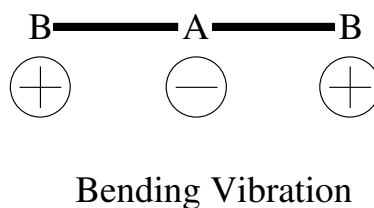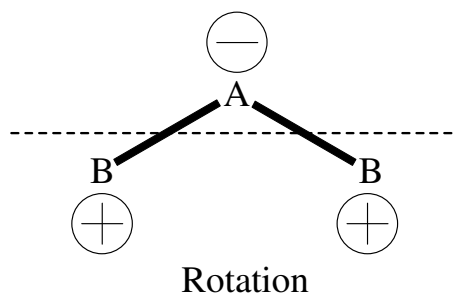# Degrees of Freedom and Vibrational Modes

1. Every atom in a molecule can move in three possible directions relative to a Cartesian coordinate, so for a molecule of n atoms there are $3n$ degrees of freedom.

2. For a linear molecule, there are 3 translations and 2 rotations of the system, so the number of normal modes is $3n - 5$.

3. For a nonlinear molecule, there are 3 translations and 3 rotations of the system, so the number of normal modes is $3n - 6$.

Why is there an "extra" vibration for a linear molecule of n atoms, compared to a nonlinear molecule with the same number of atoms?

Rotation

Bending Vibration

Symmetry of Degrees of Freedom

- All $3n$ degrees of freedom — normal modes, translations, and rotations — have symmetry relationships consistent with the irreducible representations (species) of the molecule's point group.

- We can catalogue the species of all degrees of freedom by making a set of $3n$ vectors (3 along the Cartesian coordinates of each atom) a basis for a representation of the group:

$$\Gamma_{3n}$$

- By inspecting the unit vector and rotational vector transformation properties listed in the character table, we can identify the species of the nonvibrational degrees of freedom and subtract them:

$$\Gamma_{vib} = \Gamma_{3n} - \Gamma_{trans} - \Gamma_{rot}$$

- Knowing the symmetry species of Γ_{vib}, we can apply symmetry-based quantum mechanical *selection rules* to predict which normal modes will be observable (*active*) in the infrared spectrum and the Raman spectrum.

- Matching predicted spectroscopic activity with observed spectra can be useful in determining structure.
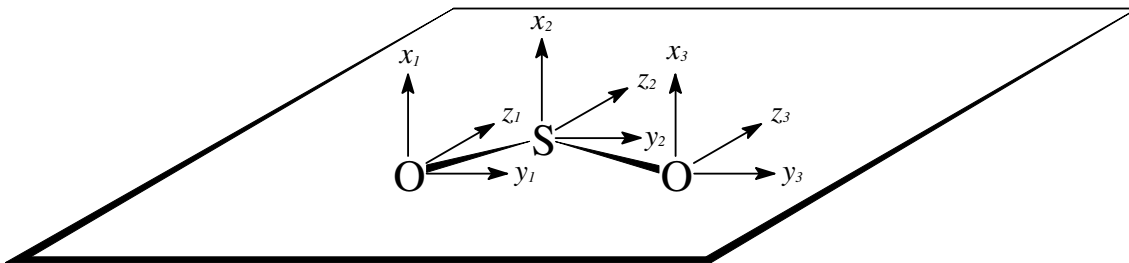
Determining Γ_{3n}
Example: SO_2 (C_{2v})
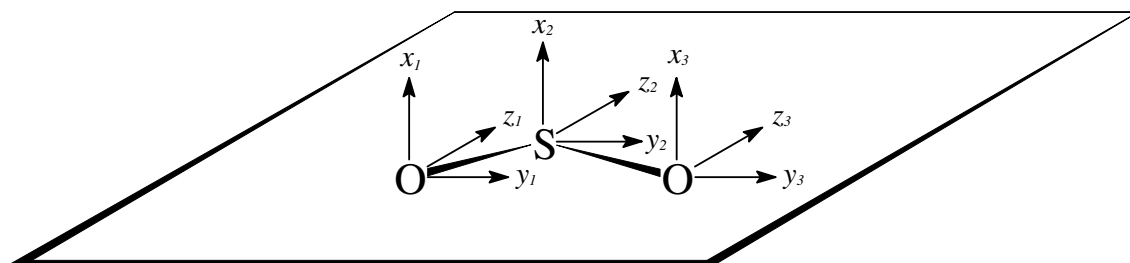
E:

$$\begin{Vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{Vmatrix} \begin{Vmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{Vmatrix} = \begin{Vmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{Vmatrix}$$

$$\chi_E = 9 = 3n$$

Determining Γ_{3n}
Example: SO_2 (C_{2v})

C_2:

$$
\begin{Vmatrix}
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0
\end{Vmatrix}
\begin{Vmatrix}
x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3
\end{Vmatrix}
=
\begin{Vmatrix}
-x_3 \\ -y_3 \\ z_3 \\ -x_2 \\ -y_2 \\ z_2 \\ -x_1 \\ -y_1 \\ z_1
\end{Vmatrix}
$$

$$\chi_{C_2} = -1$$

Determining Γ_{3n}
Example: SO_2 (C_{2v})

$\sigma_v = \sigma(xz)$:

$$
\begin{array}{|ccccccccc|}
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\begin{array}{|c|}
x_1 \\
y_1 \\
z_1 \\
x_2 \\
y_2 \\
z_2 \\
x_3 \\
y_3 \\
z_3 \\
\end{array}
=
\begin{array}{|c|}
x_3 \\
-y_3 \\
z_3 \\
x_2 \\
-y_2 \\
z_2 \\
x_1 \\
-y_1 \\
z_1 \\
\end{array}
$$

$$\chi_{\sigma(xz)} = 1$$

$\sigma_v' = \sigma(yz)$:

$$
\begin{vmatrix}
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{vmatrix}
\begin{vmatrix}
x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3
\end{vmatrix}
=
\begin{vmatrix}
-x_1 \\ y_1 \\ z_1 \\ -x_2 \\ y_2 \\ z_2 \\ -x_3 \\ y_3 \\ z_3
\end{vmatrix}
$$

$$\chi_{\sigma(yz)} = 3$$

Gathering all χ_R:

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
Γ_{3n}	9	-1	1	3

Determining Γ_{3n}
A General Simplification

- In the SO_2 example, note that each 9 x 9 operation matrix contains three 3 x 3 block operation matrices, one for each atom. Such 3 x 3 matrices will occur in the full matrix for any molecule.

- For any operation R_i, all the individual-atom operation matrices (3 x 3 matrices) have identical form and therefore have the same character, χ_i.

- Only individual-atom block matrices that lie along the diagonal of the full operation matrix contribute to the overall character for the operation, χ_R.

- Only those 3 x 3 block matrices for atoms that are *not shifted* by the operation fall along the trace of the full matrix and contribute to the character of the overall matrix.

☞ *To find χ_R, the character for the overall operation, count the number of atoms that remain nonshifted by the operation, N_i, and multiply by the contribution per nonshifted atom, χ_i; i.e.,*

$$\chi_R = N_i \chi_i$$

Determining Γ_{3n}
Obtaining Values of χ_i

- Values of χ_i for all operations can be tabulated[1], but they can also be obtained by inspecting a character table for a group that includes the operation of interest.

- The contribution per nonshifted atom for a particular operation, χ_i, is the same regardless of the orientation of its associated symmetry element.

- The value of the contribution per nonshifted atom for a particular operation is the same in any point group in which that kind of operation is found.

- Individual elements c_{11}, c_{22}, c_{33} along the trace of the 3 x 3 matrix indicate the effects of the operation on the coordinates x, y, z, respectively, of the atom on which they operate.

- The values for these elements will be identical to the characters for the operation in the irreducible representations by which the unit vectors x, y, and z transform.

☞ *To find a needed value of χ_i add up the characters in the character table under the operation for the irreducible representations by which all three unit vectors transform.*

---

[1]See Table 6-1 in E. B. Wilson, J.C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955, p. 105 (available in reprint from Dover Publications, New York).

Determining Γ_{3n}
Obtaining Values of χ_i
Examples: x, y, z nondegenerate

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
A_1	1	1	1	1	z
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y
χ_i	3	-1	1	1	

C_{2h}	E	C_2	i	σ_h	
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y
B_u	1	-1	-1	1	x, y
χ_i	3	-1	-3	1	

C_i	E	i	
A_u	1	-1	x, y, z
A_u	1	-1	x, y, z
A_u	1	-1	x, y, z
χ_i	3	-3	

Determining Γ_{3n}
Obtaining Values of χ_i
Examples: x, y, z degenerate

D_{2d}	E	$2S_4$	C_2	$2C_2{}'$	$2\sigma_d$	
B_2	1	-1	1	-1	1	z
E	2	0	-2	0	0	(x, y)
χ_i	3	-1	-1	-1	1	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
T_2	3	0	-1	-1	1	(x, y, z)
χ_i	3	0	-1	-1	1	

Determining Γ_{3n} and Obtaining Γ_{vib}
Example: SO_2
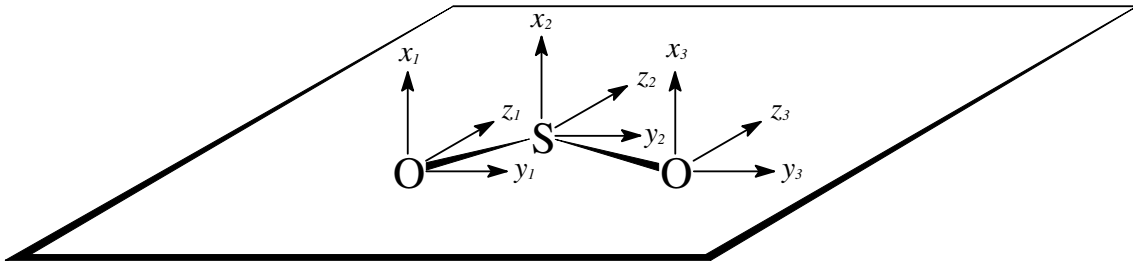
C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	Σ	n_i	
N_i	3	1	1	3			
χ_i	3	-1	1	1			
Γ_{3n}	9	-1	1	3			
A_1	9	-1	1	3	12	3	z
A_2	9	-1	-1	-3	4	1	R_z
B_1	9	1	1	-3	8	2	x, R_y
B_2	9	1	-1	3	12	3	y, R_x

$$\Gamma_{3n} = 3A_1 + A_2 + 2B_1 + 3B_2$$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Symmetries of the 3*n*-6 Vibrations

$$\Gamma_{3n-6} = \Gamma_{3n} - \Gamma_{trans} - \Gamma_{rot}$$

☞ To determine the symmetries of the translations and rotations, which must be subtracted from Γ_{3n} to obtain Γ_{3n-6}, look at the unit vector transformations (x, y, z) to identify the species of Γ_{trans}, and look at the rotational vector transformations (R_x, R_y, R_z) to identify the species of Γ_{rot}, as listed in the penultimate column of the character table.

From the listed unit vector transformations in C_{2v}:
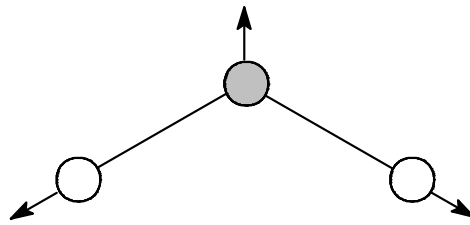
$$\Gamma_{trans} = A_1 + B_1 + B_2$$

From the listed rotational vector transformations in C_{2v}:

$$\Gamma_{rot} = A_2 + B_1 + B_2$$

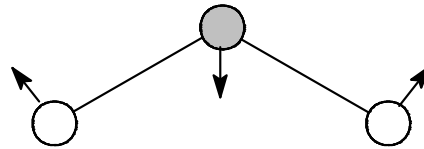Therefore for SO_2:

$$\Gamma_{vib} = \Gamma_{3n} - \Gamma_{trans} - \Gamma_{rot}$$

$$= (3A_1 + A_2 + 2B_1 + 3B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2)$$
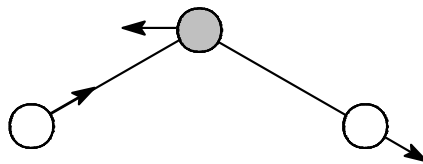
$$= 2A_1 + B_2$$

Normal Modes of SO_2

$\nu_1 \ (A_1)$
symmetric stretch

$\nu_2 \ (A_1)$
bend

$\nu_3 \ (B_2)$
antisymmetric stretch

$\nu_1 = 1151 \ \text{cm}^{-1}$, $\nu_2 = 519 \ \text{cm}^{-1}$, and $\nu_3 = 1361 \ \text{cm}^{-1}$

Systematic Numbering of Frequencies
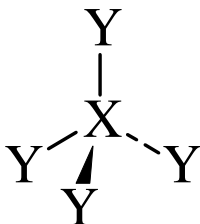## for Normal Modes

Frequencies associated with normal modes are numbered (ν_1, ν_2, ν_3, ...) in descending order of symmetry species (as listed down the left column of the appropriate character table), and among modes of the same symmetry species in descending order of vibrational frequency.

Common structures not following this convention:

- XY_6 octahedral (O_h)

- XY_4 square planar (D_{4h})

- ZXY_2 planar (C_{2v})

- ethane-type X_2Y_6 (D_{3d})

- nonlinear X_2Y_2 (planar C_{2v} or non-planar C_2)

Determining Γ_{3n} and Obtaining Γ_{vib}
Degenerate Normal Modes of Vibration
Example: Tetrahedral XY_4 (T_d)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$			
N_i	5	2	1	1	3			
χ_i	3	0	-1	-1	1			
Γ_{3n}	15	0	-1	-1	3	Σ	n_i	
A_1	15	0	-3	-6	18	24	1	
A_2	15	0	-3	6	-18	0	0	
E	30	0	-6	0	0	24	1	
T_1	45	0	3	-6	-18	24	1	(R_x, R_y, R_z)
T_2	45	0	3	6	18	72	3	(x, y, z)

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)

Symmetries of the 3*n*-6 Vibrations

From the reduction of Γ_{3n}, we have

$$\Gamma_{3n} = A_1 + E + T_1 + 3T_2$$

These fifteen degrees of freedom include three translations and three rotations.

From the listed vector transformation properties:

$$\Gamma_{trans} = T_2 \quad \text{and} \quad \Gamma_{rot} = T_1$$

Subtracting the translations and rotations:

$$\Gamma_{3n\text{-}6} = A_1 + E + 2T_2$$

Thus, we predict that there should be four frequencies:

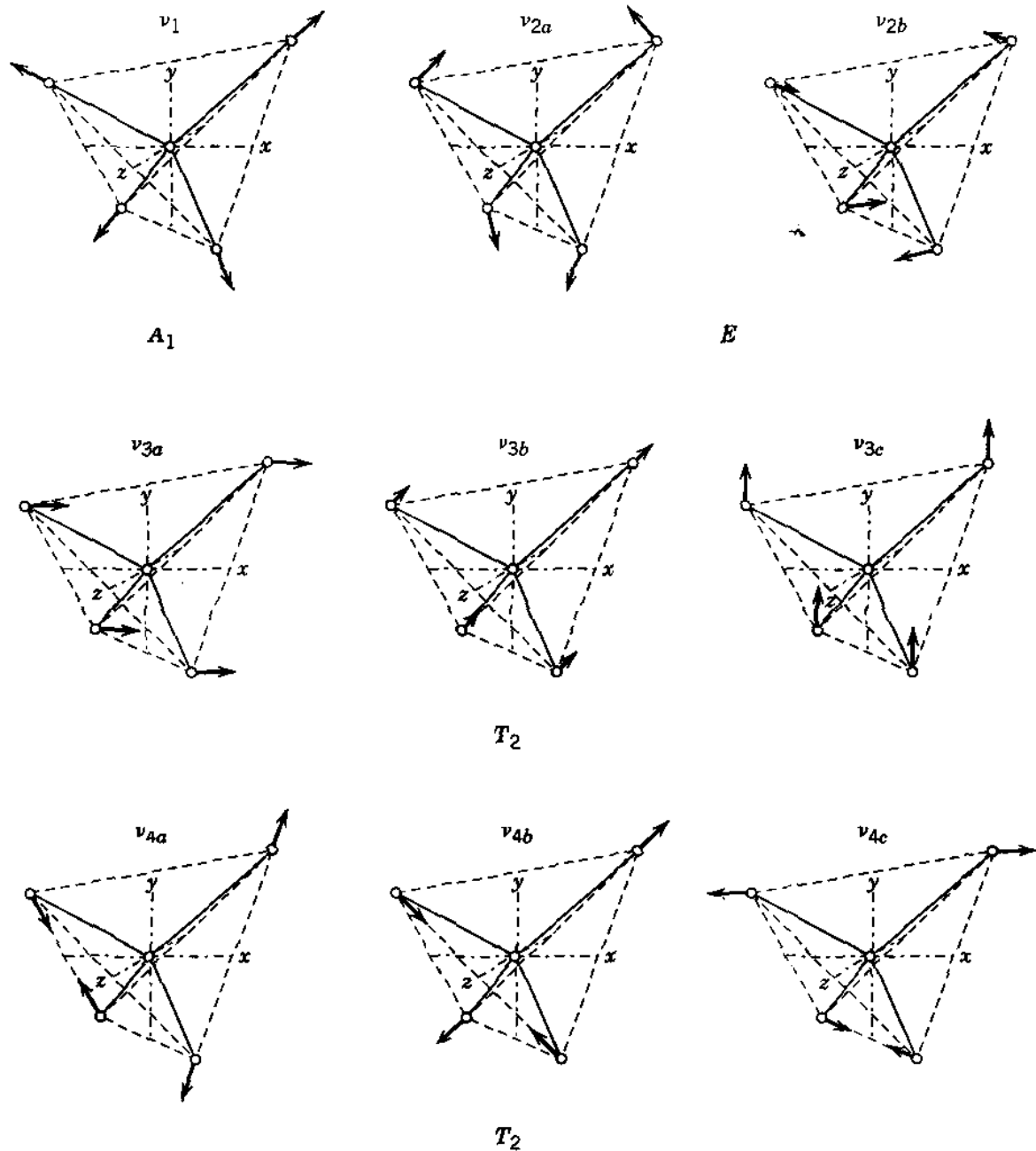$$\nu_1(A_1),\ \nu_2(E),\ \nu_3(T_2),\ \nu_4(T_2)$$

Figure 6.10 Normal modes of vibration of a tetrahedral XY_4 molecule. [Adapted with permission from G. Herzberg, *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules*, reprint 1991 with corrections, Krieger Publishers, Malabar, FL.]