

From the first part of the selection rules we learned that transitions would not happen unless the transition dipole moment is not zero.

We now know that light can drive a transition when the frequency of the light matches the energy difference between two levels. The energy of the light field is written very compactly as:

$$H_{Light} = -\vec{E} \cdot \sum_i \vec{r}_i q_i = -\vec{E} \cdot \vec{\mu}$$

$$\vec{\mu} = \sum_i \vec{r}_i q_i$$

$$\vec{E} = \vec{E}_o \cos(\omega_L t)$$

The term that drives the transition, as learned from before is:

$$(\hbar\omega_{drive})^2 = \frac{1}{4} \vec{E}_o \cdot \langle \phi_1 | \vec{\mu} | \phi_2 \rangle \langle \phi_2 | \vec{\mu} | \phi_1 \rangle \cdot \vec{E}_o$$

$$\vec{\beta} \vec{\beta}^\dagger = \langle \phi_1 | \vec{\mu} | \phi_2 \rangle \langle \phi_2 | \vec{\mu} | \phi_1 \rangle$$

$$|\vec{\beta}| = |\langle \phi_1 | \vec{\mu} | \phi_2 \rangle|$$

So the frequency driving transitions between two energy levels is proportional to the magnitude of the coupling matrix between the two levels, or the integral that involves the wave functions from the initial and final states times a quantity proportional to position (r). The operator coupling the two levels is the dipole moment operator. So now we consider when the matrix element is zero and not zero. This depends on the form of the wave function and the form of the dipole operator. The wave function has four terms in it, as described by the Born-Oppenheimer separation. The first is the electronic wave function, which defines the state of the N electrons of the molecule with respect to the nuclear geometry. The next term is the center of mass of the molecule. This describes the molecule as a single entity moving through space (like a free particle) at the center of mass. The next term is the rotation. This rotates the molecule from the lab frame to the molecular frame. In addition to the electronic wave function being in the molecular frame, the nuclear vibrations are in the molecular frame as well. The nuclear vibrations however are described in terms of the coordinates of the normal modes, as expanded about the equilibrium nuclear geometry, and as such the direct relation between the coordinates that specify the nuclear position and those for the normal modes, some algebraic relations are required to identify the nuclear coordinate in terms of the normal mode coordinates.

So the wave function as a product function looks like:

$$\varphi = \psi_{Elec}(r) \psi_{Trans}(R) \psi_{Rot}(\Omega) \psi_{Nuc}(Q)$$

Notice carefully how the coordinates are chosen. The system is in the laboratory but we first translate to the center of mass coordinates (R), and then rotate into the frame of

molecule by rotation Ω , and the electrons are written in terms of the equilibrium nuclear geometry $Q = 0$, where the normal modes are zero, at coordinates (r).

We translate to the center of mass coordinates where the center of mass moves as a particle in free space.

$$M \cdot \bar{R} = \sum_i m_i \cdot \bar{r}_{i,Lab} \quad \text{and} \quad M = \sum_i m_i$$

The coordinates in the molecule are given by the laboratory coordinates corrected for the center of mass and rotated to a convenient reference state in the molecules:

$$\bar{r} = \mathfrak{R}(\Omega) \cdot (\bar{r}_{Lab} - \bar{R})$$

And the coordinates in the lab, \bar{r}_{Lab} , are corrected from the center of mass coordinates, \bar{R} , (which is defined in terms of the laboratory coordinates) and rotated from the lab frame into the molecular frame by $\mathfrak{R}(\Omega)$, which is the 3 by 3 rotation matrix which has sines and cosines of the three Euler angles $\Omega = \{\alpha, \theta, \phi\}$ for the rotation. The rotational wave function, $\psi_{rot}(\Omega)$, is written precisely in terms of these same angles.

To illustrate a bit of how this works, consider a diatomic molecule (like N_2 or HCl). The normal coordinate, $Q = (r_A - r_B) - r_{AB}^o$, where $r_{AB}^o = r_A^o - r_B^o$, and Q is along the z axis in the molecule and is the deviation from equilibrium: Q . The equilibrium distance is r_{AB}^o for a homo nuclear diatomic like N_2 , the center of mass is in the middle, so it is possible to reconstruct the individual nuclear coordinates relative to the center of mass (and rotated) from the normal coordinates.

$$r_A = r_A^o + \frac{1}{2}Q$$

$$r_B = r_B^o - \frac{1}{2}Q$$

For HCl the relation is more complex, as the masses of the two nuclei are quite different and the mass weighted normal coordinates must be used. For a given normal mode displacement, the H atom would move much more than the Cl atom because it weighs so much less. Despite this complexity, it appears that the nuclear coordinates would be linearly related to the normal mode coordinates. Using the series expansion formalism then we can reconstruct the individual nuclear coordinates in terms of the equilibrium coordinates and the normal mode coordinates:

$$r_n = r_n^o + \sum_p \left. \frac{\partial r_n}{\partial Q_p} \right|_{Q=0} Q_p$$

Now we are ready to analyze the dipolar operator in a similar fashion. The dipolar operator is written in terms of the laboratory frame (where the light field is located), and must be transformed to the same frame as the molecule. This is pretty straightforward to do. The first thing to notice is that for a neutral molecule the translation does not matter and so the light field does not affect translation. This follows because:

$$\begin{aligned}
H_{\text{Light}} &= -\vec{E}_{\text{Lab}} \cdot \vec{\mu}_{\text{Lab}} \\
\vec{\mu}_{\text{Lab}} &= \sum_i \vec{r}_{i,\text{Lab}} q_i = \sum_i (\vec{r}_{i,\text{Lab}} - \vec{R}) q_i + \sum_i \vec{R} q_i \\
\sum_i \vec{R} q_i &= \vec{R} \sum_i q_i = 0 \\
\vec{\mu}_{\text{Lab}} &= \sum_i (\vec{r}_{i,\text{Lab}} - \vec{R}) q_i
\end{aligned}$$

We are now ready to move into the frame of the molecule by the rotation we defined above:

$$\begin{aligned}
\vec{r} &= \mathfrak{R}(\Omega) \cdot (\vec{r}_{\text{Lab}} - \vec{R}) \\
\vec{\mu}_{\text{Lab}} &= \mathfrak{R}^\dagger(\Omega) \cdot \sum_i \mathfrak{R}(\Omega) \cdot (\vec{r}_{i,\text{Lab}} - \vec{R}) q_i = \mathfrak{R}^\dagger(\Omega) \cdot \sum_i \vec{r}_i q_i \\
\vec{\mu}_{\text{Molec}} &= \sum_i \vec{r}_i q_i
\end{aligned}$$

So now we have the dipole operator written in terms of the molecular frame for both the nuclei and the electrons. The electrons are understood to mean the electron coordinates when the nuclei are not moving. The nuclear coordinates are written in terms of the equilibrium coordinates (for which the electrons are evaluated) and the normal mode coordinates. We can be clearer about that, if we sum over electrons and nuclei separately.

$$\begin{aligned}
\vec{\mu}_{\text{Molec}} &= \vec{\mu}_{\text{elect}} + \vec{\mu}_{\text{nuc}} \\
\vec{\mu}_{\text{elect}} &= \sum_{i,\text{elec}} \vec{r}_i q_{\text{ele}} \\
\vec{\mu}_{\text{nuc}} &= \sum_{i,\text{nuc}} \vec{r}_i q_i
\end{aligned}$$

Of course they are tied together as the difference (it is really the sum as the electron has negative sign) in the center of the electric charge minus the difference in the center of the nuclear charge must be the net dipole. The sum of all the nuclear charges (as all positive numbers) must be the same as the sum of all the electronic charges or must equal the number of electrons:

$$\sum_{\text{nuclei}} q_i = N_{\text{elec}} = - \sum_{\text{electron}} q_{\text{electron}}$$

The nuclear coordinates are now written in terms of the equilibrium coordinates and the normal mode coordinates:

$$\bar{\mu}_{nuc} = \sum_{n,nuc} \bar{r}_n q_n = \sum_{n,nuc} \bar{r}_n^o q_n + \sum_{n,p} q_n \left. \frac{\partial r_n}{\partial Q_p} \right|_{Q=0} Q_p$$

$$\bar{\mu}_{nuc}^o = \sum_{n,nuc} \bar{r}_n^o q_n$$

$$\bar{\mu}_{nuc}(Q) = \sum_{n,p} \left\{ q_n \left. \frac{\partial r_n}{\partial Q_p} \right|_{Q=0} \right\} Q_p$$

$$\bar{\mu}_{Molec} = \bar{\mu}_{elect} + \bar{\mu}_{nuc} = \bar{\mu}_{elect} + \bar{\mu}_{nuc}^o + \bar{\mu}_{nuc}(Q)$$

Now we have the dipolar operator written in terms of the electron coordinates and the nuclear displacement coordinates. We are now ready to evaluate the matrix element to see which terms survive and which vanish. The above equations are summarized as:

$$\beta = \langle \phi_1 | \bar{\mu}_{Lab} | \phi_2 \rangle$$

$$\varphi = \psi_{Elec}(r) \psi_{Trans}(R) \psi_{Rot}(\Omega) \psi_{Nuc}(Q)$$

$$\bar{\mu}_{Lab} = \mathfrak{R}^\dagger(\Omega) \cdot \bar{\mu}_{Molec}$$

$$\bar{\mu}_{Molec} = \bar{\mu}_{elect} + \bar{\mu}_{nuc}^o + \bar{\mu}_{nuc}(Q)$$

The two wave functions may be different, so we must label each term of each wave function by different indices and use the expanded version of the operator.

$$\beta = \langle \psi_{1,Elec}(r) \psi_{1,Trans}(R) \psi_{1,Rot}(\Omega) \psi_{1,Nuc}(Q) | \hat{\mu}_{Lab} | \psi_{2,Elec}(r) \psi_{2,Trans}(R) \psi_{2,Rot}(\Omega) \psi_{2,Nuc}(Q) \rangle$$

$$\bar{\mu}_{Lab} = \mathfrak{R}^\dagger(\Omega) \cdot \bar{\mu}_{Molec}$$

$$\bar{\mu}_{Molec} = \bar{\mu}_{elect} + \bar{\mu}_{nuc}^o + \bar{\mu}_{nuc}(Q)$$

Because the operator does not depend on the center of mass coordinates the integral over the coordinates of the center of mass (which affects the translational wave function only) can be factored; i.e. that integral can be done on its own. The rotation of the dipole operator can be factored with the rotational term. There can be no change in the translational energy of the molecule during absorption of light if it is a neutral molecule:

$$\beta = \langle \psi_{1,Trans}(R) | \psi_{2,Trans}(R) \rangle \langle \psi_{1,Rot}(\Omega) | \mathfrak{R}^\dagger(\Omega) | \psi_{2,Rot}(\Omega) \rangle \langle \psi_{1,Elec}(r) \psi_{1,Nuc}(Q) | \bar{\mu}_{Molec} | \psi_{2,Elec}(r) \psi_{2,Nuc}(Q) \rangle$$

The translational and rotational terms are now separated out, and can be done independently of the molecule. Because there is no translational operator the two translational wave functions must be the same. The rotational ones have a rotation operation mixed in with them. The elements of the rotation must contain either a sine or cosine and so they mix nearest neighbor rotational states (see later). The molecular part may now be treated separately:

$$\begin{aligned}
\langle \bar{\mu}_{Molec} \rangle &= \langle \psi_{1,Elec}(r) \psi_{1,Nuc}(Q) | \{ \bar{\mu}_{elect} + \bar{\mu}_{nuc}^o + \bar{\mu}_{nuc}(Q) \} | \psi_{2,Elec}(r) \psi_{2,Nuc}(Q) \rangle \\
&= \langle \psi_{1,Elec}(r) (\Omega) | \bar{\mu}_{elect} | \psi_{2,Elec}(r) \rangle \langle \psi_{1,Nuc}(Q) | \psi_{2,Nuc}(Q) \rangle \\
&+ \bar{\mu}_{nuc}^o \langle \psi_{1,Elec}(r) | \psi_{2,Elec}(r) \rangle \langle \psi_{1,Nuc}(Q) | \psi_{2,Nuc}(Q) \rangle \\
&+ \langle \psi_{1,Elec}(r) | \psi_{2,Elec}(r) \rangle \langle \psi_{1,Nuc}(Q) | \bar{\mu}_{nuc}(Q) | \psi_{2,Nuc}(Q) \rangle
\end{aligned}$$

The molecular dipole term is the sum of three terms: The first term is the center of all the electrons (times the charge) and the second term is the charge-weighted center of all the nuclei. The sum of the first and second terms is the intrinsic dipole moment of the molecule. This is true if there is no electronic or nuclear transition. If there is an electronic transition then the first term is the electronic transition dipole of the molecule, and the second (and third) term vanishes. If there is a vibrational transition then the permanent dipole term vanishes. You cannot have a nuclear (i.e. vibrational) and an electronic transition at the same time.

For the case where there is no electronic transition:

$$\langle \bar{\mu}_{Molec} \rangle = \bar{\mu}_{Molec}^o \delta_{1,2,nuc} + \langle \psi_{1,Nuc}(Q) | \bar{\mu}_{nuc}(Q) | \psi_{2,Nuc}(Q) \rangle$$

So the molecule can show a transition in the nuclear part or just give the permanent dipole moment of the molecule. If there is no nuclear (vibrational) transition then the molecule must have a dipole moment to have a rotational transition. That is all that can happen.

If the molecule has a nuclear transition, the permanent dipole is not necessary and there must be an accompanying rotational transition to have a vibrational transition, otherwise the entire matrix element will vanish.

The pure rotational transition matrix element is:

$$\beta = \langle \psi_{1,Rot}(\Omega) | \mathfrak{R}^\dagger(\Omega) | \psi_{2,Rot}(\Omega) \rangle \bar{\mu}_{Molec}^o$$

The combined rotational-vibrational transition matrix element is:

$$\beta = \langle \psi_{1,Rot}(\Omega) | \mathfrak{R}^\dagger(\Omega) | \psi_{2,Rot}(\Omega) \rangle \langle \psi_{1,Nuc}(Q) | \bar{\mu}_{nuc}(Q) | \psi_{2,Nuc}(Q) \rangle$$

The selection rules then can be obtained from the simple rotational rules and the vibrational rules. For the rotation we can concluded that

$$\langle \psi_{1,Rot}(\Omega) | \mathfrak{R}^\dagger(\Omega) | \psi_{2,Rot}(\Omega) \rangle \neq 0 \text{ when } Rot_1 = Rot_2 \pm 1$$

And is zero otherwise. This follows from the fact that the rotational wave functions are spherical harmonics, and the rotation operator is either a sine or cosine function.

$$\langle \psi_{1,Rot}(\Omega) | \mathfrak{R}^\dagger(\Omega)_{i,j} | \psi_{2,Rot}(\Omega) \rangle \propto \langle Y_{m_1}^{\ell_1}(\Omega) | Y_m^1(\Omega) | Y_{m_2}^{\ell_2}(\Omega) \rangle$$

which has the (selection) rule that the matrix element in terms of the spherical harmonics vanishes unless $m_1 = m + m_2$ and $\ell_1 = \ell_2 \pm 1$.

The nuclear term works exactly the same way: only up or down by one transition is allowed, and the case where no transition occurs is also forbidden. This follows from the fundamental rules of harmonic oscillator functions.

$$\langle \psi_{1,Nuc}(\mathcal{Q}) | \bar{\mu}_{nuc}(\mathcal{Q}) | \psi_{2,Nuc}(\mathcal{Q}) \rangle \neq 0 \text{ only if } Nuc_1 = Nuc_2 \pm 1$$

and is zero otherwise.