

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, ψ_i) to a vibrationally excited state (final vibrational state wave function, ψ_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 (μ) 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 μ can be split into three components, μ_x , μ_y , and μ_z along the Cartesian coordinate axes, and only one of the three integrals needs to be non-zero:

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

Symmetry Selection Rules for Infrared and Raman Spectra

Infrared Spectra

The vibrational ground state wave function, ψ_i belongs to the totally symmetric representation.

The symmetry properties of the components of the dipole moment (μ_x, μ_y, μ_z) are the same as those of the translation vectors along the same axes: T_x, T_y, T_z .

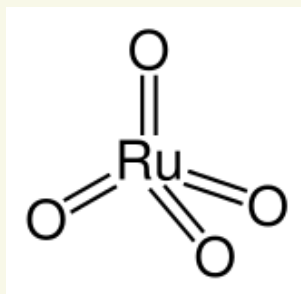
The symmetry of the vibrationally excited state wave function, ψ_f are the same as the symmetry which describes the vibrational mode.

Therefore, it is necessary to form direct products of the totally symmetric representation of ground state vibrational wave function (ψ_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.

1. ψ_i has A_1 symmetry.
2. The character table for T_d shows that T_x, T_y, T_z together have T_2 symmetry.

The direct products are then

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

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.

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 α 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.

α 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

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

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

A_1 :	$x^2 + y^2 + z^2$	Raman Only
E :	$2z^2 - x^2 - y^2, \quad x^2 - y^2$	Raman Only
T_2 :	$(\mathbf{T}_x, \mathbf{T}_y, \mathbf{T}_z), (xy, yz, zx)$	Infrared and Raman Active

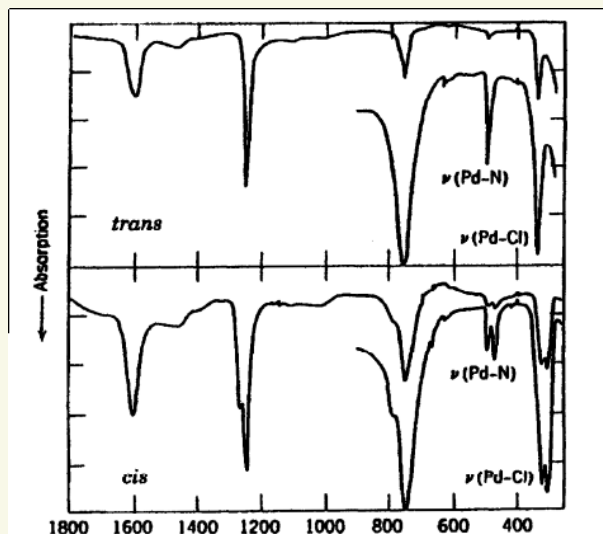
The Infrared Spectrum of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$

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 ($\nu_{\text{Pd-Cl}}$) around 350 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

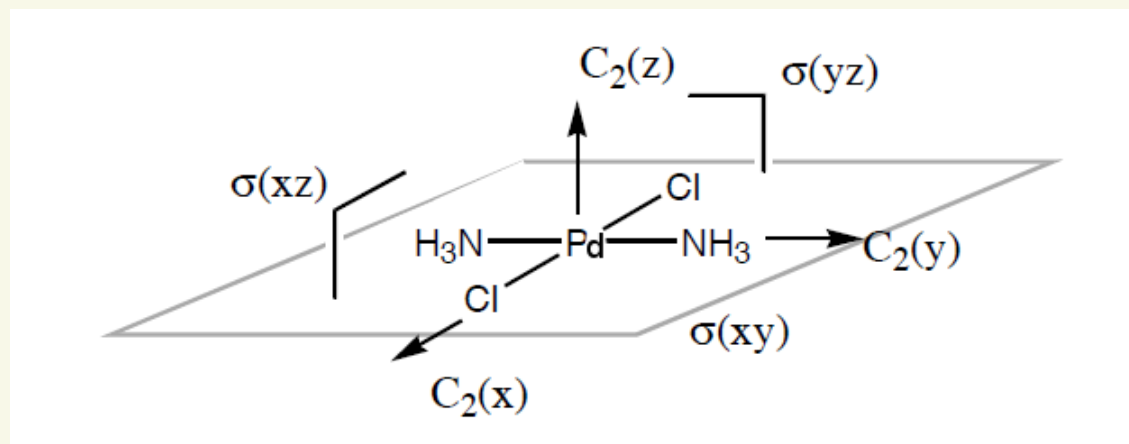
Active M-X Stretching Modes for ML_2X_2 Complexes



IR Spectrum of *cis* and *trans* $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ from Kazuo Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edition (1997), Part B, p. 10, Fig. III-5, John Wiley & Sons, New York

The Infrared Spectrum of *trans* Pd(NH₃)₂Cl₂

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



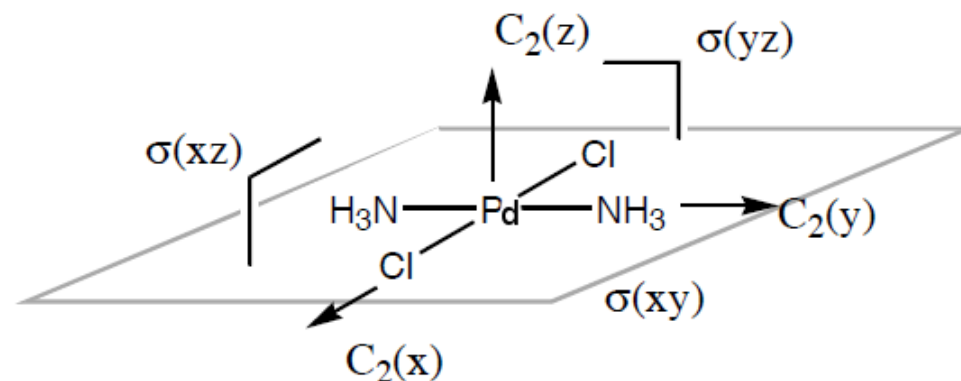
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{Pd-Cl}^{vib}	2	0	0	2	0	2	2	0

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

- IR active modes have the same symmetry as translational vectors ($\Gamma(\text{IR}) = B_{1u}, B_{2u}, B_{3u}$) while Raman modes have the same symmetry as binary functions ($\Gamma(\text{Raman}) = A_g, B_{1g}, B_{2g}, B_{3g}$).
- Trans* Pd(NH₃)₂Cl₂ 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 polarized active Raman mode and one active infrared mode
 $\Gamma_{Pd-Cl}^{vib} = A_g(\text{polarized}) + B_{3u}(\text{IR})$

The Infrared Spectrum of *cis* Pd(NH₃)₂Cl₂

Determine the contributions to Pd-Cl stretching modes for the *cis* Pd(NH₃)₂Cl₂ complex.



C_{2v}	E	C_2	$\sigma(xz)$	$\sigma'(yz)$
Γ_{Pd-Cl}^{vib}	2	0	0	2

$$\Gamma_{Pd-Cl}^{vib} = A_1 + B_2$$

- 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 polarized are expected. Both modes will be present in both the IR and Raman spectra:

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

Summary

- For the higher symmetry *trans* Pd(NH₃)₂Cl₂ 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(NH₃)₂Cl₂ complex
- The next step will be to construct and optimize the *cis* and *trans* Pd(NH₃)₂Cl₂ complexes, obtain the vibrational modes, and compare the results with the experimental spectrum.