The Laporte Rule is a selection rule in electron absorption spectroscopy that applies to centrosymmetric molecules. It says that transitions between states of the same symmetry with respect to inversion are forbidden. Using the mathematical concept of even and odd functions, the Laporte Rule can be derived and summarized as follows: Electronic transitions from wavefunctions with \( g \) symmetry to wavefunctions with \( g \) symmetry are forbidden, as are transitions from wavefunctions with \( u \) symmetry to wavefunctions with \( u \) symmetry. Transitions from \( g \) to \( u \) and \( u \) to \( g \), where the symmetry switches, may be (but are not necessarily) allowed.

Introduction

When an incident photon is absorbed by an electron, the electron is excited from a lower energy state to a higher energy, excited state. Although there are multiple higher energy excited states, not all are available to the electron, and only certain transitions are allowed. Electron absorption spectroscopy measures the intensity of transmitted photons as a function of wavelength. From this the energy of absorbed photons is determined, and transitions are assigned using selection rules. Selection rules are the guidelines for determining if a transition will be allowed or forbidden. This module will further discuss the orbital selection rule called the Laporte Rule, but will leave the spin selection rule to be discussed in another module. Specifically, the Laporte selection rule determines whether an electronic transition is orbitally allowed or forbidden. The Laporte Rule applies only to centrosymmetric molecules, or those that contain a center of inversion. An electronic transition is forbidden by the Laporte Rule if the ground and excited states have the same symmetry with respect to an inversion center. Electronic transitions are described by the transition moment integral.

\[
\int_{-\infty}^{\infty} \Psi_{el} \hat{M} \Psi_{ex}^{*} \, d\tau = |\left \langle i | \hat{M} | f \right \rangle|
\] (\( \Psi \) is the wavefunction, \( M \) is the transition dipole moment operator, \( i \) refers to the initial state and \( f \) refers to the final state). The Laporte Rule tells us that if the integrand of the transition moment integral does not contain the totally symmetric representation, then the transition is forbidden.

Background

In electron absorption spectroscopy, absorption of a photon excites an electron from one energy state to another. Such transitions are only detectable using optical spectroscopy when there is a corresponding change in the dipole moment of the molecule; transitions are detectable when the transition moment dipole is nonzero.

\[
\mu = \int_{-\infty}^{\infty} \Psi \hat{\mu} \Psi^{*} \, d\tau
\]

The transition moment dipole given above includes the wave functions of the final and initial states, which contain both electronic and nuclear wave functions.

\[
|\Psi = |\Psi_{nuc} \Psi_{el}\rangle
\]

The Born–Oppenheimer approximation tells us that electronic transitions happen on a faster time scale than nuclear transitions so the two can be separated, and when dealing with electronic transitions we can effectively ignore any nuclear motion. Thus, in discussing electronic spectroscopy and the "allowedness" of certain electronic transitions, we consider
only the electronic integral.

\[ \int_{-\infty}^{\infty} \Psi_{el} H \Psi_{el}^{ex} \] \[ \text{label}(4) \]

Where \( H \) is the time-dependent Hamiltonian. We can make this integral easier to work with by invoking Fermi's Golden Rule, which allows us to replace \( H \) with \( M \), the electric dipole moment operator, which is part of the time-dependent Hamiltonian.

\[ [ \hat{M} = e \sum_{i} \vec{r}_{i} ] \] \[ \text{label}(5) \]

We arrive at the following transition moment integral to describe electronic transitions from a ground state to an excited state.

\[ \int_{-\infty}^{\infty} \Psi_{el} \hat{M} \Psi_{el}^{ex} = | \langle i | \hat{M} | f \rangle | \] \[ \text{label}(6) \]

The transition moment integral describes the probability of a transition taking place. The integral must be non-zero in order for a transition to occur. In other words, the two electronic states must overlap in order for a transition to occur.

### Derivation

By the Laporte Rule in a centrosymmetric molecule, if the integrand of the transition moment integral contains the totally symmetric representation, then the transition is Laporte allowed. If the transition does not contain the totally symmetric representation, then the transition is Laporte forbidden. The totally symmetric representation is the irreducible symmetry representation that is even with respect to all symmetry operations. On a character table, this representation is usually listed first and has the designation A, A_1, or A_{1g}.

To determine if a transition is allowed, the point group of the molecule is determined, and the corresponding character table gives the symmetry representation of each electronic wavefunction. The character table is also used to determine the electric dipole moment operator, which is contained in the transition moment integral and has three parts that transform with the Cartesian x, y, and z axes.

\[ [ \hat{M} = \begin{vmatrix} \hat{M}_{x} \\ \hat{M}_{y} \\ \hat{M}_{z} \end{vmatrix} ] \] \[ \text{label}(7) \]

For calculating the integrand of the transition moment integral, the symmetry representations corresponding to x, y, and z are used for the electric dipole moment operator. The integrand of the transition moment integral is then given by the following direct products:

\[ [ \Psi_{el} \otimes \begin{vmatrix} \hat{M}_{x} \\ \hat{M}_{y} \\ \hat{M}_{z} \end{vmatrix} \otimes \Psi_{el}^{ex} ] \] \[ \text{label}(8) \]

The component of the electric dipole moment operator that gives the totally symmetric representation corresponds to the direction of polarization of the electronic transition.

For a point group of low symmetry like C_{2h}, computing the integrand for all possible transitions is a relatively short task. However, when considering a point group with a high degree of symmetry, like O_{h}, computing the integrand for all possible
transitions in a point group becomes a long and tedious task. If we examine these computations through the lens of mathematics, this problem can be simplified. The Laporte Rule applies to centrosymmetric molecules, those containing a center of inversion. All states have a symmetry with respect to the inversion center, and all representations for a given point group have either a \( g \) (gerade) or \( u \) (ungerade) designation with respect to the center of inversion. Designations of \( g \) and \( u \) refer to even and odd symmetries with respect to the inversion center. Odd and even with respect to orbital symmetry correspond to the mathematical definitions of odd and even functions. \( M \) is an odd function. For the derivation of the Laporte Rule, allow \( g \) states to be represented by the even function \( \cos(x) \), \( u \) states to be represented by the odd function \( \sin(x) \), and \( M \) to be represented by the odd function \( x \).

A transition between two even states is given by the integral

\[
F(x) = \int_{-\infty}^{\infty} \Psi_{el} \hat{M} \Psi_{el}^{ex} = \int \cos(x) \times x \times \cos(x) \, dx \quad \text{(9)}
\]

The integrand is given by

\[
G(x) = x \times \cos^2(x) \quad \text{(9)}
\]

Evaluate the integrand

\[
G(x) = x \times \cos^2(x) = \frac{x}{4} \times \cos^2(x)
\]

Evaluate the integrand

\[
G(x) = -G(-x)
\]

Thus, \( G(x) = x \times \cos^2(x) \) is an odd function, and the transition between two even states is forbidden.

Similarly, a transition between two odd states is given by the integral

\[
F(x) = \int_{-\infty}^{\infty} \Psi_{el} \hat{M} \Psi_{el}^{ex} = \int \sin(x) \times x \times \sin(x) \, dx \quad \text{(10)}
\]

The integrand is given by

\[
G(x) = x \times \sin^2(x) \quad \text{(10)}
\]

Evaluate the integrand

\[
G(x) = \frac{x}{4} \times \sin^2(x)
\]

Evaluate the integrand

\[
G(x) = \frac{x}{4} \times \sin^2(x) = -G(-x)
\]

Thus,
is an odd function, and the transition between two odd states is forbidden.

A transition between an odd and an even state is given by the integral

$$ F(x) = \int_{-\infty}^{\infty} \Psi_{el}(x) \hat{M} \Psi_{el}^{ex}(x) = \int \cos(x) \times \sin(x) \times \sin(x) \, dx \{\text{Eq. 11}\} $$

The integrand is given by

$$ G(x) = \cos(x) \times \sin(x) \times \sin(x) \{\text{Eq. 11}\} $$

Evaluate the integrand

$$ G(x = \frac{\pi}{4}) = \sin(\frac{\pi}{4}) \times \frac{\pi}{4} \times \cos(\frac{\pi}{4}) = \frac{\pi}{8} $$

$$ G(x = \frac{-\pi}{4}) = \sin(\frac{-\pi}{4}) \times \frac{-\pi}{4} \times \cos(\frac{-\pi}{4}) = \frac{\pi}{8} $$

$$ G(x) = G(-x) $$

Thus, $$ G(x) = x \times \sin(x) \times \sin(x) \{\text{Eq. 11}\} $$ is an even function, and the transition between an even and an odd state is not immediately forbidden.

These calculations can be summarized in the following set of rules:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$g \times g = g$</td>
<td>Forbidden</td>
</tr>
<tr>
<td>$u \times u = g$</td>
<td>Forbidden</td>
</tr>
<tr>
<td>$g \times u = u$</td>
<td>May be Allowed</td>
</tr>
<tr>
<td>$u \times g = u$</td>
<td>May be Allowed</td>
</tr>
</tbody>
</table>

It is shown above that the Laporte Rule expressly states that transitions between two even states or two odd states are forbidden. It should be emphasized, however, that the Laporte Rule does not state that transitions between an even and an odd state are allowed. The integrand of the transition moment integral for the transition between an odd and an even state is even, but there are multiple states with even inversion symmetry that are not the totally symmetric representation. Only an integrand that contains the totally symmetric representation is allowed. To determine which of the even transitions are actually allowed, the cross product of the representations of the initial and final electronic states with the electric dipole moment operator must be computed. All resulting cross products will be even; only those which contain the totally symmetric representation will be allowed.

Example 1: Octohedral Group
O\(_h\) (octahedral) point group

\[ M_x, M_y, M_z = T_{1u} \]

\[ A_{1g} \otimes T_{1u} \otimes A_{1g} = T_{1u} \] \hspace{1cm} \text{Equation (1)}

\[ A_{2u} \otimes T_{1u} \otimes A_{2u} = T_{1u} \] \hspace{1cm} \text{Equation (2)}

\[ A_{2g} \otimes T_{1u} \otimes A_{1g} = A_{1g} \] \hspace{1cm} \text{Equation (3)}

\[ A_{2u} \otimes T_{1u} \otimes T_{1g} = A_{2g} + E_{g} + T_{1g} + T_{2g} \] \hspace{1cm} \text{Equation (4)}

Equation (1) shows a forbidden even-even transition. Equation (2) shows a forbidden odd-odd transition. Equations (3) and (4) demonstrate the subtlety of the Laporte Rule. Both are even transitions between an odd and an even state. However, (3) contains the totally symmetric representation and is an allowed transition, while (4) does not contain the totally symmetric representation and is thereby forbidden.

### Problems

1. For the C\(_{4h}\) point group, which transitions are forbidden by the Laporte Rule? Which transitions are orbitally allowed?

2. For the C\(_{2h}\) point group, what are the polarizations of the Laporte allowed transitions?

3. Using the Laporte Rule, are transitions between d orbitals in a molecule of octahedral (O\(_h\)) symmetry allowed? Are transitions between p orbitals allowed? Are transitions between p and d orbitals allowed?

4. [Cu(H\(_2\)O)\(_6\)]\(^{2+}\) and [Cu(NH\(_3\))\(_4\)]\(^{2+}\) both appear blue in solution because of the presence of copper ions. However, the two solutions are not identical. How would the appearance of these solutions differ? If given an unlabeled sample of each, how could the two solutions be distinguished without collecting any spectra?

### Answers

1. The C\(_{4h}\) point group contains the representations A\(_g\), B\(_g\), E\(_g\), A\(_u\), B\(_u\), and E\(_u\). Via the Laporte rule: g to g and u to u transitions are orbitally forbidden. For g to u and u to g transitions, the integrand of the transition moment integral must contain the totally symmetric representation, which is A\(_g\) in this case.

<table>
<thead>
<tr>
<th>[ A_g \otimes A_g ]</th>
<th>Laporte Forbidden</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ A_g \otimes B_g ]</td>
<td>Laporte Forbidden</td>
</tr>
<tr>
<td>$\mathbf{A}_g \otimes \mathbf{E}_g$</td>
<td>Laporte Forbidden</td>
</tr>
<tr>
<td>$\mathbf{A}_g \otimes \mathbf{A}_u$</td>
<td>Laporte Allowed</td>
</tr>
<tr>
<td>$\mathbf{A}_g \otimes \mathbf{B}_u$</td>
<td>Laporte Forbidden</td>
</tr>
<tr>
<td>$\mathbf{A}_g \otimes \mathbf{E}_u$</td>
<td>Laporte Allowed</td>
</tr>
<tr>
<td>$\mathbf{B}_g \otimes \mathbf{B}_g$</td>
<td>Laporte Forbidden</td>
</tr>
<tr>
<td>$\mathbf{B}_g \otimes \mathbf{E}_g$</td>
<td>Laporte Forbidden</td>
</tr>
<tr>
<td>$\mathbf{B}_g \otimes \mathbf{A}_u$</td>
<td>Laporte Forbidden</td>
</tr>
<tr>
<td>$\mathbf{B}_g \otimes \mathbf{E}_u$</td>
<td>Laporte Allowed</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\langle E_{g} \otimes E_{g} \rangle & \quad \text{Laporte Forbidden} \\
\langle E_{g} \otimes A_{u} \rangle \\
\langle E_{g} \begin{vmatrix} E_{u} \\ A_{u} \end{vmatrix} A_{u} = \\
\begin{vmatrix} A_{g} + A_{u} + 2B_{g} \\ E_{g} \end{vmatrix} & \quad \text{Laporte Allowed} \\
\langle E_{g} \otimes B_{u} \rangle \\
\langle E_{g} \begin{vmatrix} E_{u} \\ A_{u} \end{vmatrix} B_{u} = \\
\begin{vmatrix} B_{u} + B_{g} + 2A_{g} \\ E_{g} \end{vmatrix} & \quad \text{Laporte Allowed} \\
\langle E_{g} \otimes E_{u} \rangle \\
\langle E_{g} \begin{vmatrix} E_{u} \\ A_{u} \end{vmatrix} E_{u} = \\
\begin{vmatrix} E_{g} + E_{u} + 2E_{g} \\ A_{g} + A_{u} + 2B_{g} \end{vmatrix} \quad \text{Laporte Allowed} \\
\langle A_{u} \otimes A_{u} \rangle & \quad \text{Laporte Forbidden} \\
\langle A_{u} \otimes B_{u} \rangle & \quad \text{Laporte Forbidden} \\
\langle A_{u} \otimes E_{u} \rangle & \quad \text{Laporte Forbidden} \\
\langle B_{u} \otimes B_{u} \rangle & \quad \text{Laporte Forbidden} \\
\langle B_{u} \otimes E_{u} \rangle & \quad \text{Laporte Forbidden} \\
\langle E_{u} \otimes E_{u} \rangle & \quad \text{Laporte Forbidden}
\end{align*}
\]

2. The \( C_{2h} \) point group contains \( A_{g}, B_{g}, A_{u}, \) and \( B_{u} \) representations. By the Laporte rule \( g \) to \( g \) and \( u \) to \( u \) transitions are orbitally forbidden. For \( g \) to \( u \) and \( u \) to \( g \) transitions, the integrand of the transition moment integral must contain the totally symmetric representation, which is \( A_{g} \) in this case. The component of the transition moment operator that gives the totally symmetric representation dictates the polarization of the transition.
3. Using the character table, we see that d-orbitals in octahedral have the following symmetries:

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Character Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>([ z^2, x^2 - y^2 ])</td>
</tr>
<tr>
<td>T&lt;sub&gt;2g&lt;/sub&gt;</td>
<td>([ xy, xz, yz ])</td>
</tr>
</tbody>
</table>

Possible transitions are \([ E_.(g) \times{ E_.(g)} ]\), \([ E_.(g) \times{ T_.(2g)} ]\), \([ T_.(2g) \times{ T_.(2g)} ]\). All possible transitions are g to g, and are thus forbidden by the Laporte Rule.

P-orbitals have the following symmetries:

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Character Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>x, y, z</td>
<td>([T_.(1u)])</td>
</tr>
</tbody>
</table>

All possible transitions are u to u, and are thus forbidden by the Laporte Rule.

P-orbital to d-orbital transitions would all be u to g, and are not forbidden by the Laporte Rule.
4. \([\text{Cu(NH}_3\text{)}_4]^{2+}\) is a tetrahedral complex and is therefore non-centrosymmetric. Since it is non-centrosymmetric, it is not Laporte forbidden. \([\text{Cu(H}_2\text{O)}_6]^{2+}\) is an octahedral complex whose d-d transitions are Laporte forbidden. \([\text{Cu(NH}_3\text{)}_4]^{2+}\) will be a darker shade of blue in solution because its d-d transitions are not forbidden, and \([\text{Cu(H}_2\text{O)}_6]^{2+}\) will be a paler shade of blue in solution because its d-d transitions are Laporte forbidden. Coloration and absorption of \([\text{Cu(H}_2\text{O)}_6]^{2+}\) in the ultraviolet-visible range is attributed to vibronic coupling.

References


Contributors

- Kathryn A. Newton