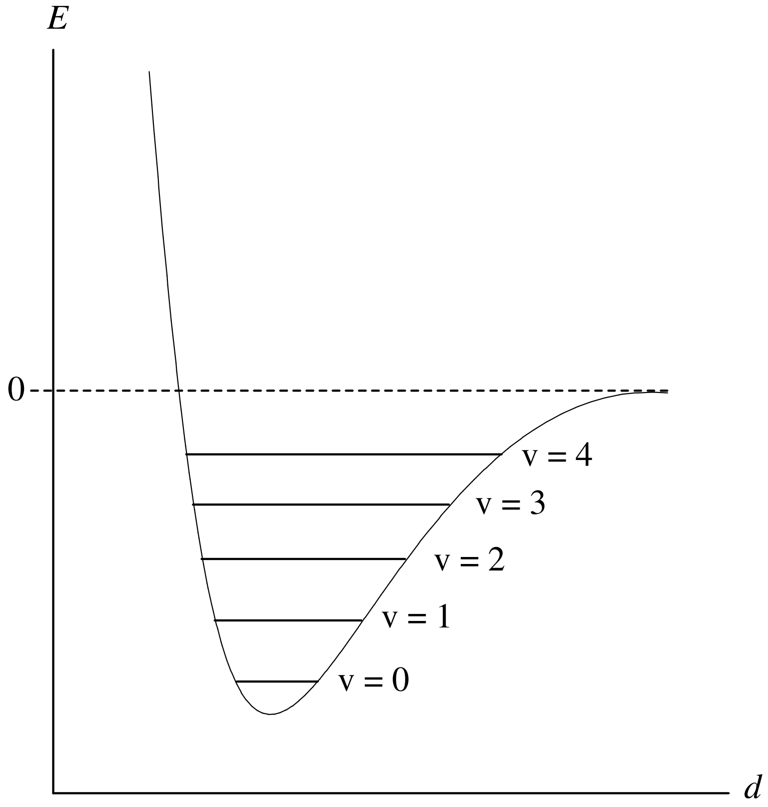
Spectroscopic Selection Rules



- For a vibrational fundamental ($\Delta\mathbf{v} = \pm 1$), the transition will have nonzero intensity in either the infrared or Raman spectrum if the appropriate transition moment is nonzero.

- If the transition moment for infrared absorption or Raman scattering is ***nonzero*** for a particular normal mode, the mode is said to be ***allowed*** or ***active*** in the associated kind of spectrum (i.r. or Raman).

- If the transition moment for infrared absorption or Raman scattering is ***zero*** for a particular normal mode, the mode is said to be ***forbidden*** or ***inactive*** in the associated kind of spectrum (i.r. or Raman).

Spectroscopic Selection Rules
Symmetry Analysis of Transition Moment Integrals

- An integral of the product of two functions, $\int f_A f_B d\tau$, can be nonzero only if it is invariant under all operations of the molecule's point group.

- This can occur only if the direct product of $f_A f_B$ is or contains the totally symmetric representation of the point group.

- In terms of the symmetry of f_A and f_B, the direct product of $f_A f_B$ is or contains the totally symmetric representation only if f_A and f_B belong to the same symmetry species.

  Only the direct product of a symmetry species with itself
  is or contains the totally symmetric representation.

Spectroscopic Selection Rules
Infrared Activity

- For infrared absorption to occur, the normal mode must have an oscillating molecular dipole moment with the same frequency as the oscillating electric field of the radiation.

- The transition moment for the fundamental of a normal mode (**v** = 0 → **v** = 1) can be written

$$M(0,1) = \int \psi_0 \mu \psi_1 d\tau$$

  where ψ_0 and ψ_1 are wave functions for the ground and excited vibrational states, and μ is the oscillating electric dipole moment vector as a function of the *normal coordinate*, Q, for the normal mode.
- The vector μ is a resultant of its components μ_x, μ_y and μ_z, so we may write

$$M_x = \int \psi_0 \mu_x \psi_1 d\tau$$
$$M_y = \int \psi_0 \mu_y \psi_1 d\tau$$
$$M_z = \int \psi_0 \mu_z \psi_1 d\tau$$

- If any one of these components is nonzero, the entire transition moment will be nonzero.

- We can determine if any of these components is nonzero on the basis of the symmetries of the wave functions and the dipole moment components.

Spectroscopic Selection Rules
Evaluating the Infrared Transition Moment Expression

- If the integral for the transition moment transforms as the totally symmetric representation the vibrational transition will be infrared allowed.

- The ground state vibrational wave function ψ_0 is totally symmetric for all molecules (except free radicals) and the excited state wave function ψ_1 has the symmetry of the normal mode.

- Therefore, by itself the product $\psi_0\psi_1$ has the symmetry of ψ_1.

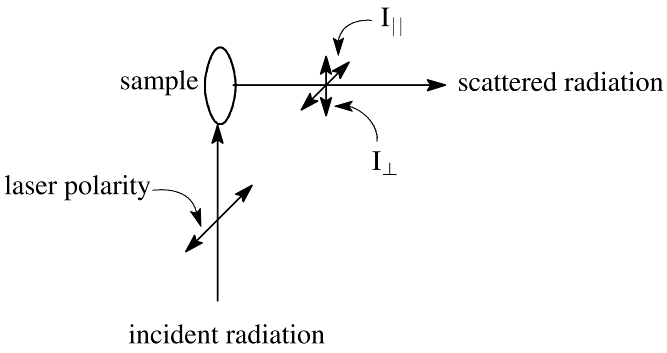
  The direct product of the totally symmetric representation with any non-totally symmetric representation is the non-totally symmetric representation (e.g., in C_{2v}, $A_1 \times B_1 = B_1$).

- If any component of μ has the same symmetry as ψ_1 the product $\mu\psi_1$ will be totally symmetric and the integral will be nonvanishing.

- The symmetry species of μ_x, μ_y, and μ_z are the same as the unit vector transformations *x, y,* and *z*, as listed in the character table.

☞ ***A normal mode belonging to the same symmetry species as any of the unit vectors x, y, or z will be active in the infrared spectrum.***

Spectroscopic Selection Rules
Raman Activity



- The induced moment is related to the field strength of the incident radiation by

$$P = \alpha E$$

where the proportionality constant α is the *polarizability*, whose magnitude changes as the molecule oscillates.

- For a normal mode to be Raman active there must be a nonzero change in the polarizability with the normal coordinate at the equilibrium configuration; i.e., $(\partial\alpha/\partial Q)_0 \neq 0$.

- The polarizability is best expressed as a tensor, so $P = \alpha E$ becomes

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

where $\alpha_{ij} = \alpha_{ji}$.

- If the change in any one of these components is nonzero $[(\partial\alpha_{ij}/\partial Q)_0 \neq 0]$ then the mode will be Raman active.

Spectroscopic Selection Rules
The Raman Transition Moment Expression

- The transition moment for Raman activity of a fundamental may be expressed as

$$P(0,1) = \int \psi_0 \alpha E \psi_1 d\tau = E \int \psi_0 \alpha \psi_1 d\tau$$

- An integral of this form can be written for every component α_{ij}, giving components P_{ij}.

$$P_{ij} = E \int \psi_0 \alpha_{ij} \psi_1 d\tau$$

- If there is any component for which $P_{ij} \neq 0$, then the entire moment will be nonvanishing ($P(0,1) \neq 0$), and the transition will be Raman active.

Spectroscopic Activity
Evaluating The Raman Transition Moment Expression

- The integral will be nonzero if it is totally symmetric.

- As before, ψ_0 is totally symmetric and ψ_1 has the symmetry of the normal mode.

- The integral will be nonzero if ψ_1 and any component α_{ij} have the same symmetry.

- The symmetries of the α_{ij} components are the same as the binary direct products of vectors, whose transformation properties are listed in the last column of the character table.

☞ ***A normal mode will be Raman active if it belongs to the same symmetry species as one of the binary direct products of vectors listed in the character table for the molecule.***

Spectroscopic Selection Rules
Normal Modes of SO_2: $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(B_2)$

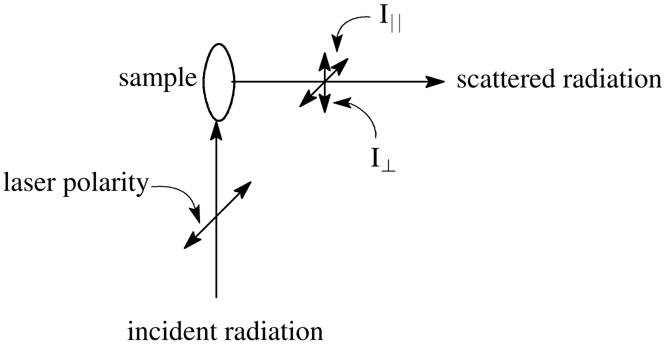
Looking at the character table for C_{2v}, we find the following unit vector and direct product transformation properties:

C_{2v}		
A_1	z	x^2, y^2, z^2
A_2		xy
B_1	x	xz
B_2	y	yz

- Both A_1 and B_2, the species of the three normal modes, have listings for unit vectors and direct products.

- Therefore, all three modes are active in both the infrared and Raman spectra. In other words, we should be able to observe the same three frequencies in both the infrared and Raman spectra.

Spectroscopic Selection Rules
Experimental Identification of Totally Symmetric Modes by Raman Spectroscopy



The polarizability ratio:

$$\rho = \frac{I_{\perp}}{I_{\parallel}}$$

- A band for which $0 < \rho < 3/4$ is said to be *polarized* and arises from a totally symmetric vibration.

- A band for which $\rho = 3/4$ is said to be *depolarized* and arises from a non-totally symmetric vibration.

Spectroscopic Selection Rules
Normal Modes of XY_4: $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(T_2)$, $\nu_4(T_2)$

Looking at the character table for T_d we find the following unit vector and direct product transformation properties:

T_d		
A_1		$x^2 + y^2 + z^2$
A_2		
E		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1		
T_2	(x, y, z)	(xy, xz, yz)

- All three unit vectors transform degenerately as T_2, so only normal modes with T_2 symmetry can be infrared active.

- For tetrahedral XY_4 this means that only ν_3 and ν_4 can be observed by infrared spectroscopy.

- In contrast, A_1, E, and T_2 all have direct product listings, which means modes with these symmetries will be Raman active. Thus, we should be able to observe all four frequencies by Raman spectroscopy.

Spectroscopic Selection Rules
Normal Modes of XY_4: $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(T_2)$, $\nu_4(T_2)$

A_1	E	$2T_2$
ν_1	ν_2	ν_3, ν_4
Raman	Raman	i.r., & Raman

- Only the Raman spectrum allows observation of all four fundamental frequencies.

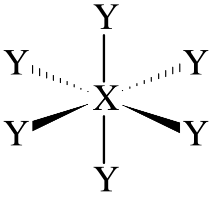
- The infrared spectrum will show only the frequencies for the two sets of triply degenerate modes, ν_3 and ν_4

- The ν_3 and ν_4 modes are ***coincident*** in both spectra. This means that we should expect to find a band for ν_3 at the same frequency in both the infrared and Raman spectra. The same is true for ν_4.

Vibrational Frequencies of Methane

Mode	Frequency (cm^{-1})	Activity
ν_1 (A_1)	3025.5	R (pol)
ν_2 (E)	1582.7	R
ν_3 (T_2)	3156.8	i.r., R
ν_4 (T_2)	1367.4	i.r., R

Spectroscopic Selection Rules
Normal Modes and Spectroscopic Activity of XY_6 (O_h)



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h =$	48
N_i	7	1	1	3	3	1	1	1	5	3		
χ_i	3	0	-1	1	-1	-3	-1	0	1	1		
Γ_{3n}	21	0	-1	3	-3	-3	-1	0	5	3	Σ	n_i
A_{1g}	21	0	-6	18	-9	-3	-6	0	15	18	48	1
A_{2g}	21	0	6	-18	-9	-3	6	0	15	-18	0	0
E_g	42	0	0	0	-18	-6	0	0	30	0	48	1
T_{1g}	63	0	6	18	9	-9	-6	0	-15	-18	48	1
T_{2g}	63	0	-6	-18	9	-9	6	0	-15	18	48	1
A_{1u}	21	0	-6	18	-9	3	6	0	-15	-18	0	0
A_{2u}	21	0	6	-18	-9	3	-6	0	-15	18	0	0
E_u	42	0	0	0	-18	6	0	0	-30	0	0	0
T_{1u}	63	0	6	18	9	9	6	0	15	18	144	3
T_{2u}	63	0	-6	-18	9	9	-6	0	15	-18	48	1

$$\Gamma_{3n} = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$$

$$\Gamma_{\text{trans}} = T_{1u} \qquad \Gamma_{\text{rot}} = T_{1g}$$

$$\Gamma_{3n-6} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$$

Spectroscopic Selection Rules
Normal Modes and Spectroscopic Activity of XY_6 (O_h)

$$\Gamma_{3n-6} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$$

Species	ν_n	Transformations	Activity
A_{1g}	ν_1	$x^2 + y^2 + z^2$	Raman
E_g	ν_2	$(2z^2 - x^2 - y^2, x^2 - y^2)$	Raman
T_{2g}	ν_5	(xz, yz, xy)	Raman
$2T_{1u}$	ν_3, ν_4	(x, y, z)	i.r.
T_{2u}	ν_6	—	—

- Raman-active modes are not i.r.-active and vice versa. (*Mutual exclusion*)

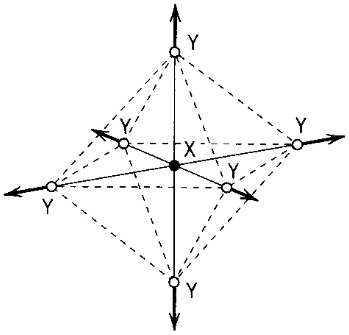
- Only *gerade* species A_{1g}, E_g, and T_{2g} are Raman active.

- Only the *ungerade* species T_{1u} is i.r. active.

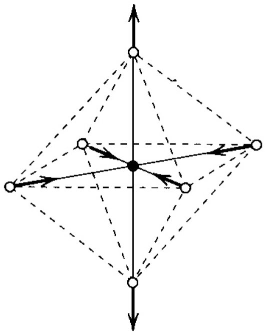
- The degenerate modes that comprise ν_6 (T_{2u}) are not active in either Raman or i.r. (*Silent modes*).

Vibrational Frequencies of SF_6

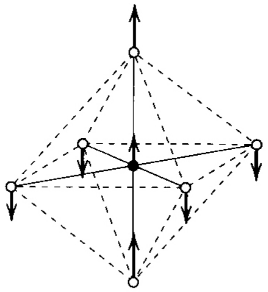
Mode	Frequency (cm^{-1})	Activity
ν_1 (A_{1g})	775	R (pol)
ν_2 (E_g)	643	R
ν_3 (T_{1u})	948	i.r.
ν_4 (T_{1u})	615	i.r.
ν_5 (T_{2g})	524	R
ν_6 (T_{2u})	346	—



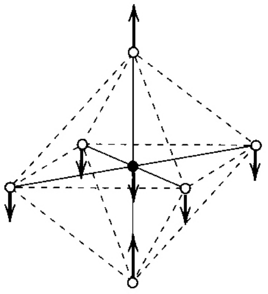
$\nu_1(A_{1g})$



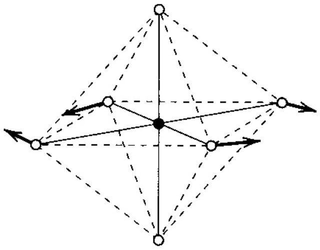
$\nu_2(E_g)$



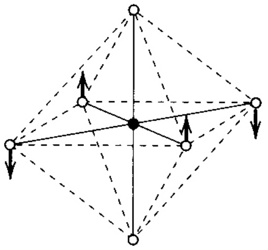
$\nu_3(T_{1u})$



$\nu_4(T_{1u})$



$\nu_5(T_{2g})$



$\nu_6(T_{2u})$

Spectroscopic Selection Rules
General Results

- Infrared-active modes can be distributed among no more than three symmetry species, because activity is associated with the transformation properties of the three unit vectors.

- Raman-active modes can be distributed among as many as four symmetry species, depending on the point group, because the direct products typically span two to four species.

- In centrosymmetric point groups (those that have inversion, *i*), unit vectors transform as *ungerade* species, and direct products transform as *gerade* species. Therefore, *infrared-active modes will be Raman inactive, and vice versa, for centrosymmetric molecules*. This requirement is known as the ***rule of mutual exclusion***.

- Unit vector and direct product transformations do not span all species in some groups. Thus, *it is possible to have some normal modes that cannot be observed as fundamentals in either the infrared or Raman spectra*. These spectroscopically inactive modes are often called ***silent modes***.

- The totally symmetric representation in every point group is associated with one or more direct product transformations. Therefore, *normal modes that are totally symmetric will always be Raman active*. Totally symmetric modes may or may not be infrared active, depending on the point group.