

# Symmetry and Group Theory for Computational Chemistry Applications

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## Symmetry Selection Rules for Infrared and Raman Spectra

### Infrared Spectra

A **Fundamental Transition** consists of a transition from a molecule in a vibrational ground state (initial vibrational state wave function,  $\psi_i$ ) to a vibrationally excited state (final vibrational state wave function,  $\psi_f$ ) where the molecule absorbs one quantum of energy in one vibrational mode.

A vibrational transition in the infrared occurs when the molecular dipole moment ( $\mu$ ) interacts with incident radiation which occurs with a probability which is proportional to the transition moment:

$$\int \psi_i \mu \psi_f d\tau$$

- A transition is said to be *forbidden* in the infrared if the value of this integral is zero because the probability of that transition is zero and no absorption will be observed.
- The integral will be zero unless the direct product of  $\psi_i \mu \psi_f$  contains the totally symmetric representation which has the character +1 for all symmetry operations for the molecule under consideration.

The vector  $\mu$  can be split into three components,  $\mu_x$ ,  $\mu_y$ , and  $\mu_z$  along the Cartesian coordinate axes, and only one of the three integrals needs to be non-zero:

$$\int \psi_i \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} \psi_f d\tau$$

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## Symmetry Selection Rules for Infrared and Raman Spectra

### Infrared Spectra

The vibrational ground state wave function,  $\psi_i$  belongs to the totally symmetric representation.

The symmetry properties of the components of the dipole moment ( $\mu_x$ ,  $\mu_y$ ,  $\mu_z$ ) are the same as those of the translation vectors along the same axes:  $T_x$ ,  $T_y$ ,  $T_z$ .

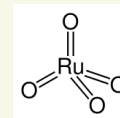
The symmetry of the vibrationally excited state wave function,  $\psi_f$  are the same as the symmetry which describes the vibrational mode.

Therefore, it is necessary to form direct products of the totally symmetric representation of ground state vibrational wave function ( $\psi_i$ ), the irreducible representations of each of the translation vectors ( $T_x$ ,  $T_y$ ,  $T_z$ ), and the irreducible representation of the excited vibration under consideration.

## Symmetry Selection Rules for Infrared and Raman Spectra

### Infrared Spectra

Consider the vibrations of the tetrahedral molecule, ruthenium tetroxide ( $T_d$  symmetry).



where there are vibrations of  $A_1$ , E, and  $T_2$ , and deduce the infrared activity of each of them.

- $\psi_i$  has  $A_1$  symmetry.
- The character table for  $T_d$  shows that  $T_x$ ,  $T_y$ ,  $T_z$  together have  $T_2$  symmetry.

The direct products are then

$$\begin{array}{llll} A_1 \text{ vibration:} & A_1 \otimes T_2 \otimes A_1 & = & T_2 \\ E \text{ vibration:} & A_1 \otimes T_2 \otimes E & = & T_2 \otimes E = T_1 + T_2 \\ T_2 \text{ vibration:} & A_1 \otimes T_2 \otimes T_2 & = & T_2 \otimes T_2 = A_1 + E + T_1 + T_2 \end{array}$$

Thus, the  $T_2$  vibrations are infrared active because the direct products produce an  $A_1$  representation, but the E and  $T_2$  vibrations will not appear in the infrared spectrum.

An important result of the above analysis is that if an excited vibrational mode has the same symmetry as the translation vectors,  $T_x$ ,  $T_y$ ,  $T_z$ , for that point group, then the totally symmetric irreducible representation is present and a transition from the vibrational ground state to that excited vibrational mode will be infrared active.

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## Symmetry Selection Rules for Infrared and Raman Spectra

### Raman Spectra

The probability of a vibrational transition occurring in Raman scattering is proportional to:

$$\int \psi_i \alpha \psi_f d\tau$$

where  $\alpha$  is the **polarizability** of the molecule.

The Raman effect depends on a molecular dipole induced by the electromagnetic field of the incident radiation and is proportional to the polarizability of the molecule which is a measure of the ease with which the molecular electron distribution can be distorted.

$\alpha$  is a tensor, i.e. a 3 x 3 array of components

$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

so there will be six distinct components

$$\int \psi_i \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \psi_f d\tau$$

where one non-zero integral is needed to have an allowed Raman transition.

## Symmetry Selection Rules for Infrared and Raman Spectra

### Raman Spectra

For the ruthenium tetroxide molecule with  $T_d$  symmetry, the components of polarizability have the following symmetries:

$$\begin{array}{ll} A_1 & x^2 + y^2 + z^2 \\ E & 2z^2 - x^2 - y^2, \quad x^2 - y^2 \\ T_2 & xy, yz, zx \end{array}$$

The vibrations are  $A_1$ ,  $E$ , and  $T_2$ , and it is possible to deduce the infrared activity of each of them. The direct products are then

$$\begin{array}{ll} A_1 \otimes \begin{pmatrix} A_1 \\ E \\ T_2 \end{pmatrix} \otimes A_1 & = A_1, E, T_2; \quad A_1 \text{ vibration is possible.} \\ A_1 \otimes \begin{pmatrix} A_1 \\ E \\ T_2 \end{pmatrix} \otimes E & = E, (A_1 + A_2 + E), (T_1 + T_2); \quad E \text{ vibrations are possible.} \\ A_1 \otimes \begin{pmatrix} A_1 \\ E \\ T_2 \end{pmatrix} \otimes T_2 & = T_2, (T_1 + T_2), (A_1 + E + T_1 + T_2); \quad T_2 \text{ vibrations are possible.} \end{array}$$

Thus, all of the vibrations in the  $RuO_4$  molecule are Raman active.

A summary of the infrared and Raman activity is given as

$$\begin{array}{ll} A_1: & x^2 + y^2 + z^2 \quad \text{Raman Only} \\ E: & 2z^2 - x^2 - y^2, \quad x^2 - y^2 \quad \text{Raman Only} \\ T_2: & (T_x, T_y, T_z), (xy, yz, zx) \quad \text{Infrared and Raman Active} \end{array}$$

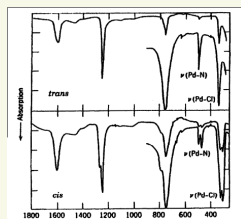
## The Infrared Spectrum of $Pd(NH_3)_2Cl_2$

One can determine which isomer (*cis* or *trans*) is present in a sample from the IR spectrum by determining the contribution to the spectrum of the Pd-Cl stretching modes for both the *cis* and *trans* complexes.

The *trans* isomer exhibits a single Pd-Cl stretching vibration ( $\nu_{Pd-Cl}$ ) around  $350 \text{ cm}^{-1}$ , while the *cis* isomer exhibits two stretching modes.

M-X Vibrations		
	IR	Raman
<i>trans</i> isomer, $D_{2h}$	$B_{2u}$	$A_u$
<i>cis</i> isomer, $C_{2v}$	$A_1, B_2$	$A_1, B_2$

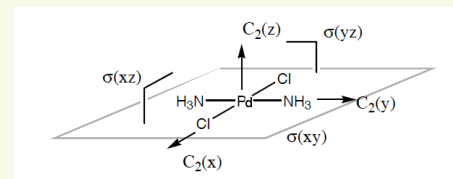
Active M-X Stretching Modes for  $ML_2X_2$  Complexes



IR Spectrum of *cis* and *trans*  $Pd(NH_3)_2Cl_2$  from Kazuo Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5<sup>th</sup> Edition (1997), Part B, p. 10, Fig. III-5, John Wiley & Sons, New York

## The Infrared Spectrum of *trans* $Pd(NH_3)_2Cl_2$

Determine the contribution of the Pd-Cl stretching modes in the *trans* complex.



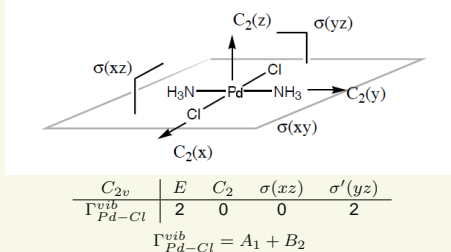
$D_{2h}$	$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{Pd-Cl}^{vib}$	2	0	0	2	0	2	2	0

$$\Gamma_{Pd-Cl}^{vib} = A_g + B_{3u}$$

- IR active modes have the same symmetry as translational vectors ( $\Gamma(IR) = B_{1u}, B_{2u}, B_{3u}$ ) while Raman modes have the same symmetry as binary functions ( $\Gamma(Raman) = A_g, B_{1g}, B_{2g}, B_{3g}$ ).
- Trans*  $Pd(NH_3)_2Cl_2$  has a center of symmetry, and the rule of mutual exclusion indicates that no vibrational modes will be present in **both** the Raman and IR spectra.
- Thus, there should be one polarised active Raman mode and one active infrared mode  $\Gamma_{Pd-Cl}^{vib} = A_g(\text{polarised}) + B_{3u}(IR)$

## The Infrared Spectrum of *cis* Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>

Determine the contributions to Pd-Cl stretching modes for the *cis* Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> complex.



- IR active modes have the same symmetry as translational vectors ( $\Gamma(\text{IR}) = A_1, B_1, B_2$ ) while Raman modes have the same symmetry as binary functions ( $\Gamma(\text{Raman}) = A_1, A_2, B_1, B_2$ ).
- Two infrared active modes and two Raman active modes, one of which will be polarised are expected. Both modes will be present in both the IR and Raman spectra:

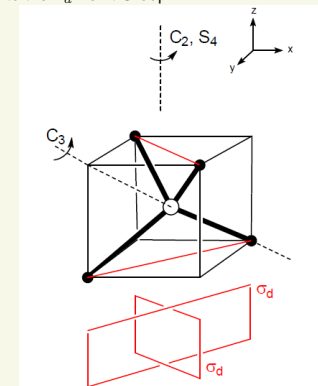
$$\Gamma_{Pd-Cl}^{vib} = A_1(\text{IR, polarised}) + B_2(\text{IR, depolarized})$$

### Summary

- For the higher symmetry *trans* Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> complex, a single mode Pd-Cl stretching vibration is expected in the IR spectrum, while two Pd-Cl stretching modes are expected in the IR spectrum for the lower symmetry *cis* Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> complex
- The next step will be to construct and optimize the *cis* and *trans* Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> complexes, obtain the vibrational modes, and compare the results with the experimental spectrum.

## The Methane Molecule

The methane molecule belongs to the  $T_d$  Point Group.



Symmetry Operations for the CH<sub>4</sub> Tetrahedral Molecule

## Reducible Representations of 4 x H1s Orbitals on Methane

As an example, consider the irreducible representations spanned by the set of 4 H 1s basis functions in the methane molecule.

### Character Table for $T_d$ Symmetry

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$A_1$	1	1	1	1	1	$x^2+y^2+z^2$
$A_2$	1	1	1	-1	-1	
E	2	-1	2	0	0	$(2z^2-x^2-y^2, x^2-y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$
$T_2$	3	0	-1	-1	1	$(x, y, z)$ $(xy, xz, yz)$
$\Gamma(\text{H1s})$	4	1	0	0	2	

Reducible Representations of the 4 x H1s on CH<sub>4</sub>

## The Reduction Formula and Basis Functions

The reduction formula

$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

provides a procedure for reducing the representation spanned by a set of basis functions in a molecule.

- $n(i)$  - number of times the  $i^{\text{th}}$  irreducible representation occurs in the representation  $r$  that is being reduced.
- $h$  - the order of the group, i.e. the number of operations in the group.
- $\sum_R$  - summation of all  $R$  operations in the group. If there is more than one operation in a given class, each operation must be included in the summation.
- $\chi_r(R)$  - character of the reducible representation  $r$  under the symmetry operator  $R$ .
- $\chi_i(R)$  - character of the irreducible representation  $i$  under the symmetry operator  $R$ .

$$\begin{aligned} n(A_1) &= \frac{1}{24} [(4 \times 1 \times 1) + (1 \times 1 \times 8) + (0 \times 1 \times 3) + (0 \times 1 \times 6) + (2 \times 1 \times 6)] = 1 \\ n(A_2) &= \frac{1}{24} [(4 \times 1 \times 1) + (1 \times 1 \times 8) + (0 \times -1 \times 3) + (2 \times -1 \times 6) + (2 \times 1 \times 6)] = 0 \\ n(E) &= \frac{1}{24} [(4 \times 2 \times 1) + (1 \times -1 \times 8) + (0 \times 2 \times 3) + (0 \times 0 \times 6) + (2 \times 0 \times 6)] = 0 \\ n(T_1) &= \frac{1}{24} [(4 \times 3 \times 1) + (1 \times 0 \times 8) + (0 \times -1 \times 3) + (0 \times 1 \times 6) + (2 \times -1 \times 6)] = 0 \\ n(T_2) &= \frac{1}{24} [(4 \times 3 \times 1) + (1 \times 0 \times 8) + (0 \times -1 \times 3) + (0 \times -1 \times 6) + (2 \times 1 \times 6)] = 1 \end{aligned}$$

$$\Gamma(\text{H1s}) = A_1 + T_2$$

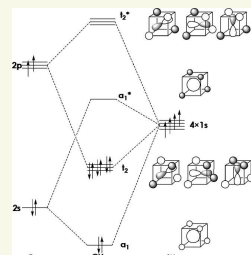
## Symmetry Adapted Linear Combinations of Orbitals (SALCs)

### SLACs and MO Diagram for the Methane Molecule

Inspection of the character table for the  $T_d$  point group shows that the p orbitals on the central C atom of  $CH_4$  transform as  $T_2$ . It's easy to show that the  $T_2$  SALC of the 4 H 1s functions match to the three orthogonal  $T_2$  C 2p orbitals.

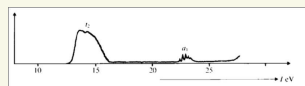
In addition, the  $A_1$  SALC of the H 1s orbitals match with the C 2s orbital.

This yields the interaction diagram below for  $CH_4$  with occupied MOs of two different energies as shown below:



MO Diagram for  $CH_4$  Showing the SALCs

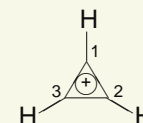
The above description of the MO diagram is confirmed below in the photoelectron spectrum for  $CH_4$ .



The Photoelectron Spectrum of  $CH_4$

## The Cyclopropenium Ion

The cyclopropenium ion ( $C_3H_3^+$ ) provides an excellent example of how to determine the symmetry of the MOs of a molecular species from Group Theory.



The  $C_3H_3^+$  ion belongs to the  $D_{3h}$  point group.

## The Cyclopropenium Ion: Secular Determinant

For  $C_3H_3^+$ , the secular determinant in the Hückel approximation becomes

$$\begin{vmatrix} \alpha - \epsilon & \beta & \beta \\ \beta & \alpha - \epsilon & \beta \\ \beta & \beta & \alpha - \epsilon \end{vmatrix} = 0$$

This is only a  $3 \times 3$  determinant which is not difficult to evaluate explicitly.

However, group theory can be used to simplify this, and the same ideas can be applied to larger molecules leading to substantial reduction in effort.

## The Cyclopropenium Ion: $D_{3h}$ Character Table

### The $D_{3h}$ Character Table

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	$x^2 + y^2, z^2$
$A_2'$	1	1	-1	1	1	-1	$R_z$
$E'$	2	-1	0	2	-1	0	$(x, y)$
$A_1''$	1	1	1	-1	-1	-1	
$A_2''$	1	1	-1	-1	-1	1	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$
$\phi_1$	$\phi_1$	$\phi_2, \phi_3$	$-\phi_1$	$-\phi_1$	$\phi_2, \phi_3$	$\phi_1$	
$\phi_2$	$\phi_2$	$\phi_3, \phi_1$	$-\phi_2$	$-\phi_2$	$\phi_3, \phi_1$	$\phi_2$	
$\phi_3$	$\phi_3$	$\phi_1, \phi_2$	$-\phi_3$	$-\phi_3$	$\phi_1, \phi_2$	$\phi_3$	
$\Gamma_{\text{reducible}}$	3	0	-1	-3	0	1	

## The Cyclopropenium Ion: Reducible Representations

To use group theory to simplify MOs, we must first determine the irreducible representations spanned by the AOs.

For example, a  $C_mH_m$  polyene would require matrices of size  $m \times m$  to be constructed, but a simple set of rules for determining the characters that may be derived from these matrices are:

1. If an orbital is unchanged after applying a symmetry operation, a value of +1 per orbital is assigned to the character.
2. If the orbital changes sign, a value of -1 per orbital is assigned to the character.
3. If the orbital changes location, a value of 0 per orbital is assigned to the character.

## The Cyclopropenium Ion: Reducible Representations

Applying these rules to  $C_3H_3$  for the reducible representation yields

$$\begin{array}{c|cccccc} D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\ \hline \Gamma_{\text{reducible}} & 3 & 0 & -1 & -3 & 0 & 1 \end{array}$$

$$\begin{aligned} a_{A'_1} &= \frac{1}{12} [(1)(3) + (2)(0) + (3)(-1) + (1)(-3) + (2)(0) + (3)(1)] = 0 \\ a_{A'_2} &= \frac{1}{12} [(1)(3) + (2)(0) + (-3)(-1) + (1)(-3) + (2)(0) + (-3)(1)] = 0 \\ a_{E'} &= \frac{1}{12} [(2)(3) + (-2)(0) + (0)(-1) + (2)(-3) + (-2)(0) + (0)(1)] = 0 \end{aligned}$$

MOs of  $C_3H_3$  cannot have  $A'$  symmetry.

$$\begin{aligned} a_{A''_1} &= \frac{1}{12} [(1)(3) + (2)(0) + (3)(-1) + (-1)(-3) + (-2)(0) + (-3)(1)] = 0 \\ a_{A''_2} &= \frac{1}{12} [(1)(3) + (2)(0) + (-3)(-1) + (-1)(-3) + (-2)(0) + (3)(1)] = 1 \\ a_{E''} &= \frac{1}{12} [(2)(3) + (-2)(0) + (0)(-1) + (-2)(-3) + (2)(0) + (0)(1)] = 1 \end{aligned}$$

Thus,  $\Gamma_{\text{reducible}} = A''_2 + E''$ .

## The Cyclopropenium Ion: Secular Determinant in Terms of SLACs

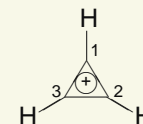
To apply Hückel theory, we can automatically separate out the  $A''_2$  symmetry sub-block of the secular determinant from the  $E''$  symmetry sub-block.

### Secular Determinant in Terms of SLACs

$$\begin{aligned} \psi_1 &= \psi_{A''_2} = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3) \\ \psi_2 &= \psi_{E''}^{(1)} = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3) \\ \psi_3 &= \psi_{E''}^{(2)} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) \end{aligned}$$

$$\begin{vmatrix} \langle \psi_1 | H | \psi_1 \rangle - \epsilon & 0 & 0 \\ 0 & \langle \psi_2 | H | \psi_2 \rangle - \epsilon & \langle \psi_2 | H | \psi_3 \rangle \\ 0 & \langle \psi_3 | H | \psi_2 \rangle & \langle \psi_3 | H | \psi_3 \rangle - \epsilon \end{vmatrix} = 0$$

## Energy-Level Diagram for $C_3H_3$



$$e'' \quad \text{-----} \quad \alpha - \beta$$

$$a''_2 \quad \text{-----} \quad \alpha + 2\beta$$

## Using the Projection Operator Method to Generate MOs as Bases for Irreducible Representations

It is not always possible to deduce the form of an SALC by matching the central atom orbital of appropriate symmetry.

However, the **projection operator method** can be used to generate symmetry adapted molecular orbital (MO) from atomic orbitals (AOs) that form a basis for a given representation.

A projection operator projects a certain part a symmetry orbital from another orbital.

$$\psi^{\text{SALC}} = P_i \phi_a = \sum_R R \phi_a \chi_i(R)$$

where

- $\psi^{\text{SALC}}$  is the wave function for the SALC belonging to the  $i^{\text{th}}$  irreducible representation.
- $P_i$  is the projection operator for the  $i^{\text{th}}$  irreducible representation.
- $\phi_a$  is one of the basis functions.
- $\sum_R$  represents a summation over all operations in the group.
- $R \phi_a$  indicates the atomic basis function generated by the operation  $R$  on  $\phi_a$ .
- $\chi_i(R)$  is the character of the  $i^{\text{th}}$  irreducible representation under  $R$ .

## Using the Projection Operator Method to Generate MOs That are Bases for Irreducible Representations

A simple set of rules for determining the MO which forms a basis for a given symmetry representation can be used:

1. Choose an AO on an atom and determine into which AO it is transformed by each symmetry operator of that group.
2. Multiply the AO of the transformed species by the character of the operator in the representation of interest for each symmetry operator.
3. The resulting linear combination of AOs forms an MO that is a basis for that representation.

The method will be applied to the cyclopropenium ion which belongs to the  $D_{3h}$  point group.

## Using the Projection Operator Method to Generate MOs as Bases for Irreducible Representations

Obtain the projection operator for the  $A_2''$  symmetry representation:

$$P^{A_2''} = \frac{1}{12} [E + C_3 + C_3^2 - C_2^{(1)} - C_2^{(2)} - C_2^{(3)} - \sigma_h - S_3 - S_3^2 + \sigma_v^{(1)} + \sigma_v^{(2)} + \sigma_v^{(3)}]$$

Project out MOs for the  $A_2''$  symmetry representation

$$\begin{aligned} P^{A_2''} \phi_1 &= \frac{1}{12} (\phi_1 + \phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2 + \phi_1 + \phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2) = \frac{1}{3} (\phi_1 + \phi_2 + \phi_3) \\ P^{A_2''} \phi_2 &= \frac{1}{12} (\phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2 + \phi_1 + \phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2 + \phi_1) = \frac{1}{3} (\phi_1 + \phi_2 + \phi_3) \\ P^{A_2''} \phi_3 &= \frac{1}{12} (\phi_3 + \phi_1 + \phi_2 + \phi_2 + \phi_1 + \phi_3 + \phi_3 + \phi_1 + \phi_2 + \phi_2 + \phi_1 + \phi_3) = \frac{1}{3} (\phi_1 + \phi_2 + \phi_3) \end{aligned}$$

The normalized symmetry adapted linear for  $A_2''$  is given as

$$\psi_{A_2''} = \frac{1}{\sqrt{3}} (\phi_1 + \phi_2 + \phi_3)$$

## Using the Projection Operator Method to Generate MOs as Bases for Irreducible Representations

Obtain the projection operator for the  $E''$  symmetry representation:

$$P^{E''} = \frac{2}{12} [2E - C_3 - C_3^2 - 2\sigma_h + S_3 + S_3^2]$$

Project out MOs for the  $E''$  symmetry representation

$$\begin{aligned} P^{E''} \phi_1 &= \frac{2}{12} (2\phi_1 - \phi_2 - \phi_3 + 2\phi_1 - \phi_2 - \phi_3) = \frac{1}{3} (2\phi_1 - \phi_2 - \phi_3) \\ P^{E''} \phi_2 &= \frac{2}{12} (2\phi_2 - \phi_1 - \phi_3 + 2\phi_2 - \phi_1 - \phi_3) = \frac{1}{3} (2\phi_2 - \phi_1 - \phi_3) \\ P^{E''} \phi_3 &= \frac{2}{12} (2\phi_3 - \phi_1 - \phi_2 + 2\phi_3 - \phi_1 - \phi_2) = \frac{1}{3} (2\phi_3 - \phi_1 - \phi_2) \end{aligned}$$

From the above, it is possible to form two linear independent functions:

$$\begin{aligned} \psi_{E''}^{(1)} &= P^{E''} \phi_1 = \frac{1}{\sqrt{6}} (2\phi_1 - \phi_2 - \phi_3) \\ \psi_{E''}^{(2)} &= P^{E''} \phi_2 - P^{E''} \phi_3 = \frac{1}{\sqrt{2}} (\phi_2 - \phi_3) \end{aligned}$$

## Franck-Condon Factors

Within the Born-Oppenheimer approximations, the electric-dipole transition moment which provides the probability of a transition from the ground-electronic state,  $\psi_i$ , to an excited electronic state,  $\psi_f$ , is given by

$$\mu_{f \leftarrow i} = -e \sum_i \underbrace{\langle \psi_f | \mathbf{r}_i | \psi_i \rangle}_{\text{Electric Dipole Transition Moment}} \underbrace{\langle \nu_f | \nu_i \rangle}_{\text{Franck-Condon Overlap Integral } S(\nu_f, \nu_i)}$$

The intensity of a transition is proportional to the square of the transition moment,  $|S(\nu_f, \nu_i)|^2$

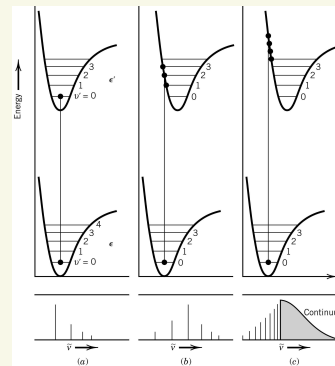
The upper and lower vibrational wavefunctions,  $\nu_f$  and  $\nu_i$ , are approximately harmonic-oscillator-like functions, so that the largest overlap of probabilities for the ground-state and excited-state vibrations will occur for a vibrational quantum number greater than 0.

This leads to the fact that the absorption probability is largest into that vibrational state of the excited electronic states whose probability is largest directly above the equilibrium internuclear distance.

## Electronic Absorption Spectra of Molecules

Potential energy curves and absorption spectra for three electronic transitions (vertical lines).

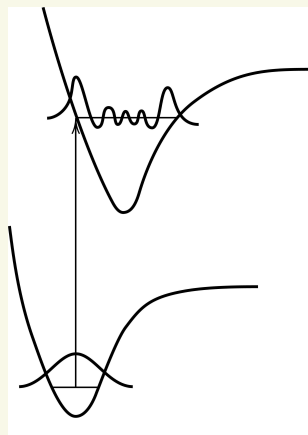
- The minimum in the potential in the excited state coincides with the ground state.
- The minimum in the potential in the excited state is at a larger internuclear distance than in the ground state.
- The absorption may raise the excited state to a higher energy than its dissociation energy so that the absorption is continuous.



## The Franck-Condon Principle

The Franck-Condon principle states that in an electronic transition, the overlap of the ground vibrational wavefunction in the lower electronic state.

The various vibrational wavefunctions in the upper electronic state is greatest for the vibrational level whose classical turning point is at the equilibrium separation in the lower state.



## Fluorescence and Phosphorescence

Excited-state molecules in a crystal, in solution, or in a gas undergo frequent collisions with other molecules in which they lose energy and return to the lowest vibrational state of  $S_1$ .

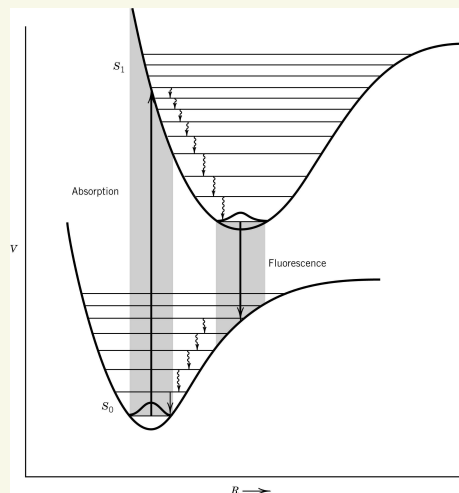
**Internal conversion** is a nonradiative transition induced by collisions and involves a decay from a higher vibrational state to the ground vibrational state of the same multiplicity.

Once in the lowest vibrational state of  $S_1$ , the molecule can undergo a radiative transition to a vibrational state in  $S_0$  (fluorescence), or it can make a nonradiative transition to an excited vibrational state of  $T_1$  in a process called **intersystem crossing** which can lead to **phosphorescence**.

Because internal conversion to the ground vibrational state of  $S_1$  is generally fast in comparison with fluorescence to  $S_0$ , the vibrationally excited-state molecule will relax to the ground vibrationally state of  $S_1$  before undergoing fluorescence.

As a result of the relaxation, the **fluorescence spectrum is shifted to lower energies relative to the absorption**.

## Absorption and Fluorescence



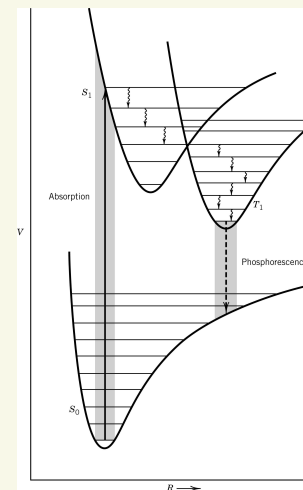
## Absorption and Phosphorescence

Absorption from  $S_0$  leads to a population of excited vibrational states in  $S_1$ .

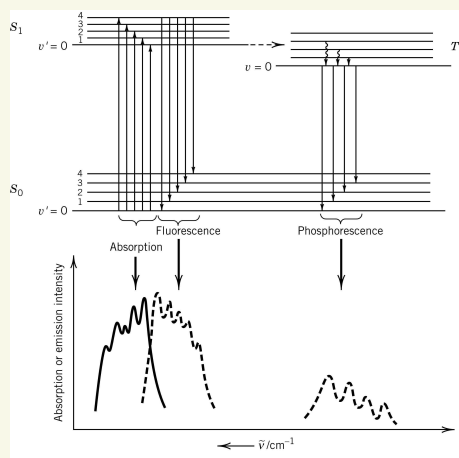
The molecule has a finite probability of making a transition to an excited vibrational state of  $T_1$ , if it has the same geometry in both states and if there are vibrational levels of the same energy in both states.

The dashed arrow indicates the coincidence of vibrational levels in  $T_1$  and  $S_1$ .

The initial excitation to  $S_1$  occurs to a vibration of maximum overlap with the ground state of  $S_0$ .



## Absorption, Fluorescence, and Phosphorescence



## Lifetimes for Fluorescence and Phosphorescence

In **fluorescence**, the radiation is emitted during a transition between electronic states of the **same spin or multiplicity**.

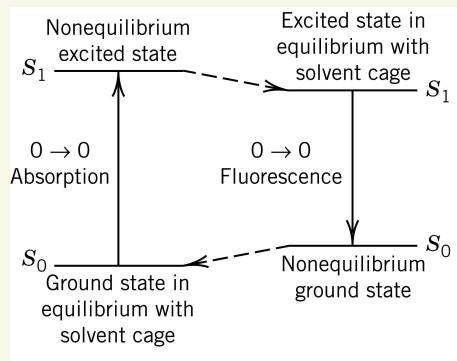
In **phosphorescence** the radiation is emitted in a transition between states of **different multiplicities**.

- The lifetime of excited singlet states is short, i.e. usually between  $10^{-6}$  s and  $10^{-9}$  s.
- The lowest triplet state of a molecule with a singlet ground state is long ( $10^{-4}$  s to 100 s) because the transitions between states of different multiplicity are forbidden, and the rate is slow leading to a longer lifetime.



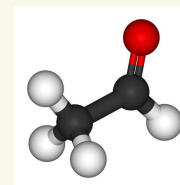
## Effect of Solute-Solvent Equilibrium on Absorption and Fluorescence Transition

The small difference on the 0-0 bands for absorption and fluorescence is due to the difference in the solvation of the initial and final states.



## Calculations of Excited States

### Acetaldehyde



## Jahn-Teller Effects

Start by assuming a particular configuration of the molecule in a certain point group.

The Schrödinger equation is assumed to be solved giving rise to eigenvalues ( $E_0, E_1, \dots, E_n$ ), and to the corresponding wave functions ( $\psi_0, \psi_1, \dots, \psi_n$ ).

After distortion by displacement of the normal coordinate,  $Q$ , from the original position, the change in energy is given by:

$$E = E_0 + \underbrace{\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_0 \right\rangle Q}_{\text{FOJT}} + \underbrace{\left[ \frac{1}{2} \left\langle \psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \psi_0 \right\rangle - \sum_k \left( \frac{\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle^2}{E_k - E_0} \right) \right] Q^2}_{\text{SOJT}}$$

where  $U$  is the nuclear-nuclear and nuclear-electronic potential energy

A first-order Jahn-Teller distortion (FOJT) states that a nonlinear molecule with an incompletely filled, degenerate HOMO level is susceptible to a structural distortion which removes the degeneracy. This structural distortion is related to a degenerate electronic state with partially filled highest occupied molecular orbitals which are degenerate.

A structural distortion arising from a second-order energy change in the HOMO is termed a second-order Jahn-Teller (SOJT) distortion.

## First-Order Jahn-Teller Effects

Consider a  $d^8$  transition metal complex which has the electronic configuration  $t_{2g}^6 e_g^{*2}$

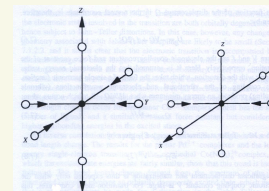
A distortion coordinate is needed such that the matrix element  $\langle \psi_0 | \frac{\partial U}{\partial Q} | \psi_0 \rangle \neq 0$ .

Then,  $\Gamma_e \otimes \Gamma_e = {}^1A_{1g} + {}^3A_{2g} + {}^1E_g$

If  $\Gamma_{E_g}$  is the symmetry species of the degenerate state, and  $\Gamma_Q$  is the distortion coordinate, then the symmetry representation of the distortion coordinate must contain the totally symmetric representation,  $A_{1g}$ :

$$\Gamma_{E_g} \otimes \Gamma_Q \otimes \Gamma_{E_g} \subset \Gamma_{A_{1g}}$$

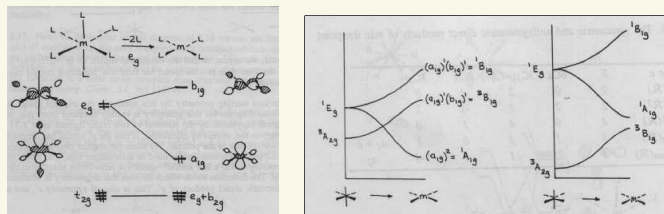
which implies that the distortion is  $\Gamma_Q = \Gamma_{E_g}$  as shown below:



## First-Order Jahn-Teller Effects: $\text{Ni}(\text{H}_2\text{O})_6^{2+}$

$\text{Ni}(\text{H}_2\text{O})_6^{2+}$  complex is a  $d^8$  complex with the electronic configuration  $t_{2g}^6 e_g^{*2}$  which splits into  $^1A_{1g} + ^3A_{2g} + ^1E_g$  states. The triplet state will probably be lowest in energy, and the doubly degenerate singlet state is next in energy. The  $^1E_g$  state is Jahn-Teller unstable and splits apart in energy during an  $e$  vibration. Stretching of two *trans* ligands will lead to a drop in the energy of the  $d_{z^2}$  orbital while the shrinking of four equatorial bonds leads to destabilization of the  $d_{x^2-y^2}$  orbital, as shown in the graph on the left. The energetic behavior of the two states closest in energy as a result of this distortion is shown in the graph on right.

If the splitting between the singlet and triplet states is small, the singlet state crosses the triplet state somewhere along the reaction coordinate. If the splitting is large, it is expected to find an octahedral triplet as in  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ .



## Second Order Jahn-Teller Effects

The symmetry species of the distortion which allows the mixing of the HOMO and LUMO is derived from group theory.

A distortion coordinate is needed such that the matrix element

$$\langle \psi_{\text{HOMO}} | \frac{\partial U}{\partial Q} | \psi_{\text{LUMO}} \rangle \neq 0.$$

If  $\Gamma_{\text{HOMO}}$  and  $\Gamma_{\text{LUMO}}$  are the symmetry species of the HOMO and LUMO, respectively and  $\Gamma_Q$  is the distortion coordinate, then the symmetry representation of the distortion coordinate must contain the totally symmetric representation,  $a_1$ :

$$\Gamma_{\text{HOMO}} \otimes \Gamma_Q \otimes \Gamma_{\text{LUMO}} \subset \Gamma_{a_1}$$

This then implies that the distortion coordinate  $Q$  has the symmetry representation:

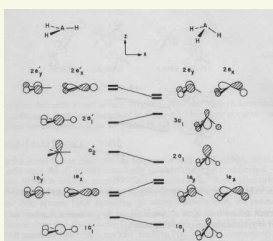
$$\Gamma_Q = \Gamma_{\text{HOMO}} \otimes \Gamma_{\text{LUMO}}$$

## Second Order Jahn-Teller Effects

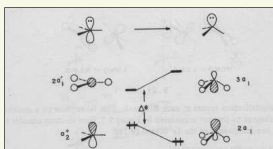
### Why is $\text{NH}_3$ Pyramidal?

$$\Gamma_{\text{HOMO}} \otimes \Gamma_{\text{LUMO}} = \Gamma_{a_2''} \otimes \Gamma_{a_1'} \subset \Gamma_{a_2''}$$

so the distortion coordinate is  $a_2''$ , in the z-direction.



Calculations show that the inversion barriers are 5.8 kcal/mol, 30 kcal/mol, and 46 kcal/mol while the HAH angles are  $106.7^\circ$ ,  $93.3^\circ$ , and  $92.1^\circ$  for  $\text{NH}_3$ ,  $\text{PH}_3$ , and  $\text{AsH}_3$ , respectively.

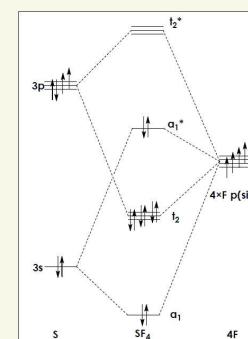


The  $2a_1'$  orbital is stabilized by mixing with the  $a_2''$  orbital. The magnitude of the stabilization is inversely proportional to the energy gap between the  $2a_1'$  and  $a_2''$  orbitals:  $E_{\text{INV}} \propto e(a_2'') - e(2a_1') \propto \frac{1}{\Delta E}$ .



## Second Order Jahn-Teller Effects

An MO diagram of the  $\sigma$  bonding in the  $\text{SF}_4$  constructed in a hypothetical tetrahedral geometry is shown below.



1. The bonding  $a_1$  and  $t_2$  levels are occupied as in the  $\text{CF}_4$  molecule, but there is also an occupied antibonding orbital,  $a_1^*$ .
2. In addition, there is an unoccupied antibonding  $t_2^*$  level at higher energy.
3. Consider a distortion to a lower symmetry than  $T_d$ . During descent of symmetry, the  $a_1$  orbital remains totally symmetric. But, the threefold degeneracy of the  $t_2^*$  level will be lifted.
4. Provided that one of the lowest unoccupied molecular orbital (LUMO,  $t_2^*$ ) orbitals is also totally symmetric, the highest occupied antibonding molecular orbital (the HOMO,  $a_1^*$ ) can mix together to stabilize the lower level.

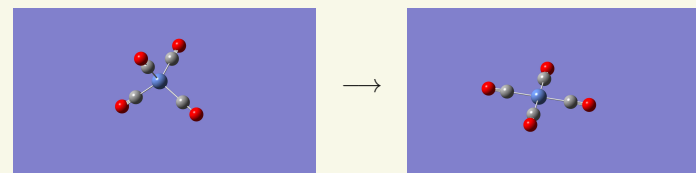
## Distortion of SF<sub>4</sub> from T<sub>d</sub> to Lower Symmetry

T <sub>d</sub>	T	D <sub>2d</sub>	C <sub>3v</sub>	C <sub>2v</sub>
A <sub>1</sub>	A	A <sub>1</sub>	A <sub>1</sub>	A <sub>1</sub>
A <sub>2</sub>	A	B <sub>1</sub>	A <sub>2</sub>	A <sub>2</sub>
E	E	A <sub>1</sub> + B <sub>1</sub>	E	A <sub>1</sub> + A <sub>2</sub>
T <sub>1</sub>	T	A <sub>2</sub> + E	A <sub>2</sub> + E	A <sub>2</sub> + B <sub>1</sub> + B <sub>2</sub>
T <sub>2</sub>	T	B <sub>2</sub> + E	A <sub>1</sub> + E	A <sub>1</sub> + B <sub>1</sub> + B <sub>2</sub>

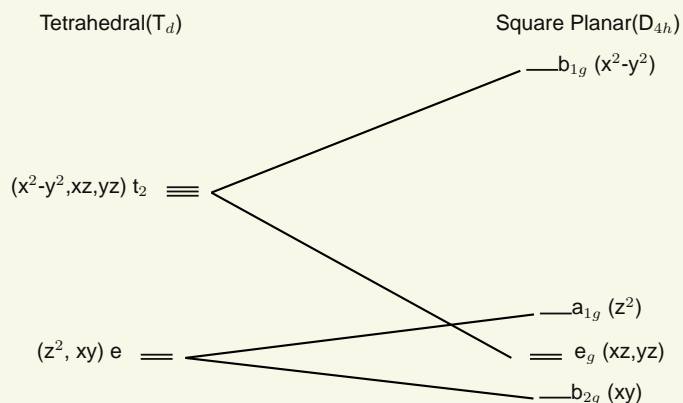
Distortions to C<sub>2v</sub> or C<sub>3v</sub> symmetry would lower the electronic energy, but distortion to either D<sub>2d</sub> or D<sub>4h</sub> symmetry would not.

The C<sub>2v</sub> and C<sub>3v</sub> structures are similar to those predicted by VSEPR arguments.

## Can Ni(CO)<sub>4</sub> Distort from T<sub>d</sub> to D<sub>4h</sub> Symmetry?



## Orbital Correlation Diagram for the Distortion of Ni(CO)<sub>4</sub> from T<sub>d</sub> to D<sub>4h</sub> Symmetry



The above graph is called an orbital correlation diagram. It is related to a Walsh diagram which is a plot of orbital energies of a molecular transformation as a function of some variable.

## Distortion of Ni(CO)<sub>4</sub> from T<sub>d</sub> to D<sub>4h</sub> Symmetry

T <sub>d</sub>	D <sub>4h</sub>
<b>Unfilled Orbitals</b>	
t <sub>2</sub> (4p <sub>x</sub> , 4p <sub>y</sub> , 4p <sub>z</sub> )	a <sub>2u</sub> + e <sub>u</sub>
a <sub>2</sub> (4s)	a <sub>1g</sub>
<b>Filled Orbitals</b>	
t <sub>2</sub> (d <sub>x2-y2</sub> , d <sub>xz</sub> , d <sub>yz</sub> )	b <sub>1g</sub> + e <sub>g</sub>
e (d <sub>z2</sub> , d <sub>xy</sub> )	a <sub>1g</sub> + b <sub>2g</sub>

During the descent to lower symmetry there is no lower unoccupied orbital that can mix and stabilize the occupied orbitals.