



## Molecular Spectroscopy Workbench

# Practical Group Theory and Raman Spectroscopy, Part I: Normal Vibrational Modes

Group theory is an important component for understanding the fundamentals of vibrational spectroscopy. The molecular or solid state symmetry of a material in conjunction with group theory form the basis of the selection rules for infrared absorption and Raman scattering. Here we investigate, in a two-part series, the application of group theory for practical use in laboratory vibrational spectroscopy.

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In part I of this two-part series we present salient and beneficial aspects of group theory applied to vibrational spectroscopy in general and Raman spectroscopy in particular. We highlight those aspects of molecular symmetry and group theory that will allow readers to beneficially apply group theory and polarization selection rules in both data acquisition and interpretation of Raman spectra. Small-molecule examples are presented that show the correlation between depictions of normal vibrational modes and the mathematical descriptions of group theory.

### Why Would I Want to Use Group Theory?

Many of us learned group theory in undergraduate or graduate school. For some, the last time that they used or understood group theory was in preparation for a final exam. Furthermore, the application of group theory to anything other than the small molecules covered in textbooks can seem like an ordeal in tedious mathematics and bookkeeping. But, it doesn't have to be that way. So, let's brush up on those aspects of group theory that apply to vibrational spectroscopy, and you'll soon find that there is a lot more information to be gained through the application of group theory and Raman

polarization selection rules in both data acquisition and interpretation of the spectra.

There are so many good instructional and reference materials in books (1–11) and articles (12–15) on group theory that there did not seem to be any good reason to attempt to duplicate that work in this installment. Rather, I would like to summarize and present the most salient and beneficial aspects of group theory when it is applied to vibrational spectroscopy in general and Raman spectroscopy in particular.

The character table is at the heart of group theory and contains a great deal of information to assist vibrational spectroscopists. Thus, let's examine and describe in detail one of the most simple character tables — the  $C_{2v}$  point group, which is shown in Table I. The top row consists of the type and number of symmetry operations that form a symmetry class. The first column lists the symmetry species (represented by their Mulliken symbols) that comprise the  $C_{2v}$  point group. The symmetry species' irreducible representations of characters appear in the rows immediately to the right of the Mulliken shorthand symbols. The individual characters indicate the result of the symmetry operation at the top of the column on the molecular basis for that symmetry

$C_{2v}$	$E$	$C_2$	$\nu(xz)$	$\nu'(yz)$	IR Activity	Raman Activity
$A_1$	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	$y, R_x$	$yz$

Mulliken Symbols of Symmetry Species (Column 1 in Character Table)	Meaning
$A$	Symmetric with respect to principal axis of symmetry
$B$	Antisymmetric with respect to principal axis of symmetry
$E$	Doubly degenerate, two-dimensional irreducible representation
$T$	Triply degenerate, three-dimensional irreducible representation
$g$	Symmetric with respect to a center of symmetry
$u$	Antisymmetric with respect to a center of symmetry
1 (subscript)	Symmetric with respect to a $C_2$ axis that is perpendicular to the principal axis. Where there is no such axis the subscript indicates that reflection in a $\nu$ plane of symmetry is symmetric.
2 (subscript)	Antisymmetric with respect to a $C_2$ axis that is perpendicular to the principal axis. Where there is no such axis the subscript indicates that reflection in a $\nu$ plane of symmetry is antisymmetric.
' (prime)	Symmetric with respect to reflection in a horizontal plane of symmetry
'' (double prime)	Antisymmetric with respect to reflection in a horizontal plane of symmetry

species. In vibrational spectroscopy, each normal mode of vibration consists of stretches, bends, and other motions that form a basis for an irreducible representation in the character table of the point group with the same symmetry as that of the molecule. The individual characters in the table indicate the effect of the symmetry operation in the top row on the symmetry species in the first column. Each normal vibrational mode of the molecule will conform to the irreducible representation of a symmetry species in the point group of the molecule. Consequently, the effect of the symmetry operations on the vibrational mode must match the character value of that irreducible representation for the symmetry species to be a valid or correct construction of the vibrational mode. What that means is that only those

vibrational motions with the symmetry properties described in the character table are allowed.

And speaking of being allowed, it is important to note that not all vibrational modes of a molecule are spectroscopically active. The complete set of normal vibrational modes of a molecule will belong to one of the following three categories: Raman active, infrared active, or silent. Here is where the last two columns of the character table become particularly helpful to the spectroscopist. The next to last column indicates the axes along which a change in the dipole moment will occur with molecular vibration and thereby allow that vibration to be infrared (IR) active (that is, will absorb IR radiation at the frequency of the changing dipole moment). Only the  $A_1$ ,  $B_1$ , or  $B_2$  species of normal

vibrational modes of a molecule in this  $C_{2v}$  point group will be IR active. Likewise, all four symmetry species may be Raman active. The last column indicates the axes along which a change in polarizability will occur with molecular vibration and thereby allow that vibration to be Raman active (that is, will scatter radiation at the frequency of the vibrational modulation of the polarizability). One final point here is that any Raman bands belonging to the totally symmetric  $A_1$  (or  $A_g$ ) symmetry species will be polarized; that is, allowed and observed with the Raman analyzer in a configuration parallel to the incident polarization, but absent or weak when the analyzer is configured perpendicular to the incident polarization. We will have more to say on the practical application of the Raman polarization selection rules in the second installment of this two-part series.

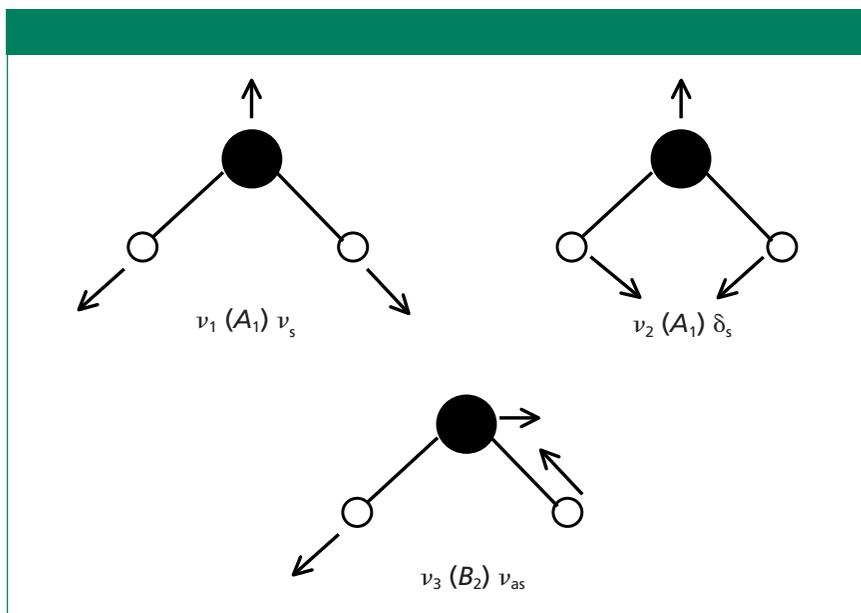
## Symbols in Group Theory and Spectroscopy

The literature of atomic and molecular spectroscopy is filled with symbols that can sometimes seem to be an unfathomable, cryptic code. In reality, the symbolism of spectroscopy is a logical and systematic shorthand way of communicating a great deal of information about the interaction of light with matter and the subsequent response by the material. In vibrational spectroscopy, each normal mode of vibration must derive from a basis (for example, atomic positions, bond stretches, and bond angles) that conforms to an irreducible representation in the character table of that point group with the same symmetry as that of the molecule. When an author provides an accepted or newly assigned Mulliken symbol to a spectroscopic band, they are communicating information to you about the particular vibrational mode from which the band has its origin and perhaps even the symmetry of the molecule.

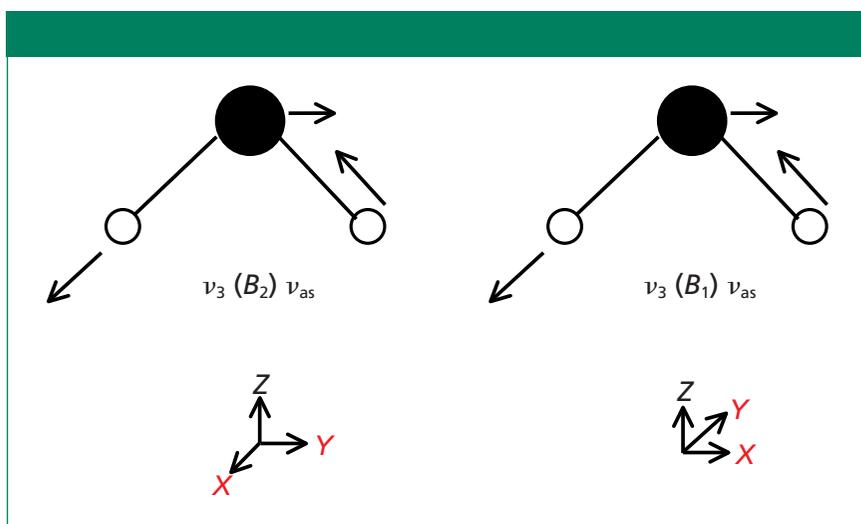
The first column of the character table lists the Mulliken symbols frequently used in the designation

**Table III: The vibrational mode symbols used to describe the motion and symmetry of a normal vibrational mode associated with a specific spectroscopic band**

Symbol	Description of Vibrational Mode
	Stretching
	Deformation (bending)
w	Wagging
r	Rocking
t	Twisting
$\varpi$	Out of plane
as	Antisymmetric
s	Symmetric
d	Degenerate



**Figure 1:** Normal vibrational modes of H<sub>2</sub>O.



**Figure 2:** Different coordinate systems for the molecule lead to different species assignments for the antisymmetric stretch of H<sub>2</sub>O. Both coordinate systems obey the right-hand rule.

of spectroscopic band symmetry species. The last two columns for the band's symmetry species pertain to IR and Raman activity of that species, respectively. A list of Mulliken symbols and the meaning of each is given in Table II. Here are a few examples that you may have encountered in the past. A Raman band designated as  $A_1$  can be either a totally symmetric stretch or bend with respect to the principal axis of symmetry in a molecule without a center of symmetry. A band designated  $A_g$  can also be either a totally symmetric stretch or bend, and here the subscript  $g$  informs us that the molecule is centrosymmetric. We will have more to say about centrosymmetric molecules and the rule of mutual exclusion later. A  $B_2$  designation indicates that the stretching or bending mode is antisymmetric with respect to the principal axis of symmetry and antisymmetric with respect to either a vertical reflection plane or a  $C_2$  axis perpendicular to the principal axis of symmetry.

In addition to the Mulliken symbols of character tables used to describe the symmetries of the vibrational modes, spectroscopists often use symbols to describe the type of motion (stretching, bending, twisting, and so on) associated with a particular band in the vibrational spectrum. A list of vibrational mode symbols and the description of each is given in Table III. These symbols supplement those of the character table symmetry species and the motions they describe are often useful in understanding changes to band position and width because of effects of the molecular environment such as solvation, H bonding, and molecular aggregation on the molecular vibrations.

### Normal Vibrational Modes of Water

Let's continue working with the  $C_{2v}$  point group and analyze the normal vibrational modes of the water molecule. It is not the purpose of this installment to take the reader step-by-step through the process

of determining all the normal vibrational modes of a molecule. Excellent guidance for that activity can be found in the books listed in the references. Rather, we want to highlight those aspects of molecular symmetry and group theory that will allow the reader to beneficially apply group theory and polarization selection rules in both data acquisition and interpretation of the spectra.

Choosing the  $x$ ,  $y$ , and  $z$  axes of each atom in the molecule as a basis, the reducible representation for the displacement of the water molecule is

$$3N = 3A_1 + A_2 + 2B_1 + 3B_2. \quad [1]$$

The translation and rotation species from the second-to-last column of the  $C_{2v}$  character table are

$$\begin{matrix} (T+R) \\ (A_1 + B_1 + B_2) + (A_2 + B_1 + B_2), \end{matrix} \quad [2]$$

with the species in the first and second parentheses corresponding to the translational and rotational degrees of freedom, respectively. Consequently, the complete set of vibrational modes is given by

$$vib = 3N - (T+R) = 2A_1 + B_2. \quad [3]$$

The three (two  $A_1$  and one  $B_2$ ) normal modes of vibration for water are shown in Figure 1. The  $\nu_1$  and  $\nu_2$  bands are of  $A_1$  symmetry, a symmetric stretch and symmetric bending mode, respectively. The  $\nu_3$  band is an antisymmetric stretch of species  $B_2$ .

Now let's confirm our normal vibrational mode symmetry assignments. The  $A_1$  species are totally symmetric. That means that if we apply any of the  $C_{2v}$  symmetry operations to a basis of the molecule, the basis will remain unchanged. Let's designate the directional arrows in Figure 1 as bases for the molecular point group. If we apply the  $E$ ,  $C_2$ ,  $\sigma_v(xz)$ , and  $\sigma_v(yz)$  symmetry operations to both vibrational modes the directional arrows re-

Table IV: Character table for the $C_{3v}$ point group.					
$C_{3v}$	$E$	$2C_3$	$3\sigma_v$	IR Activity	Raman Activity
$A_1$	1	1	1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	$xy$
$E$	2	-1	0	$(x,y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$

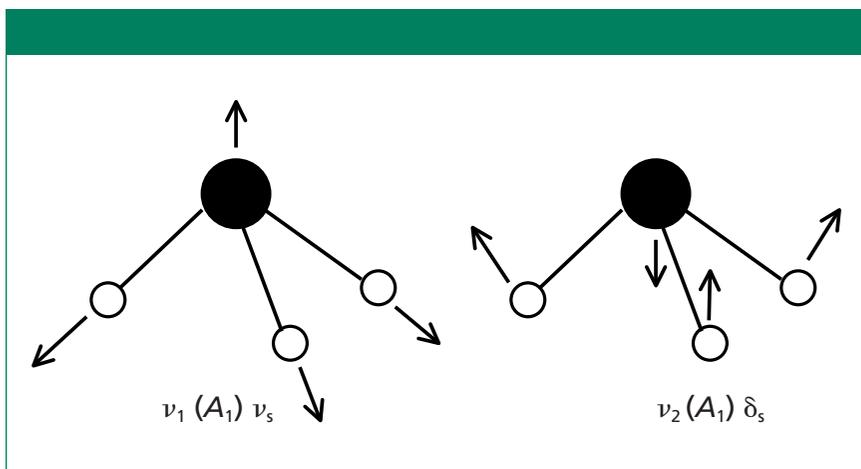


Figure 3:  $A_1$  symmetric stretching and bending modes of  $NH_3$ .

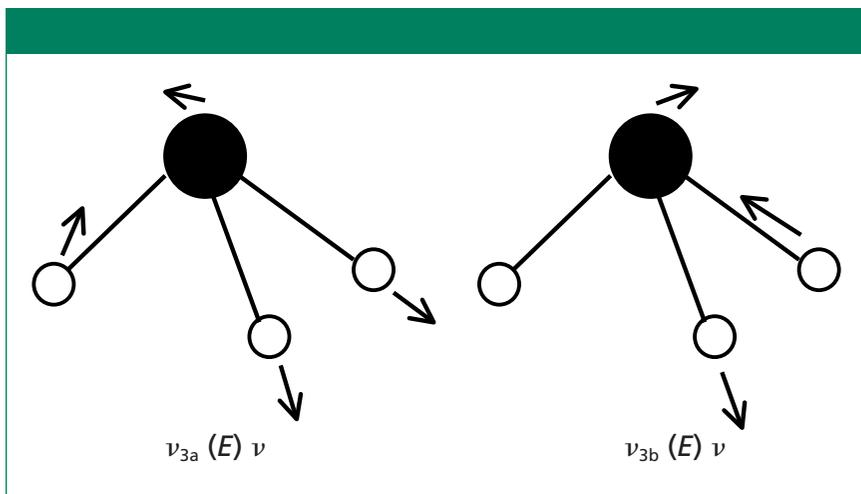


Figure 4: N-H doubly degenerate stretching modes of  $NH_3$ .

main unchanged, thereby confirming the modes as  $A_1$  species. If we apply those same symmetry operations to the  $\nu_3$  mode we see that the characters for  $C_2$  and  $\sigma_v(xz)$  are -1, and so the antisymmetric stretch is consistent with the  $B_2$  assignment because the characters of  $B_2$  under the symmetry operations  $C_2$  and  $\sigma_v(xz)$  are both -1. Inspection of the last two columns of the  $C_{2v}$  character table indicates that both  $A_1$  and  $B_2$  species, and therefore all three

vibrational modes of water are IR and Raman active.

Remember that group theory only predicts whether or not a vibrational mode will be Raman or IR active. It does not predict the strength of the corresponding bands in the spectra. The strength of an individual IR or Raman band depends on the corresponding vibrational transition dipole moment or Raman polarizability, respectively. Therefore, group theory can account for

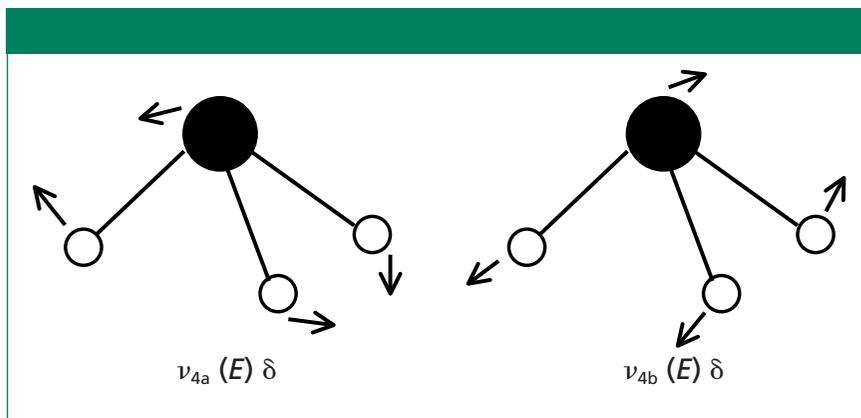


Figure 5: H-N-H doubly degenerate bending modes of  $\text{NH}_3$ .

$C_{2h}$	$E$	$C_2$	$i$	$h$	IR Activity	Raman Activity
$A_g$	1	1	1	1	$R_z$	$x^2, y^2, z^2, xy$
$B_g$	1	-1	1	-1	$R_x, R_y$	$xz, yz$
$A_u$	1	1	-1	-1	$z$	
$B_u$	1	-1	-1	1	$x, y$	

the number of bands in a vibrational spectrum, but not how strong they will be.

In writing this installment, I uncovered a somewhat confusing but interesting situation. Many of the group theory and vibrational spectroscopy books list the vibrational modes for water as  $2A_1 + B_2$  (2,5,6,7,10). However, using the exact same character table for  $C_{2v}$  other book authors list the modes as  $2A_1 + B_1$  (1,9,11). This really had me puzzled. I wondered how there could be such a difference among fine textbooks on group theory and vibrational spectroscopy, whether there was an error in one of the assignments, and whether anyone else had noticed this difference. I solved the puzzle by scrupulously working through the written descriptions by which the authors arrived at these different Mulliken symbols for the antisymmetric stretch of water.

The answer lies in the molecular coordinate systems chosen by the authors. The coordinate systems leading to the different species assignments are shown in Figure 2. Each system follows the right-hand

rule whereby the fingers originally aligned with the positive  $x$ -axis and then folded into the positive  $y$ -axis points with the thumb to the positive  $z$ -axis. The difference is that these coordinate systems are rotated  $90^\circ$  with respect to each other. Both species assignments are technically correct because in each case the  $C_2$  operation yields a character of -1 and the vertical reflection plane perpendicular to the plane of the molecule yields a character of -1.

Subsequently, I searched for a nonarbitrary basis for the assignment of molecular coordinates and found that J. Michael Hollas had encountered the same situation (16). He states, "For a planar  $C_{2v}$  molecule the convention is that the  $C_2$  axis is taken to be the  $z$  axis and the  $x$  axis is perpendicular to the plane. This is the convention used here for  $\text{H}_2\text{O}$ ." Following this convention would lead to the  $B_2$  assignment shown in Figure 2.

The take-home message of this cautionary tale is that great care and consistency need to be exercised in the designation of molecular coordinate systems and all of the symmetry elements (for example, rota-

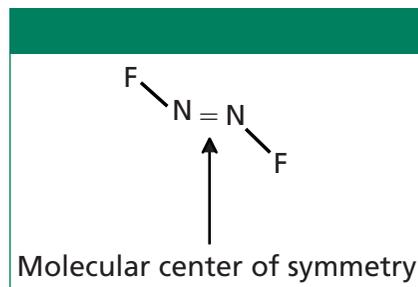


Figure 6: Molecular structure of  $\text{trans-N}_2\text{F}_2$ .

tional axes and reflection planes) in the application of group theory to molecular vibrations. Having stated that, please note that the species subscripts exceed 2 in some point groups, in which case the subscript numbering can be arbitrary.

### Degeneracy in Vibrational Modes

Degeneracy in vibrational spectroscopy pertains to multiple vibrational modes of a molecule all at the same energy state and same symmetry. Here we use the ammonia molecule  $\text{NH}_3$  of point group  $C_{3v}$  to understand the role of degeneracy in spectra. The character table for the  $C_{3v}$  point group is shown in Table IV.

Choosing the  $x$ ,  $y$ , and  $z$  axes of each atom in the molecule as a basis, the reducible representation for the displacement of the  $\text{NH}_3$  molecule is

$${}_{3N} = 3A_1 + A_2 + 4E. \quad [4]$$

The translation and rotation species from the second-to-last column of the  $C_{3v}$  character table are

$${}_{(T+R)} = (A_1 + E) + (A_2 + E), \quad [5]$$

with the species in the first and second parentheses corresponding to the translational and rotational degrees of freedom, respectively. Consequently, the complete set of vibrational modes is given by

${}_{vib} = {}_{3N} - {}_{(T+R)} = 2A_1 + 2E. \quad [6]$   
 The two  $A_1$  totally symmetric normal modes of vibration for  $\text{NH}_3$  are shown in Figure 3. The  $\nu_1$  and  $\nu_2$  bands are of  $A_1$  symmetry, a sym-

metric stretch and symmetric bending mode, respectively. Now let's confirm our normal vibrational mode symmetry assignments. The  $A_1$  species are totally symmetric. Therefore, if we apply any of the  $C_{3v}$  symmetry operations to a basis of the molecule that basis should remain unchanged. Let's designate the directional arrows in Figure 3 as bases for the molecular point group. If we apply the  $E$ ,  $C_3$ , and  $\sigma_v$  symmetry operations to both vibrational modes, the directional arrows remain unchanged, thereby confirming the modes as  $A_1$  species.

The two  $\nu_3$  doubly degenerate vibrational modes are N-H stretching modes of species  $E$  and are shown in Figure 4. The  $\nu_{3a}$  and  $\nu_{3b}$  stretching modes are doubly degenerate insofar as their excited states are of equal energy and their directional arrow bases conform to the character of the  $E$  species even though their motions are different. The interpretation of the bases and symmetries of degenerate vibrational modes is beyond the scope of this installment. To understand how to determine the character of a degenerate symmetry species, I would highly recommend the treatment of these same degenerate vibrational modes of  $NH_3$  described on pages 69–74 of the book by Hollas (3). Inspection of the last two columns of the  $C_{3v}$  character table indicates that the vibrational transition dipole moment and Raman polarizabilities occur in the  $xy$ -plane perpendicular to the principal molecular axis; therefore,  $\nu_{3a}$  and  $\nu_{3b}$  stretching modes are both IR and Raman active.

The H-N-H doubly degenerate bending modes of  $NH_3$  are shown in Figure 5. Unlike the  $\nu_{3a}$  and  $\nu_{3b}$  modes, which consist primarily of stretching motions, the  $\nu_{4a}$  and  $\nu_{4b}$  modes are primarily bending motions in which the bond angles vary. The  $\nu_{4a}$  and  $\nu_{4b}$  bending modes are doubly degenerate insofar as their excited states are of equal energy and their directional arrow bases

**Table VI: Spectral characteristics of the *trans* form of  $N_2F_2$  belonging to the  $C_{2h}$  point group**

Vibrational Mode	Symmetry Species	Band Position (cm <sup>-1</sup> )	Activity
$\nu_s$ (NF)	$A_g$	1010	Raman
(NN)	$A_g$	1636	Raman
$\nu_s$ (NNF)	$A_g$	592	Raman
$\tau$	$A_u$	360	IR
$\nu_{as}$ (NF)	$B_u$	989	IR
$\nu_{as}$ (NNF)	$B_u$	421	IR

conform to the character of the  $E$  species even though their motions are different. And, like the  $E$  stretching modes, these bending modes are both IR and Raman active in the  $xy$ -plane. In summary, both symmetry species and all six vibrational modes of  $NH_3$  are both IR and Raman active.

### Centrosymmetric Molecules and the Rule of Mutual Exclusion

Our last topic addresses the well-known rule of mutual exclusion. This rule states that for molecules with a center of symmetry all vibrational modes that are Raman active will be IR inactive and all IR-active modes will be Raman inactive. Centrosymmetric molecules possess the symmetry element  $i$  such that the process of inversion (the symmetry operation of  $i$ ) changes all molecular positions from  $(x,y,z)$  to  $(-x,-y,-z)$ . Point groups of molecules with a center of symmetry will contain the symmetry element  $i$  in the top row of the character table, and the symmetry species will have either a  $g$  or  $u$  subscript in the Mulliken symbols indicating symmetric or antisymmetric, respectively. The symbols  $g$  and  $u$  have their origin in the German words *gerade* and *ungerade*, which here mean even and odd, respectively. An example of a point group for a centrosymmetric molecule is  $C_{2h}$ , and its character table is shown in Table V.

We see that  $i$  is one of the symmetry operations and all of the symmetry species have a designation of either  $g$  or  $u$  in their Mulliken symbols. Note that consistent with the inversion operation, the character

of  $i$  is either 1 for the symmetric  $g$  species or -1 for the antisymmetric  $u$  species. Furthermore, you can see from the last two columns that no vibrational mode of a molecule belonging to the  $C_{2h}$  point group can be both IR and Raman active, thereby obeying the rule of mutual exclusion.

Let's continue working with the  $C_{2h}$  point group and analyze the normal vibrational modes of *trans*- $N_2F_2$ , the structure that is shown in Figure 6. Please note that the molecular center of symmetry need not be an atom in the molecule. As we see here, the inversion symmetry element  $i$  is the midpoint between the N=N double bond. It is worth noting that the *cis* form of  $N_2F_2$  belongs to the  $C_{2v}$  point group, and not only are the symmetry species different but so are the energies and number of spectroscopically active vibrational modes. The symmetry species, band positions, and spectroscopic activities for *trans*- $N_2F_2$  are shown in Table VI (17).

Note that both the symmetries and energies of the Raman- and IR-active vibrational modes are different. It can be helpful to think of the differences between the energies of these modes and their correlation to the entirely different symmetric and antisymmetric motions of the molecule. The vibrational modes here do not share IR and Raman activity, and so we would expect the IR and Raman spectra of *trans*- $N_2F_2$  to be different with respect to the appearance of bands at specific energies. And of course, because the only Raman bands allowed are of  $A_g$  symmetry, the entire Raman spectrum consists of polarized bands;

that is, they will be seen with the Raman analyzer oriented parallel to the incident laser polarization but will be absent or weak with the analyzer in a perpendicular configuration.

In summary, using Raman polarization selection rules in the acquisition of the Raman spectra along with the application of the rule of mutual exclusion can be a powerful and effective method of structure determination and characterization. Having said that, let me close with a word of caution: The rule of mutual exclusion does not always present or manifest itself in the most obvious ways for the easy determination of molecular structure. Weak bands or those only partially resolved from an adjacent, more intense band can easily be missed or overlooked. There is no substitute for attention to detail and careful analysis and interpretation by the spectroscopist.

## Conclusions

In part I of this two-part series we have discussed and highlighted those aspects of molecular symmetry and group theory that are of relevance to spectroscopists. An explanation of the nomenclature of group theory and vibrational spectroscopy has been provided to better equip readers with the scientific literature. Small-molecule examples have been presented on how to understand the correlation between depictions of normal vibrational modes and the

mathematical descriptions of group theory. In part II of this series, we will see how to beneficially apply the Raman polarization selection rules in the acquisition of the Raman spectra along with the application of group theory to the interpretation of the Raman spectra for structure determination and characterization.

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