_{\nu'}^x - \epsilon_\nu^0$; that is, the transition occurs between quantized states of E_0 and E_x. Combining the above two requirements on $h\nu$ gives

$$\epsilon_{\nu'}^x - \epsilon_\nu^0 = E_x(\mathbf{R}_c) - E_0(\mathbf{R}_c). \tag{B.1}$$

This very important relation shows that transitions from ϵ_ν^0 to $\epsilon_{\nu'}^x$ can occur only at molecular geometries $\{\mathbf{R}_c\}$ in which the quantum-level energy difference $\epsilon_{\nu'}^x - \epsilon_\nu^0$ is identical to the *electronic* energy difference $E_x(\mathbf{R}_c) - E_0(\mathbf{R}_c)$. Since the electronic energy functions E_x and E_0 are the potential energy functions for the vibration-rotation motion of the molecule, the vibration-rotation classical kinetic energies T are given by $\epsilon_{\nu'}^x - E_x(\mathbf{R}_c) = T_x(\mathbf{R}_c)$ and $\epsilon_\nu^0 - E_0(\mathbf{R}_c) = T_0(\mathbf{R}_c)$. Hence, the above condition can be restated as $T_x(\mathbf{R}_c) = T_0(\mathbf{R}_c)$; that is, photon absorption can occur at geometries in which the classical vibration-rotation kinetic energy is conserved.

Thus far, we have seen how to determine geometries at which the light of energy $h\nu = \epsilon^x_{v'} - \epsilon^0_v$ *can* be absorbed. To understand the rate at which such light *will* be absorbed, we need to consider what happens to the electronic and vibration-rotation wavefunctions of the molecule when a photon is absorbed.

In the approximation in which the photon-molecule interaction is treated as an electric dipole interaction, the ground-state Born-Oppenheimer wavefunction $\phi_0(\mathbf{r}|\mathbf{R})\chi^0_v(\mathbf{R})$ becomes $\phi_x(\mathbf{r}|\mathbf{R})\langle\phi_x(\mathbf{r}|\mathbf{R})|\epsilon\cdot\mathbf{r}|\phi_0(\mathbf{r}|\mathbf{R})\rangle\chi^0_v(\mathbf{R})$ when the photon $(h\nu = \epsilon^x_{v'} - \epsilon^0_v)$ is absorbed (Simons, 1982). To make a connection with the Franck-Condon picture, the **R**-dependence of the above postabsorption wavefunction $(\psi_{x,\nu})$ is expanded in terms of the complete set of vibration-rotation functions $\{\chi^x_{v'}\}$ of the excited state

$$\psi_{x,\nu}(\mathbf{r}|\mathbf{R}) = \sum_{v'}\langle\chi^x_{v'}\phi_x|\epsilon\cdot\mathbf{r}|\chi^0_v\phi_0\rangle\phi_x\chi^x_{v'}\delta\left[\nu - \left(\frac{\epsilon^x_{v'} - \epsilon^0_v}{h}\right)\right] \tag{B.2}$$

The δ function is inserted simply to insure that the energy of the photon that creates $\psi_{x,\nu}$ is equal to the quantum-state energy difference $\epsilon^x_{v'} - \epsilon^0_v$. The probability P of finding the molecule in any specific vibration-rotation state $\phi_x\chi^x_{v'}$ having energy $\epsilon^x_{v'}$ is given by the square of the amplitude of this state in the above expression for $\psi_{x,\nu}$:

$$P = \delta\left[\nu - \left(\frac{\epsilon^x_{v'} - \epsilon^0_v}{h}\right)\right]|\langle\chi^x_{v'}\phi_x|\epsilon\cdot\mathbf{r}|\chi^0_v\phi_0\rangle|^2. \tag{B.3}$$

The usual Franck-Condon factors arise by assuming that the electric-dipole-transition matrix element $\langle\phi_x(\mathbf{r}|\mathbf{R})|\epsilon\cdot\mathbf{r}|\phi_0(\mathbf{r}|\mathbf{R})\rangle \equiv \mu_{0x}(\mathbf{R})$ is relatively independent of molecular geometry $\mu_{ox}(\mathbf{R}) \cong \mu_{0x}$. With such an approximation

$$P = \delta\left[\nu - \frac{\epsilon^x_{v'} - \epsilon^0_v}{h}\right]|\langle\chi^x_{v'}|\chi^0_v\rangle|^2\mu^2_{0x},$$

which contains the Franck-Condon factors $|\langle\chi^x_{v'}|\chi^0_v\rangle|^2$. The expression for P leads to the conclusion that transitions to $\phi_x\chi^x_{v'}$ occur at a rate proportional to μ^2_{0x} times the square of the overlap between the initial vibration-rotation state χ^0_v and the final state $\chi^x_{v'}$.

Transitions for which μ_{0x} vanish are said to be electronically forbidden. Molecular point-group symmetry, which is reflected in the spatial symmetry of ϕ_0 and ϕ_x, can determine whether μ_{0x} vanishes. For example, the ${}^1A_1 \rightarrow {}^1A_2$, $n(b_2) \rightarrow \pi^*(b_1)$ electronic transition in C_{2v} H_2CO is forbidden, since $\mu_{0x} = \langle\pi^*|\epsilon\cdot\mathbf{r}|n\rangle$ vanishes. Transitions that are electronically allowed can still be forbidden if the Franck-Condon factor $|\langle\chi^x_{v'}|\chi^0_v\rangle|^2$ vanishes. Again, molecular symmetry gives rise to symmetry in $\chi^x_{v'}$ and χ^0_v, which can then be used to predict whether $\langle\chi^x|\chi^0\rangle$

equation B.3 it had not been assumed that $\mu_{0x}(\mathbf{R})$ is $\mathbf{R}$-independent, and $\mu_{0x}(\mathbf{R})$ was expanded about the equilibrium geometry $\{\mathbf{R}_e\}$ of the ground state χ_v^0,

$$\mu_{0x}(\mathbf{R}) = \mu_{0x}(\mathbf{R}_e) + (\mathbf{R} - \mathbf{R}_e)\cdot\nabla_R\mu_{0x} + \cdots, \tag{B.4}$$

then for such electronically forbidden transitions the transition probability P would reduce to

$$P = \delta\left[\nu - \left(\frac{\epsilon_{v'}^{x} - \epsilon_v^0}{h}\right)\right]|\nabla_R\mu_{0x}\cdot\langle\chi_{v'}^{x}|(\mathbf{R} - \mathbf{R}_e)|\chi_v^0\rangle|^2. \tag{B.5}$$

Because the geometrical displacements $\mathbf{R} - \mathbf{R}_e$ contain contributions from various symmetries, the integrals $\langle\chi_{v'}^{x}|\mathbf{R} - \mathbf{R}_e|\chi_v^0\rangle$ could be nonzero even though $\langle\chi_{v'}^{x}|\chi_v^0\rangle = 0$. In such cases, the intensity of the transition is said to be *borrowed*. In lowest order it is forbidden, since $\mu_{0x} \cong 0$; it is only through the $\mathbf{R}$-dependence of μ_{0x} that the transition is weakly allowed.

Although the above Franck-Condon analysis of the intensities of vibration-rotation structure in electronic absorption lines is very informative, another point of view gives additional insight. By treating the vibration-rotation kinetic-energy operator of the molecule classically, the photon-absorption probability can be rewritten as follows (Simons, 1982):

$$P = \langle\chi_v^0|\delta[\nu - (E_x(\mathbf{R}) - E_0(\mathbf{R}))/h]\mu_{0x}^2(\mathbf{R})|\chi_v^0\rangle. \tag{B.6}$$

This expression can be interpreted in terms of the probability $|\chi_v^0(\mathbf{R})|^2$ of the molecule being at geometry $\mathbf{R}$ in the ground state χ_v^0, multiplied by the electric dipole matrix element at that geometry $\mu_{0x}^2(\mathbf{R})$, and constrained (by the δ function) to allow contribution of only those geometries that obey $h\nu = E_x - E_0$. By allowing equation B.6 to apply only when $h\nu = \epsilon_{v'}^{x} - \epsilon_v^0$, a partly classical approximation of P is obtained:

$$P = \delta[\nu - (\epsilon_{v'}^{x} - \epsilon_v^0)/h]\langle\chi_v^0|\delta[\nu - (E_x - E_0)/h]\mu_{0x}^2|\chi_v^0\rangle. \tag{B.7}$$

This expression for P can be used in attempting to understand how photon absorption prepares the molecule at the excited-state potential-energy surface $E_x(\mathbf{R})$. The energy of the photon must coincide (within the spectral linewidths) with one of the energy spacings $\epsilon_{v'}^{x} - \epsilon_v^0$. For each such energy value, the molecule can absorb the light only at geometries $\{\mathbf{R}_c\}$ obeying $h\nu = E_x(\mathbf{R}_c) - E_0(\mathbf{R}_c)$; this condition preserves the vibration-rotation kinetic energy of the molecule. The relative probability that the molecule experiences each such critical geometry $\{\mathbf{R}_c\}$ is given by the square of the initial vibration-rotation wavefunction $|\chi_v^0(\mathbf{R}_c)|^2$.

$|\chi_v^0|^2$ of the absorbing molecule being at $\{\mathbf{R}_c\}$ multiplied by the relative rate $\mu_{0x}^2(\mathbf{R}_c)$ of its electronic absorption at $\{\mathbf{R}_c\}$. This interpretation of equation B.7 is a valuable one. In attempting to determine the geometries at which the system will enter the excited surface, only molecular geometries for which $|\chi_v^0|^2$ is substantial must be examined. Within such geometries, only those for which ground- and excited-state surfaces are spaced by $h\nu$ will be populated during photon absorption. Finally, the transition to the excited surface will be efficient only where $\mu_{0x}^2(\mathbf{R}_c)$ is large.

The above qualitative treatment of photon absorption was motivated by the need to guess where a molecule will enter an excited-state potential energy surface. Knowing where it enters E_x, one can then walk along the E_x surface toward the product molecule to see whether reaction barriers, surface crossings, or near-crossings occur. As illustrated in Chapters 6 and 7, the ability to explore excited surfaces in the above manner is essential if one hopes to predict the outcome of photochemically initiated reactions.

The energy of the photon $h\nu = \epsilon_{v'}^x - \epsilon_v^0$ has been treated as being *precisely* determined by the initial ϵ_v^0 and final $\epsilon_{v'}^x$ energies. However, the energy of the absorbing photons may not be precisely determined, owing to the finite bandwidth of the light source or the lifetime broadening of the excited level $\epsilon_{v'}^x$. In that case, the contributions arising from a finite range of frequencies $\nu_0 \pm \Delta\nu$ must be added up. In attempting to guess the molecular geometries at which the excited surface E_x is entered, ν must be allowed to vary (by $\Delta\nu$) about the mean value ν_0. Experiments involving high-resolution monochromators ($\Delta\nu/c \sim 0.1\ \text{cm}^{-1}$) and sharp vibrational lines $(1/hc)\Delta\epsilon_{v'}^x \sim 1\ \text{cm}^{-1}$ do not produce significant smoothing of the photon energy (i.e., $\Delta\nu$ is small). However, modern picosecond and nanosecond light sources have bandwidths of 33 cm^{-1} and 0.03 cm^{-1}, respectively, and for very short ($\sim$1–10 picosecond) light pulses, significant uncertainty in ν can occur, which then requires one to consider a spread in ν values in implementing a picture of the photon-absorption event.

Even if a highly frequency-resolved light source is employed, a reasonably short (10^{-11}–10^{-13} sec) lifetime of the final state $\epsilon_{v'}^x$ can give rise to a spread (3–333 cm^{-1}) in the allowed absorption energies. Thus, when considering excited states that decompose on a relatively fast time scale ($< 10^{-10}$ sec), one must again consider a range of ν values.

Appendix C

Review of Point-Group Symmetry Tools

In this appendix it is assumed that the reader is familiar with molecular point groups, symmetry operations, and character tables. Good introductions to these topics can be found in several references (Cotton, 1963; Eyring, Walter and Kimball, 1944; and Wilson, Decius, and Cross, 1955). In this appendix, we shall only review material that is of direct use in solving the problems in the text.

We begin by summarizing the information content of a representative character table. A fairly complete list of character tables is given at the end of this appendix. At its ground-state equilibrium geometry the ammonia molecule NH_3 belongs to the C_{3v} point group. Its symmetry operations consist of two C_3 rotation axes (rotation by 120° and 240°, respectively, about an axis passing through the nitrogen atom and lying perpendicular to the plane formed by the three hydrogen atoms), three vertical planes σ_v, $\sigma_{v'}$, $\sigma_{v''}$, and the identity operation. These symmetry elements are shown in Figure C-1.

The C_{3v} character table given at the end of the appendix lists the above symmetry operations along with the names of three irreducible representations (A_1, A_2, E) that characterize this point group. Also listed under the title of point group C_{3v} are examples of especially common and important functions [e.g., z, R_z, (x,y)] that transform according to each of the irreducible representations.

To transform according to a certain irreducible representation means that the function, when operated upon by a point-group symmetry operator, yields a linear combination of the functions that transform according to that irreducible representation. For example, a $2p_z$ orbital (z is the C_3 axis of NH_3) on the nitrogen atom belongs to the A_1 representation because it yields 1 times itself when C_3, C_3', σ_v, $\sigma_{v'}$, $\sigma_{v''}$, or the identity operation operates on it. The factor of 1 means that $2p_z$ has A_1 symmetry, since the characters (the numbers listed opposite A_1 and below E, $2C_3$, and $3\sigma_v$ in the C_{3v} character table) of all six symmetry operations are 1 for the A_1 irreducible representation.

The $2p_x$ and $2p_y$ orbitals on the nitrogen atom transform as the E representation, since C_3, C_3', σ_v, $\sigma_{v'}$, $\sigma_{v''}$, and the identity map $2p_x$ and $2p_y$ among one another. For example,

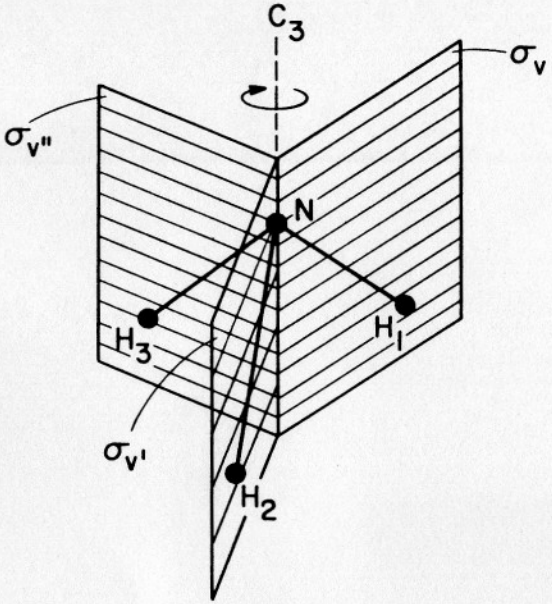

Figure C-1
Symmetry elements of NH_3.

$$C_3\begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix} = \begin{pmatrix} \cos 120^\circ & \sin 120^\circ \\ -\sin 120^\circ & \cos 120^\circ \end{pmatrix} \times \begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix}$$

$$C_{3'}\begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix} = \begin{pmatrix} \cos 240^\circ & \sin 240^\circ \\ -\sin 240^\circ & \cos 240^\circ \end{pmatrix} \times \begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix}$$

$$E\begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \times \begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix}$$

$$\sigma_v\begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix} \times \begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix}$$

$$\sigma_{v'}\begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \times \begin{pmatrix} 2p_x \\ 2p_y \end{pmatrix}$$

and

$$\sigma_{v''}\begin{pmatrix} 2p_x \\ \\ 2p_y \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \times \begin{pmatrix} 2p_x \\ \\ 2p_y \end{pmatrix}.$$

The 2×2 matrices, which indicate how each symmetry operation maps $2p_x$ and $2p_y$ into some combinations of $2p_x$ and $2p_y$, are called the representation matrices (RM) for that particular operation and for this particular irreducible representation. For example,

$$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

is $\mathrm{RM}_E(\sigma_{v''})$. The traces (sums of the diagonal elements) of these matrices are called characters (e.g., $\chi_E(\sigma_{v''})$) and are the entries in the character tables.

A shortcut device exists for evaluating the trace of the representation matrices (that is, for computing the characters). The diagonal elements of the representation matrices are the projections along each orbital of the effect of the symmetry operation acting on that orbital. For example, a diagonal element of the C_3 matrix is the component of $C_3 2p_y$ along the $2p_y$ direction. More rigorously, it is $\int 2p_y^* C_3 2p_y \, d\mathbf{r}$. Thus, the character of the C_3 matrix is the sum of $\int 2p_y^* C_3 2p_y \, d\mathbf{r}$ and $\int 2p_x^* C_3 2p_x \, d\mathbf{r}$. In general, the character χ of a symmetry operation S can be computed by allowing S to operate on each orbital ϕ_i, projecting $S\phi_i$ along ϕ_i (forming $\int \phi_i^* S \phi_i \, d\mathbf{r}$), and summing these terms, $\Sigma_i \int \phi_i^* S \phi_i \, d\mathbf{r} = \chi(S)$. If these rules are applied to the $2p_x$ and $2p_y$ orbitals of nitrogen within the C_{3v} point group, then

$$\chi(E) = 2, \quad \chi(C_3) = \chi(C_{3'}) = -1, \qquad \text{and}$$

$$\chi(\sigma_v) = \chi(\sigma_{v'}) = \chi(\sigma_{v''}) = 0.$$

This set of characters agrees with those of the E representation for the C_{3v} point group, so $2p_x$ and $2p_y$ belong to or transform as the E representation. This is why (x, y) is to the left of the row of characters for the E representation in the C_{3v} character table.

In similar fashion, the C_{3v} character table states that $d_{x^2-y^2}$ and d_{xy} orbitals on nitrogen transform as E, as do d_{xz} and d_{yz}, but d_{z^2} transforms as A_1.

To illustrate a somewhat more complicated situation, we consider how the three $1s_H$ orbitals on the hydrogen atoms transform. Using the shortcut rule just described, the traces (characters) of the 3×3 representation matrices formed are computed by allowing E, $2C_3$, and $3\sigma_v$ to operate on $1s_{H_1}$, $1s_{H_2}$, and $1s_{H_3}$. The resulting characters are $\chi(E) = 3$, $\chi(C_3) = \chi(C_{3'}) = 0$, and $\chi(\sigma_v) = \chi(\sigma_{v'}) = \chi(\sigma_{v''}) = 1$. The C_{3v} character table shows that these characters (3,0,1) do not match the characters of any *one irreducible* representation, though the sums of the characters of the A_1 and E representations do give these characters. Hence, the hydrogen $1s_H$ orbital set forms a *reducible* representation consisting of the sum of A_1 and E. This means that the three $1s_H$ orbitals can be combined to yield one orbital of A_1 symmetry and a *pair* that each transforms according to the E representation.

To generate the A_1 and E symmetry-adapted orbitals, the symmetry-projection operators P_E and P_{A_1} are used. These operators are given in terms of linear combinations of products of characters times elementary symmetry operations as follows:

$$P_{A_1} = \sum_S \chi_{A_1}(S)S \tag{C.1}$$

$$P_E = \sum_S \chi_E(S)S \tag{C.2}$$

The result of applying P_{A_1} to, say, $1s_{H_1}$ is

$$\begin{aligned} P_{A_1} 1s_{H_1} &= 1s_{H_1} + 1s_{H_2} + 1s_{H_3} + 1s_{H_2} + 1s_{H_3} + 1s_{H_1} \\ &= 2(1s_{H_2} + 1s_{H_2} + 1s_{H_3}) = \phi_{A_1}, \end{aligned}$$

which is an (unnormalized) orbital having A_1 symmetry. Clearly, this same ϕ_{A_1} would be generated by P_{A_1} acting on $1s_{H_2}$ or $1s_{H_3}$. Hence, only one A_1 orbital exists.

Likewise,

$$P_E 1s_{H_1} = (2 \times 1s_{H_1}) - 1s_{H_2} - 1s_{H_3} \equiv \phi_{E,1}$$

which is *one* of the symmetry-adapted orbitals having E symmetry. The other E orbital can be obtained by allowing P_E to act on $1s_{H_2}$ or $1s_{H_3}$:

$$P_E 1s_{H_2} = (2 \times 1s_{H_2}) - 1s_{H_1} - 1s_{H_3} \equiv \phi_{E,2}$$

$$P_E 1s_{H_3} = (2 \times 1s_{H_3}) - 1s_{H_1} - 1s_{H_2} = \phi_{E,3}.$$

It might seem as though *three* orbitals having E symmetry were generated, but only two of these are really independent functions. For example, $\phi_{E,3}$ can be expressed in terms of $\phi_{E,1}$ and $\phi_{E,2}$ as

$$\phi_{E,3} = -(\phi_{E,1} + \phi_{,2}).$$

Thus, only $\phi_{E,1}$ and $\phi_{E,2}$ are needed to span the two-dimensional space of the E representation.

In summary, a given set of atomic orbitals $\{\phi_i\}$ can be used as a basis for the symmetry operations of the point group of the molecule. The characters $\chi(S)$ belonging to the operations S of this point group can be found by summing the integrals $\int \phi_i^* S \phi_i \, d\mathbf{r}$ over all the atomic orbitals. The resultant characters will, in general, be reducible to a combination of the characters of the irreducible representations $\chi_i(S)$. To decompose the characters $\chi(S)$ of the reducible representation to a sum of characters $\chi_i(S)$ of the irreducible representation $\chi(S) = \Sigma_i n_i \chi_i(S)$, it is necessary to determine how many times, n_i, the ith irreducible representation occurs in the reducible representation. The expression for n_i is (Cotton, (1963))

$$n_i = \frac{1}{g} \sum_S \chi(S) \chi_i(S) \qquad \text{(C.3)}$$

in which g is the order of the point group—that is, g is simply the total number of symmetry operations in the group (e.g., $g = 6$ for C_{3v}). The reducible representation $\chi(E) = 3$, $\chi(C_3) = 0$, and $\chi(\sigma_v) = 1$ formed by the three $1s_H$ orbitals discussed above can be decomposed as follows:

$$n_{A_1} = \frac{1}{6}(3 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot 1) = 1$$

$$n_{A_1} = \frac{1}{6}(3 \cdot 1 + 2 \cdot 0 \cdot 1 + 3 \cdot 1 \cdot (-1)) = 0$$

$$n_E = \frac{1}{6}(3 \cdot 2 + 2 \cdot 0 \cdot (-1) + 3 \cdot 1(0)) = 1,$$

These equations state that the three $1s_H$ orbitals can be combined to give one A_1 orbital and (since E is degenerate), one *pair* of E orbitals, as established above. With knowledge of the n_i, the symmetry-adapted orbitals can be formed by allowing the projectors

$$P = \sum \chi(S) S \qquad \text{(C.4)}$$

to operate on each of the primitive atomic orbitals. How this is carried out was illustrated for these $1s_H$ orbitals after equation C.2. These tools allow a symmetry decomposition of any set of atomic orbitals into appropriate symmetry-adapted orbitals.

Before considering other concepts and group-theoretical machinery, it should be pointed out that these same tools can also be used in symmetry analysis of the translational, vibrational, and rotational motions of a molecule. The twelve motions of NH_3 (three translations, three rotations, six vibrations) can be described in terms of combinations of displacements of each of the four atoms in each of three (x, y, z) directions. Hence, unit vectors placed on each atom directed in the x, y, and z directions form a basis for action by the operations (S) of the point group. In the case of NH_3, the characters of the resultant 12×12 representation matrices form a reducible representation in the C_{2v} point group: $\chi(E) = 12, \chi(C_3) = \chi(C_{3'}) = 0, \chi(\sigma_v) = \chi(\sigma_{v'}) = \chi(\sigma_{v''}) = 2$. This representation can be decomposed as follows:

$$n_{A_1} = \frac{1}{6}[1\cdot 1\cdot 12 + 2\cdot 1\cdot 0 + 3\cdot 1\cdot 2] = 3$$

$$n_{A_2} = \frac{1}{6}[1\cdot 1\cdot 12 + 2\cdot 1\cdot 0 + 3\cdot(-1)\cdot 2] = 1$$

$$n_E = \frac{1}{6}[1\cdot 2\cdot 12 + 2\cdot(-1)\cdot 0 + 3\cdot 0\cdot 2] = 4.$$

From the information on the left side of the C_{3v} character table, translations of all four atoms in the z, x and y directions transform as $A_1(z)$ and $E(x, y)$, respectively, whereas rotations about the $z(R_z)$, $x(R_x)$, and $y(R_y)$ axes transform as A_2 and E. Hence, of the twelve motions, three translations have A_1 and E symmetry and three rotations have A_2 and E symmetry. This leaves six vibrations, of which two have A_1 symmetry, none have A_2 symmetry, and two (pairs) have E symmetry. We could evaluate the symmetry-adapted vibrations and rotations by allowing symmetry-projection operators of the irreducible-representation symmetries to operate on various elementary cartesian (x, y, z) atomic displacement vectors. Both Cotton (1963) and Wilson, Decius and Cross (1955) show in detail how this is accomplished.

We now return to the symmetry analysis of atomic orbitals by considering how the symmetries of individual orbitals give rise to symmetry characteristics of orbital products. Such knowledge is important because one is routinely faced with constructing symmetry-adapted electronic configurations that consist of products of N individual orbitals. A point-group symmetry operator S, when acting on such a product of orbitals, gives the product of S acting on each of the individual

$$S\phi_1\phi_2\phi_3 \cdots \phi_N = (S\phi_1)(S\phi_2)(S\phi_3) \cdots (S\phi_N). \tag{C.5}$$

For example, reflection of an N-orbital product through the σ_v plane in NH_3 utilizes reflection operations for all N electrons.

Just as the atomic orbitals formed a basis for action of the point-group operators, the configurations (N-orbital products) form a basis for the action of these same point-group operators. Hence, the various electronic configurations (orbital occupancies) can be treated as functions on which S operates, and the machinery illustrated earlier for decomposing orbital symmetry can then be used to carry out a symmetry analysis of configurations. However, another shortcut makes this task easier. Since the individual orbitals $\{\phi_i, i = 1, \ldots, M\}$ transform according to irreducible representations, we form the direct product of the symmetries of the N orbitals that appear in any configuration. This direct product can then be symmetry-analyzed in a straightforward manner, as discussed earlier. For example, if one is interested in knowing the symmetry of an orbital product involving $a_1^2a_2^2e^2$ occupancy in C_{3v} symmetry, the procedure used is the following. For each of the six symmetry operations in the C_{3v} point group, the *product* of the characters associated with each of the *six* spin orbitals (orbital multiplied by α or β spin) is formed

$$\chi(S) = \prod_{i=1}^{6} \chi_i(S) = \chi_{A_1}^2(S)\chi_{A_2}^2(S)\chi_E^2(S). \tag{C.6}$$

In the specific case considered here, $\chi(E) = 4$, $\chi(C_3) = 1$, and $\chi(\sigma_v) = 0$. Notice that the contributions of any doubly occupied nondegenerate orbitals (e.g., a_1^2, and a_2^2) to these direct-product characters $\chi(S)$ are unity because for *all* operators S, $\chi_k^2(S) = 1$ for any nondegenerate irreducible representation k. As a result, only the singly occupied or degenerate orbitals need to be considered when forming the characters of the reducible direct-product representation $\chi(S)$. In this example, the direct-product characters can be determined from the characters $\chi_E(S)$ of the two active (non-closed-shell) orbitals—the e^2 orbitals. That is, $\chi(S) = \chi_E(S) \cdot \chi_E(S)$.

From the direct-product characters $\chi(S)$ that belong to a particular electronic configuration (e.g., $a_1^2a_2^2e^2$), one must still decompose this list of characters into a sum of irreducible characters using equation C.3. For the example at hand, the direct-product characters $\chi(S)$ decompose into one A_1, one A_2, and one E representation. This means that the e^2 configuration contains A_1, A_2, and E symmetry elements. The e^2 configuration contains all determinants that can be formed by placing two electrons into the *pair* of degenerate orbitals. There are six such determinants. In Chapter 4 we show how to these pure (A_1, A_2, and E) symmetries and that possess either singlet or triplet spin (which are the only possibilities for the two e^2 electrons).

In summary, we have reviewed how to make a symmetry decomposition of a basis of atomic orbitals into their irreducible representation components. This tool is most helpful when constructing the orbital-correlation diagrams that form the basis of the Woodward-Hoffman rules. We also learned how to form the direct-product symmetries that arise when considering configurations that consist of products of symmetry-adapted spin orbitals. This step is essential for the construction of configuration- and state-correlation diagrams upon which one ultimately bases a prediction about whether a reaction is allowed or forbidden.

C_1	E
A	1

C_2			E	C_2
x^2, y^2, z^2, xy	R_z, z	A	1	1
xz, yz	x, y R_x, R_y	B	1	-1

C_3			E	C_3	C_3^2	
x^2+y^2, z^2	R_z, z	A	1	1	1	
(xz, yz)	(x, y)	E	1	ω	ω^2	$(\omega = e^{2\pi i/3})$
(x^2-y^2, xy)	(R_x, R_y)		1	ω^2	ω	

C_4			E	C_2	C_4	C_4^3
x^2+y^2, z^2	R_z, z	A	1	1	1	1
x^2-y^2, xy		B	1	1	-1	-1
(xz, yz)	(x, y)	E	1	-1	i	$-i$
	(R_x, R_y)		1	-1	$-i$	i

C_5			E	C_5	C_5^2	C_5^3	C_5^4	
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1	1	
(xz, yz)	(x, y) (R_x, R_y)	E'	1	ω	ω^2	ω^3	ω^4	
			1	ω^4	ω^3	ω^2	ω	$(\omega = e^{2\pi i/5})$
$(x^2 - y^2, xy)$		E''	1	ω^2	ω^4	ω	ω^3	
			1	ω^3	ω	ω^4	ω^2	

C_6			E	C_6	C_3	C	C_5^2	C_6^5	
$x^2 + y^2, z^2$	R_z, z	A	1	1	1	1	1	1	
		B	1	-1	1	-1	1	-1	
(xz, yz)	(x, y) (R_x, R_y)	E'	1	ω	ω^2	ω^3	ω^4	ω^5	$(\omega = e^{2\pi i/6})$
			1	ω^5	ω^4	ω^3	ω^2	ω	
$(x^2 - y^2, xy)$		E''	1	ω^2	ω^4	1	ω^2	ω^4	
			1	ω^4	ω^2	1	ω^4	ω^2	

C_{2v}			E	C_2	σ_v	σ_v'
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	-1	-1
xz	R_y, x	B_1	1	-1	1	-1
yz	R_x, y	B_2	1	-1	-1	1

C_{3v}			E	$2C_3$	$3\sigma_v$
$x^2 + y^2, z^2$	z	A_1	1	1	1
	R_z	A_2	1	1	-1
$(x^2 - y^2, xy)$ (xz, yz)	(x, y) (R_x, R_y)	E	2	-1	0

C_{4v}			E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
$x^2 + y^2, z^2$	z	A_1	1	1	1	1	1
	R_z	A_2	1	1	1	-1	-1
$x^2 - y^2$		B_1	1	1	-1	1	-1
xy		B_2	1	1	-1	-1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	-2	0	0	0

C_{5v}			E	$2C_5$	$2C_5^2$	$5\sigma_v$	
x^2+y^2, z^2	z	A_1	1	1	1	1	
	R_z	A_2	1	1	1	-1	$x = \frac{2\pi}{5}$
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	$2\cos x$	$2\cos 2x$	0	
(x^2-y^2, xy)		E_2	2	$2\cos 2x$	$2\cos 4x$	0	

C_{6v}			E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$
x^2+y^2, z^2	z	A_1	1	1	1	1	1	1
	R_z	A_2	1	1	1	1	-1	-1
		B_1	1	-1	1	-1	-1	1
		B_2	1	-1	1	-1	1	-1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	-2	-1	1	0	0
(x^2-y^2, xy)		E_2	2	2	-1	-1	0	0

C_{1h}			E	σ_h
x^2, y^2, z^2, xy	R_z, x, y	A'	1	1
xz, yz	R_x, R_y, z	A''	1	-1

C_{2h}			E	C_2	σ_h	i
x^2, y^2, z^2, xy	R_z	A_g	1	1	1	1
	z	A_u	1	1	-1	-1
xz, yz	R_x, R_y	B_g	1	-1	-1	1
	x, y	B_u	1	-1	1	-1

$C_{3h} = C_3 \times \sigma_h$			E	C_3	C_3^2	σ_h	S_3	$(\sigma_h C_3^2)$	
$x^2 + y_2, z^2$	R_z	A'	1	1	1	1	1	1	
	z	A''	1	1	1	-1	-1	-1	
(x^2-y^2, xy)	(x, y)	E'	1	ω	ω^2	1	ω	ω^2	$(\omega = e^{2\pi i/3})$
			1	ω^2	ω	1	ω^2	ω	
(xz, yz)	(R_x, R_y)	E''	1	ω	ω^2	-1	$-\omega$	$-\omega^2$	
			1	ω^2	ω	-1	$-\omega^2$	$-\omega$	

$$\mathrm{C}_{4h} = \mathrm{C}_4 \times i$$

$$\mathrm{C}_{5h} = \mathrm{C}_5 \times \sigma_h$$

$$\mathrm{C}_{6h} = \mathrm{C}_6 \times i$$

S_2			E	i
x^2, y^2, z^2, xy xz, yz	R_x, R_y, R_z	A_g	1	1
	x, y, z	A_u	1	-1

S_4			E	C_2	S_4	S_4^3
x^2+y^2, z^2	R_z	A	1	1	1	1
	z	B	1	1	-1	-1
(xz, yz)	(x, y)	E	1	-1	i	$-i$
(x^2-y^2, xy)	(R_x, R_y)		1	-1	$-i$	i

$$\mathrm{S}_6 = \mathrm{C}_3 \times i$$

D_2			E	C_2^z	C_2^y	C_2^x
x^2, y^2, z^2		A_1	1	1	1	1
xy	R_z, z	B_1	1	1	-1	-1
xz	R_y, y	B_2	1	-1	1	-1
yz	R_x, x	B_3	1	-1	-1	1

D_3			E	$2C_3$	$3C_2'$
x^2+y^2, z^2		A_1	1	1	1
	R_z, z	A_2	1	1	-1
(xz, yz) (x^2-y^2, xy)	(x, y) (R_x, R_y)	E	2	-1	0

D_4			E	C_2	$2C_4$	$2C_2'$	$2C_2''$
x^2+y^2, z^2		A_1	1	1	1	1	1
	R_z, z	A_2	1	1	1	-1	-1
		B_1	1	1	-1	1	-1
		B_2	1	1	-1	-1	1
(xz, yz) (x^2-y^2, xy)	(x, y) (R_x, R_y)	E	2	-2	0	0	0

D_5			E	$2C_5$	$2C_5^2$	$5C_2'$	
x^2+y^2, z^2		A_1	1	1	1	1	
	R_z, z	A_2	1	1	1	-1	
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	$2\cos x$	$2\cos 2x$	0	$x = \frac{2\pi}{5}$
(x^2-y^2, xy)		E_2	2	$2\cos 2x$	$2\cos 4x$	0	

D_6			E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
x^2+y^2, z^2		A_1	1	1	1	1	1	1
	R_z, z	A_2	1	1	1	1	-1	-1
		B_1	1	-1	1	-1	1	-1
		B_2	1	-1	1	-1	-1	1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	-2	-1	1	0	0
(x^2-y^2, xy)		E_2	2	2	-1	-1	0	0

D_{2d}			E	C_2	$2S_4$	$2C_2'$	$2\sigma_d$
x^2+y^2, z^2		A_1	1	1	1	1	1
	R_z	A_2	1	1	1	-1	-1
x^2-y^2		B_1	1	1	-1	1	-1
xy	z	B_2	1	1	-1	-1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	-2	0	0	0

$$D_{3d} = D_3 \times i$$

$$D_{2h} = D_2 \times i$$

$D_{3h} = D_3 \times \sigma_h$			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
$x^2 + y^2, z^2$		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	−1	−1
		A_1''	1	−1	1	−1	1	−1
	z	A_2''	1	−1	1	−1	−1	1
$(x^2 - y^2, xy)$	(x, y)	E'	2	2	−1	−1	0	0
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0

$D_{4h} = D_4 \times i$

$D_{5h} = D_5 \times \sigma_h$

$D_{6h} = D_6 \times i$

T			E	$3C_2$	$4C_3$	$4C_3'$	
Active		A	1	1	1	1	
Active		E	1 1	1 1	ω ω^2	ω^2 ω	$\omega = e^{2\pi i/3}$
Active	(R_x, R_y, R_z) (x, y, z)	T	3	−1	0	0	

$T_h = T \times i$

O			E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Active		A_1	1	1	1	1	1
Inactive		A_2	1	1	1	−1	−1
Active		E	2	−1	2	0	0
Active	(R_x, R_y, R_z) (x, y, z)	T_1	3	0	−1	−1	+1
Active		T_2	3	0	−1	+1	−1

$O_h = O \times i$

T_d			E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
Active		A_1	1	1	1	1	1
Inactive		A_2	1	1	1	−1	−1
Active		E	2	−1	2	0	0

$C_{\infty v}$			E	$2C_\varphi$	σ_v
x^2+y^2, z^2	z	A_1	1	1	1
	R_z	A_2	1	1	-1
(xz, yz)	(x, y) (R_x, R_y)	E_1	2	$2 \cos \varphi$	0
(x^2-y^2, xy)		E_2	2	$2 \cos 2\varphi$	0
		. .	......	......	......

$D_{\infty h}$			E	$2C_\varphi$	C_2'	i	$2iC_\varphi$	iC_2'
x^2+y^2, z^2		A_{1g}	1	1	1	1	1	1
		A_{1u}	1	1	1	-1	-1	-1
		A_{2g}	1	1	-1	1	1	-1
	z	A_{2u}	1	1	-1	-1	-1	1
(xz, yz)	(R_x, R_y)	E_{1g}	2	$2 \cos \varphi$	0	2	$2 \cos \varphi$	1
	(x, y)	E_{1u}	2	$2 \cos \varphi$	0	-2	$-2 \cos \varphi$	0
(x^2-y^2, xy)		E_{2g}	2	$2 \cos 2\varphi$	0	2	$2 \cos 2\varphi$	0
		E_{2u}	2	$2 \cos 2\varphi$	0	-2	$-2 \cos 2\varphi$	0
		. .	......	......	......	......	......	......