# The Unshifted Atom-A Simpler Method of Deriving Vibrational Modes of Molecular Symmetries 

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#### Abstract

The infrared and Raman spectroscopy are widely utilized to study molecular structures. Of great interest is the great interest is the striking correlation between the molecular geometry and the infrared and Raman spectra of simple molecules and ions. This incredible correlation tends to be shadowed by deep theoretical and mathematical principles such that a good number of scholars are denied the joy of appreciating the correlation between molecular symmetry and infrared and Raman spectra. The 'unshifted atom' method presents a highly simplified approach based on basic knowledge of symmetry elements and the effect of symmetry operations on molecular geometries to determine the number of unshifted atoms (US) . Inserting the Cartesian coordinates $(\mathrm{X}, \mathrm{Y}, \mathrm{Z})$ on an unshifted atom and applying symmetry operations, the contributions to the character $\left(\mathrm{X}_{\mathrm{so}}\right)$ by the symmetry operations are obtained. A simple multiplication of the numbers of unshifted atoms ( $\mathrm{US}_{\mathrm{a}}$ ) in a point group with the corresponding numbers of $\left(\mathrm{X}_{\mathrm{so}}\right)$ generates a REDUCIBLE REPRESENTATION from which the VIBRATIONAL MODES of a molecule/ion are deduced. Examples of different molecular geometries have been presented to illustrate the simplicity, flexibility and viability of the method.


Key words: Vibrational modes, Molecular symmetries, Spectroscopy.

## INTRODUCTION

Infrared spectroscopy has been extensively used for both military and civilian purposes since its discovery by Herschel ${ }^{1}$ in 1800. In chemistry, it has been utilized for the characterization of molecular structures of simple and complex molecules ${ }^{2-6}$. From the study of infrared spectra of a vast range of molecules, scientists have been able to design a chart of characteristic absorption frequencies of molecular functional groups ${ }^{7}$. Such an infrared chart is extremely useful
in predicting the type of functional groups from the infrared spectrum of an unknown sample or the expected absorption ranges of a sample whose molecular formula is known.

Symmetry and group theory principles have been utilized to interpret the bonding and the infrared and Raman spectra mainly of simple molecules ${ }^{2,8-11}$. In the case of bonding, the molecular bonds are regarded as the basis set or vectors from which a Reducible Representation is generated ${ }^{12}$. This is then decomposed into appropriate

Irreducible Representations from bonding information is derived. But in the case of infrared or Raman Spectroscopy, three Cartesian coordinates ( $x, y, z$ ) are inserted on each atom of the molecule or ion under consideration ${ }^{8-9,11,13}$. The reason for this is that a molecule possesses Translational, Rotational and Vibrational energies. These are resolved into $x, y$ and $z$ vectors for each of the atom in the molecule. This set of $x, y$ and $z$ coordinates form the BASIS SET for generating irreducible representation

For instance, if $\mathrm{CH}_{4}$ is being considered for bonding, only 4 vectors are taken into account whereas if IR or Raman Spectroscopy is being considered, $3 \times 5=15$ ( $3 \times \mathrm{N}, \mathrm{N}=$ number of atoms in the molecule) Cartesian coordinates will be considered. The use of 3 N vectors is not only cumbersome but also the level of mathematical theory accompanying the explanation of IR and Raman spectroscopy ${ }^{8-13}$ tend to frighten or deny the joy of enjoying the correlation between molecular symmetry and the corresponding IR/Raman spectra of molecules/ions for chemists who may not have a good depth of physical chemistry. Although the concept of unshifted atom has briefly been used before ${ }^{14-15}$ no detailed account has been given. The aim of this article is to introduce in details a condensed simple unshifted atom method of deriving the expected number of IR/Raman peaks from the symmetry of simple molecule or ion. Hence, this paper hopes to popularize the unshifted atom method so as to put to rest the cumbersome

$$
\mathrm{E}\left[\begin{array}{l}
\mathrm{x} \\
\mathrm{y} \\
\mathrm{z}
\end{array}\right]=\left[\begin{array}{lll}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{array}\right]\left[\begin{array}{l}
\mathrm{x} \\
\mathrm{y} \\
\mathrm{z}
\end{array}\right]=\left[\begin{array}{l}
\mathrm{x} \\
\mathrm{y} \\
\mathrm{z}
\end{array}\right)
$$

$$
E\left[\begin{array}{lll}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{array}\right]
$$

$$
X_{E}=3
$$

It is not necessary to be using matrices to derive the character of a symmetry operation as this can be easily extracted by inspection of the signs of the Cartesian coordinates after the effect of the symmetry operation.

## POINT OF INVERSION (i)



Hence, the contribution to character is $[(-1)+(-1)+(-1)]=-3$.

PLANE OF SYMMETRY (s) OPERATION


Contribution to character will be [(+1) $+(+1)+(-1)]=+1$. In terms of the contribution to character, $\sigma_{x y}=\sigma_{x z}=\sigma_{y z}=+1$.

## $C_{n}$ OPERATION

Consider rotation of $\mathrm{c}_{\mathrm{n}}$ clockwise through an angle $\theta$

$\mathbf{Z}$ is perpandicular
$\downarrow_{\text {Rotation through } \theta}$, clockwise by $\mathrm{c}_{\mathrm{n}}$

$\mathbf{Z}$ is perpandicular

The vector components contributions to the original directions are $\mathrm{X} \cos \theta$ by X in the original $x$-axis and $Y \cos \theta$ by $Y$ vector in the $y$-axis.

Hence, the contributions to the character by X -vector is $\cos \theta$, and the contribution to the
character by Y vector is also $\cos \theta$. The rotation is done via the principal axis $\mathrm{C}_{\mathrm{n}}$ that coincides with zaxis. There is no change in $Z$ vector since it coincides with the principal axis $\mathrm{C}_{\mathrm{n}}$.
Hence,

$$
(X, Y, Z) \xrightarrow{C_{n} \text { OPERATION }}[(\cos \theta) X,(\cos \theta) Y, Z]
$$

Ther efore, $\mathrm{X}_{\mathrm{C}_{\mathrm{n}}}=2 \cos \theta+1$.
$\mathrm{S}_{\mathrm{n}}$ OPERATION
We also know that $S_{n}=C_{n} \times \sigma_{h}$. Therefore,
its operation can be broken into the following operations.


Hence, $X_{S_{n}}=2 \cos \theta-1$.

Table 1. Summary of symmetry operation contribution to character table.

| Contribution to character, $\left(\chi\right.$ so) by unshifted atom $\left(\right.$ US $\left._{a}\right)$ |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| E | Cn | Sn | i | $\boldsymbol{\sigma}$ |
| +3 | $1+2 \operatorname{cosq}$ | $-1+2 \operatorname{cosq}$ | -3 | +1 |


| $\mathrm{n}=$ | $\mathbf{2}$ | $\mathbf{3}$ | $\mathbf{4}$ | $\mathbf{6}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}_{\mathrm{n}}$ | $\mathrm{C}_{2}=-1$ | $\mathrm{C}_{3}=0$ | $\mathrm{C}_{4}=1$ | $\mathrm{C}_{6}=2$ |
| $\mathrm{~S}_{\mathrm{n}}$ |  | $\mathrm{S}_{3}=-2$ | $\mathrm{~S}_{4}=-1$ | $\mathrm{~S}_{6}=0$ |

Examples
Let us apply the above concepts to selected molecules/ions to illustrate the power of the method. Initially, we can apply the conventional
method of using all the Cartesian coordinates on a simple molecule such as water, $\mathrm{H}_{2} \mathrm{O}$. Later on we will apply the simpler method for comparison. Consider $\mathrm{H}_{2} \mathrm{O}$ as an illustration in Fig. 1.


Fig.1: The Cartesian coordinate system of $\mathrm{H}_{2} \mathrm{O}$

Point group is $\mathrm{C}_{2 v}$. The identity symmetry operation, E leaves all the 9 Cartesian coordinates unchanged. Hence we insert 9 under $E$ in the $C_{2 v}$ character table. The $\mathrm{C}_{2}$ symmetry operation completely shifts all the Cartesian coordinates on the two H atoms. These contribute zero to the $\mathrm{C}_{2 v}$ character table. However, $\mathrm{C}_{2}(\mathrm{X}, \mathrm{Y}, \mathrm{Z})$ on the O atom gives rise to , $(-X,-Y,+Z)$. The net contribution to the character of $\mathrm{C}_{2}$ operation becomes, $[(-1)+(-1)+(+1)]$
$=-1$. The symmetry operation $\sigma_{\mathrm{xZ}}(\mathrm{X}, \mathrm{Y}, \mathrm{Z})$ for the O atom, we get ( $\mathrm{X},-\mathrm{Y}, \mathrm{Z}$ ) giving a net contribution to the $\sigma_{x z}$ character of +1 . This is the same for each of the two H atoms. Hence, $\sigma_{x z}$ the overall contribution to the character is +3 . Similarly, $\sigma_{x z}$ will have a contribution to character of +1 . The entire set of numbers generated by symmetry operations are known as REDUCIBLE REPRESENTATIONS, $\Gamma_{3 \mathrm{~s}}$. This is shown in table 2.

Table 2: The Reducible Representation of $\mathrm{H}_{2} \mathrm{O}$ and the $\mathrm{C}_{2 \mathrm{v}}$ Character Table

| $\mathrm{C}_{2 v}$ | E | $\mathrm{C}_{2}$ | $\sigma_{\mathrm{xz}}$ | $\sigma_{\mathrm{yz}}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\Gamma_{\mathrm{XN}}$ | 9 | -1 | 3 | 1 |
|  |  |  |  |  |
| $\mathrm{~A}_{1}$ | 1 | 1 | 1 |  |
| $\mathrm{~A}_{2}$ | 1 | 1 | -1 | 1 |
| $\mathrm{~B}_{1}$ | 1 | -1 | 1 | -1 |
| $\mathrm{~B}_{2}$ | 1 | -1 | -1 | -1 |
|  |  |  |  |  |

The Reducible representation is then decomposed into Irreducible representations using the following reduction formula.
$N_{\mathrm{IR}}=1 / h \Sigma X_{\mathrm{R}} \mathrm{X}_{\mathrm{IR}}$
$N_{I R}=$ Number of irreducible representations,
$h=$ order of the group(the sum of symmetry operations),
$X_{R}=$ character of reducible representation,
$\mathrm{X}_{\mathrm{IR}}=$ character of irreducible representation.
Applying the above formula, we get:
$\mathrm{N}_{\mathrm{A} 1}=1 / 4[9.1+(-1) \cdot 1+3.1+1.1]=3$
$N_{A 2}=1 / 4[9 \cdot 1+(-1) \cdot 1+3 \cdot(-1)+1 \cdot(-1)]=1$
$N_{B 1}=1 / 4[9 \cdot 1+(-1) \cdot(-1)+3 \cdot 1+1 \cdot(-1)]=3$
$N_{B 2}=1 / 4[9 \cdot 1+(-1) \cdot(-1)+3 \cdot(-1)+1 \cdot(1)]=2$
$\Gamma_{3 \mathrm{~N}}=3 \mathrm{~A}_{1}+\mathrm{A}_{2}+3 \mathrm{~B}_{1}+2 \mathrm{~B}_{2}$

## Selection rules

$\Gamma_{\text {TRANS }}=$ Transform as X, Yand $Z$
$\Gamma_{\text {ROT }}=$ Transform as $\mathrm{R}_{\mathrm{x}}$, $\mathrm{R}_{\mathrm{y}}$, and $\mathrm{R}_{\mathrm{z}}$ Hence, $\Gamma_{\text {TRANS }}=A_{1}+B_{1}+B_{2}$ since they transform as $X, Y$ and $Z$ and $\Gamma_{\text {ROT }}=\quad A_{2}+B_{1}+B_{2}$ since they transform as $R_{x}, R_{y}$, and $R_{z}$.
Since, $\Gamma_{\text {3N }}=\Gamma_{\text {TRANS }}+\Gamma_{\text {ROT }}+\Gamma_{\text {VIB }}$, then $\Gamma_{\mathrm{VIB}}=\Gamma_{3 \mathrm{~N}}-\Gamma_{\text {TRANS }}-\Gamma_{\text {ROT. }}$ Thus,
$\Gamma_{\mathrm{VIB}}=\left(3 \mathrm{~A}_{1}+\mathrm{A}_{2}+3 \mathrm{~B}_{1}+2 \mathrm{~B}_{2}\right)-\left(\mathrm{A}_{1}+\mathrm{B}_{1}+\mathrm{B}_{2}\right)-\left(\mathrm{A}_{2}+\mathrm{B}_{1}\right.$ $+B_{2}$ ) giving us,
$\Gamma_{\mathrm{VIB}}=\quad 2 \mathrm{~A}_{1}+\mathrm{B}_{1}$

## Selection rules

$\mathrm{IR}_{\text {ACtive }}$ transform as $\mathrm{x}, \mathrm{y}$, and z $\mathrm{RM}_{\text {ACTIVE }}$ transform as Products of $\mathrm{x}, \mathrm{y}$, and z . $\mathrm{IR}_{\mathrm{A}}=$ Infrared active and $\mathrm{RM}_{\mathrm{A}}=$ Raman active.
Since $A_{1}+B_{1}$ symmetries are IR and Raman active, we expect to see 3 PEAKS in both IR and Raman spectra. These are (cm ${ }^{-1}$ ) 3657, 1595 and 3756.

Applying the simpler method on $\mathrm{H}_{2} \mathrm{O}$.
$A B_{2}$ system
Table 3: Derivation of Reducible Representation of $\mathrm{H}_{2} \mathrm{O}$ using shorter and simpler method.

| $C_{2 v}$ | E | $\mathrm{C}_{2}$ | $\sigma_{\mathrm{Xz}}$ | $\sigma_{\mathrm{yz}}$ |
| :--- | :---: | :---: | :---: | :---: |
| USa | 3 | 1 | 3 | 1 |
| $\mathrm{X}_{\mathrm{SO}}$ | 3 | -1 | 1 | 1 |
| $\Gamma_{3 N}$ | 9 | -1 | 3 | 1 |

This means that determining the number of unshifted atoms ( US ${ }_{a}$ ) by each of the symmetry operations and the contribution to the character $\left(\chi_{\text {so }}\right)$ by each symmetry operation and multiplying them easily produces $\left(\Gamma_{3 N}\right)$. Thus, $\Gamma_{3 N}=\left(U S_{a}\right) X\left(\chi_{\text {sO }}\right)$. Then, $\Gamma_{3 N}$ can be decomposed into Irreducible representations in the usual way as described above.

Let us take a few more examples to illustrate the power of the method.

## $\mathrm{AB}_{3}$ SYSTEM

Consider $\mathrm{BF}_{3}$ as shown in Fig.2. This has $a D_{3 n}$ point group.


Fig. 2: The coordinate system of $\mathrm{BF}_{3}$

The starting point is to generate the number of unshifted atoms ( $\mathrm{US}_{\mathrm{a}}$ ) by each symmetry operation of the $\mathrm{D}_{3 \mathrm{~h}}$ point group. Under E operation, all atoms of $\mathrm{BF}_{3}$ are not shifted. Hence, we enter 4 under E operation. The number of unshifted atoms for $\mathrm{C}_{3}, \mathrm{C}_{2}, \sigma_{\mathrm{h}}, \mathrm{S}_{3}$, and $\sigma_{\mathrm{h}}$ are $1,2,4,1$ and 2
respectively. The corresponding contribution to character $\left(\chi_{\text {so }}\right)$ by each symmetry operation obtained from Table 1 are also recorded. The product of US ${ }_{a}$, $\chi_{\mathrm{so}}$ and the corresponding number of symmery operations, produces the row of Reducible Representation $\Gamma_{3 \mathrm{~N}}$. These are given in Table 4.

Table 4: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{BF}_{3}$

| $\mathbf{D}_{3 \mathrm{~h}}$ | $\mathbf{E}$ | $\mathbf{2 C}$ | $\mathbf{3 C}$ | $\boldsymbol{\sigma}_{\mathbf{h}}$ | $\mathbf{2 S}_{\mathbf{3}}$ | $\mathbf{3} \boldsymbol{\sigma}_{\mathrm{v}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| US $_{\mathrm{a}}$ | 4 | 1 | 2 | 4 | 1 | 2 |
| $\chi_{\text {so }}$ | 3 | 0 | -1 | 1 | -2 | 1 |
| $\Gamma_{3 \mathrm{~N}}$ | 12 | 0 | -6 | 4 | -4 | 6 |

Using the reduction formula, $\Gamma_{3 N}$ is the decomposed into Irreducible Representation symmetries which comprise of $\Gamma_{\text {TRANS }}, \Gamma_{\text {ROT, }}$ and $\Gamma_{\text {VIB }}$. The symmetries of $\Gamma_{\text {TRAN }}$ and $\Gamma_{\text {ROT }}$ are extracted from $D_{3 h}$ character table. They are then subtracted from $\Gamma_{3 N}$ leaving $\Gamma_{\text {VIB }}$ symmetries. Applying the selection rules to $\Gamma_{\mathrm{VIB}}$ symmetries, we can deduce how many are IR active or Raman active. In the case of $\mathrm{BF}_{3}$, we expect to observe 3 peaks in IR spectrum and 3 peaks in Raman spectrum with 2 peaks in common. This is what is observed* and is given in Table 5.
$\begin{array}{ll}\Gamma_{3 N} & =\mathrm{A}^{\prime}+\mathrm{A} 2^{\prime}+3 \mathrm{E}^{\prime}+2 \mathrm{~A} 2^{\prime \prime}+\mathrm{E}^{\prime \prime} \\ \Gamma_{\text {TRANS }} & = \\ \mathrm{E}^{\prime}+\mathrm{A} 2^{\prime \prime} \\ \Gamma_{\text {ROT }} & = \\ \mathrm{A}_{2}{ }^{\prime} \quad+\quad \mathrm{E}^{\prime \prime} \\ \Gamma_{\mathrm{VBB}} & =\mathrm{A}_{1}{ }^{\prime}+2 \mathrm{E}^{\prime}+\mathrm{A}^{\prime \prime} \\ \mathrm{IR}_{\mathrm{A}} & = \\ \mathrm{RM}_{\mathrm{A}} & V \sqrt{ } \quad \sqrt{ } \rightarrow 3 \text { peaks } \\ & \end{array}$

Table 5: IR and Raman Spectral data ${ }^{2}$ of $\mathrm{BF}_{3}$

| $\mathbf{B F}_{3}(\mathbf{g})$ | $\mathbf{A 1}$ | $\mathbf{A} \mathbf{n}^{\prime \prime}$ | $\mathrm{E}^{\prime}$ | $\mathbf{E}^{\prime}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{cm}^{\prime}$ | 888 | 718 | 1505 | 482 |
|  |  | $\mathrm{IR}_{\mathrm{A}}$ | $\mathrm{IR}_{\mathrm{A}}$ | $\mathrm{IR}_{\mathrm{A}}$ |
|  | $\mathrm{RM}_{\mathrm{A}}$ | $\mathrm{RM}_{\mathrm{A}}$ | $\mathrm{RM}_{\mathrm{A}}$ |  |


| $\Gamma_{3 N}$ | $=A_{1}+E+T_{1}+3 T_{2}$ |  |
| :---: | :---: | :---: |
| $\Gamma_{\text {TRANS }}$ | = |  |
| $\Gamma_{\text {ROT }}$ | T |  |
| $\Gamma_{\text {VIB }}$ | $=A_{1}+E+2 T_{2}$ |  |
| $1 \mathrm{R}_{\text {A }}$ | $=\sqrt{ }$ | $\rightarrow 2$ peaks |
| $\mathrm{RM}_{\text {A }}$ | $\checkmark \quad \checkmark \quad \checkmark$ | $\rightarrow 4$ peaks |

2 in common

As can be seen from tables 6 and 7, the theoretical model is consistent with the experimental data.

## $\mathrm{AB}_{4}$ SYSTEM

TETRAHEDRAL ( $\mathrm{T}_{\mathrm{d}}$ )
Example
The reason why this method is so easy is that it eliminates the burden of visualizing the set of all coordinates on the atoms within the molecule/ ion. It only focuses on the unshifted atom(s) by a symmetry operation $\left(\mathrm{US}_{\mathrm{a}}\right)$ and the corresponding contribution to the character $\left(\chi_{\mathrm{so}}\right)$ by the symmetry operation. When this approach is applied to $\mathrm{CH}_{4}$ shown in Fig.3. the results obtained are given in Table 6.


Fig. 3: Tetrahedral geometry of $\mathrm{CH}_{4}$

Table 6. Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{CH}_{4}$

| $\mathbf{T}_{\mathrm{d}}$ | $\mathbf{E}$ | $\mathbf{8 C}$ | $\mathbf{3 C}$ | $\mathbf{6 S}_{\mathbf{4}}$ | $\mathbf{6} \boldsymbol{\sigma}_{\mathrm{d}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{US}_{\mathrm{a}}$ | 5 | 2 | 1 | 1 | 3 |
| $X_{\mathrm{so}}$ | 3 | 0 | -1 | -1 | 1 |
| $\Gamma_{3 \mathrm{~N}}$ | 15 | 0 | -3 | -6 | 18 |

Table 7: IR and Raman Spectral data ${ }^{2}$ of $\mathbf{C H}_{4}$

| $\mathbf{C H}_{4}$ | $\mathbf{A}_{1}$ | $\mathbf{E}$ | $\mathbf{T}_{2}$ | $\mathbf{T}_{2}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{~cm}^{-1}$ | 2917 | 1534 | 3019 | 1306 |
| $\mathrm{IR}_{\mathrm{A}}$ |  |  | $\sqrt{ }$ | $\sqrt{ }$ |
| $\mathrm{RM}_{\mathrm{A}}$ | $\sqrt{ }$ | $\sqrt{ }$ | $\sqrt{ }$ | $\sqrt{ }$ |

## $\mathrm{AB}_{5}$ SYSTEM

The application of the method to $\mathrm{PF}_{5}$ shown in Fig. 4 gives us the results shown in tables 8 and 9 .


Fig. 4: The trigonal bipyramid of $\mathrm{PF}_{5}$
Table 8: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{PF}_{5}$

| $\mathrm{D}_{3 \mathrm{~h}}$ | E | $2 \mathrm{C}_{3}$ | $3 C_{2}$ | $\sigma_{\text {h }}$ | $2 S_{3}$ | $3 \sigma_{v}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| US ${ }_{\text {a }}$ | 6 | 3 | 2 | 4 | 1 | 4 |
| $\mathrm{X}_{\text {so }}$ | 3 | 0 | -1 | 1 | -2 | 1 |
| $\Gamma_{3 N}$ | 18 | 0 | -6 | 4 | -4 | 12 |
| $\Gamma_{3 N}$ | $2 \mathrm{~A}_{1}{ }^{\prime}$ | $\mathrm{A}_{2}{ }^{\prime}$ | $4 \mathrm{E}^{\prime}$ |  | $2 E^{\prime \prime}$ |  |
| $\Gamma_{\text {TRANS }}$ |  |  | E' | $\mathrm{A}_{2}{ }^{2}{ }^{2}$ |  |  |
| $\Gamma_{\text {ROt }}$ |  | $\mathrm{A}_{2}{ }^{\text {D }}$ |  |  | E" |  |
| $\Gamma_{\text {vIB }}$ | $2 A_{1}{ }^{\prime}$ |  | $3 \mathrm{E}^{\prime}$ | $2 A_{2}{ }^{\prime \prime}$ | E" |  |
| $1 \mathrm{R}_{\text {A }}$ |  |  | $\checkmark$ | $\sqrt{ }$ |  | 5 peaks |
| $\mathrm{RM}_{\text {A }}$ | $\checkmark$ |  | $\sqrt{ }$ |  | $\checkmark$ | 6 peaks |
|  |  |  | 3 COMMON |  |  |  |

Table 9: IR and Raman Spectral data² of $\mathrm{PF}_{5}$

| $\mathrm{PF}_{5}(\mathrm{~g})$ | $\mathrm{A}_{1}{ }^{\text {' }}$ | $A_{1}{ }^{\prime}$ | $\mathrm{A}_{2}{ }^{\prime \prime}$ | $\mathrm{A}_{2}{ }^{\prime \prime}$ | $E^{\prime}$ | $E^{\prime}$ | $E^{\prime}$ | E" |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 817 | 640 | 944 | 575 | 1026 | 532 | 300 | 514 |
| $1 \mathrm{R}_{\text {A }}$ |  |  | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |
| $\mathrm{RM}_{\text {A }}$ | $\checkmark$ | $\sqrt{ }$ |  |  | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |

$A B_{6}$ molecules including one lone pair


The unshifted atom method indicates that $\mathrm{BrF}_{5}$ molecule is expected to show 6 and 9 peaks in IR and Raman respectively with 6 peaks in common. This is shown in Table 10 and is consistent with the experimental data in Table11.

Fig. 5: The square pyramidal geometry of BrF5.

Table 9: IR and Raman Spectral data ${ }^{2}$ of $\mathrm{BrF}_{5}$

| $\mathrm{BrF}_{5}$ | $\mathrm{A}_{1}$ | $\mathrm{A}_{1}$ | $\mathrm{A}_{1}$ | $\mathrm{B}_{1}$ | $B_{1}$ | $\mathrm{B}_{2}$ | E | E | E |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{cm}^{-1}$ | 682 | 570 | 365 | 535 | 281 | 312 | 644 | 414 | 237 |
| $1 \mathrm{R}_{\text {A }}$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |  | $\checkmark$ | $\checkmark$ | $\checkmark$ |  |  |
| $\mathrm{RM}_{\text {A }}$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |

Table 10: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{BrF}_{5}$

| $\mathrm{C}_{4 \mathrm{v}}$ | E | $2 \mathrm{C}_{4}$ | $\mathrm{C}_{2}$ | $2 \sigma_{v}$ | $2 \sigma_{\text {d }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| US ${ }_{\text {a }}$ | 6 | 2 | 2 | 4 | 2 |  |
| $\mathrm{X}_{\text {so }}$ | 3 | 1 | -1 | 1 | 1 |  |
| $\Gamma_{3 N}$ | 18 | 4 | -2 | 8 | 4 |  |
| $\Gamma_{3 N}$ | $4 \mathrm{~A}_{1}$ | $\mathrm{A}_{2}$ | $2 \mathrm{~B}_{1}$ | $\mathrm{B}_{2}$ | 5E | $3 N=18$ |
| $\Gamma_{\text {TRANS }}$ | A |  |  |  | E |  |
| $\Gamma_{\text {ROt }}$ |  | $\mathrm{A}_{2}$ |  |  | E |  |
| $\Gamma_{\text {VIB }}$ | $3 \mathrm{~A}_{1}$ |  | $2 \mathrm{~B}_{1}$ | $\mathrm{B}_{2}$ | 3E | 3N-6=12 |
| $1 \mathrm{R}_{\text {A }}$ | $\checkmark$ |  |  |  | $\checkmark$ | 6 peaks |
| $\mathrm{RM}_{\text {A }}$ | $\checkmark$ |  | $\checkmark$ | $\checkmark$ | $\checkmark$ | 9 peaks |

ISOMERS OF $\mathrm{N}_{2} \mathrm{~F}_{2}$
TRANS ISOMER apply it to a few more molecular geometries.

The theoretical and experimental data are given in tables 10 and 11.


Fig. 6: The geometry of trans $-\mathrm{N}_{2} \mathrm{~F}_{2}$

Table 10: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{PF}_{5}$

| $\mathrm{C}_{2 \mathrm{~h}}$ | E | $\mathrm{C}_{2}$ | i | $\sigma_{\text {h }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| US ${ }_{\text {a }}$ | 4 | 0 | 0 | 4 |  |
| $\mathrm{X}_{\text {so }}{ }^{\text {a }}$ | 3 | -1 | -3 | 1 |  |
| $\Gamma_{3 N}^{\text {so }}$ | 12 | 0 | 0 | 4 |  |
| $\Gamma_{\text {3N }}{ }_{\text {J }}$ | $4 \mathrm{~A}_{\mathrm{g}}$ | $2 \mathrm{~B}_{\mathrm{g}}$ | $2 A_{u}$ | $\begin{aligned} & 4 B_{u} \\ & 2 B \end{aligned}$ | $3 \mathrm{~N}=12$ |
| ITRANS $\Gamma_{\text {ROT }}$ $\Gamma_{\text {VIB }}$ $\mathrm{IR}_{\mathrm{A}}$ | $A_{9}$ $3 A_{g}$ | $2 B_{g}$ | $\mathrm{A}_{\mathrm{u}}$ | $2 B_{u}$ | 3N-6=6 <br> 3peaks |
| $\mathrm{RM}_{\mathrm{A}}$ | no peaks in common |  |  |  | 3 peaks |

Table 11: IR and Raman Spectral data ${ }^{2}$ of Trans $\mathrm{N}_{2} \mathrm{~F}_{2}$

| Trans- $\mathrm{N}_{2} \mathrm{~F}_{2}(\mathrm{I})$ | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{A}_{\mathrm{g}}$ | $B_{u}$ | $B_{u}$ | $\mathrm{A}_{u}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{cm}^{-1}$ | 1010 | 1522 | 600 | 990 | 423 | 364 |
| $\begin{aligned} & \mathrm{IR}_{\mathrm{A}} \\ & \mathrm{RM}_{\mathrm{A}} \end{aligned}$ | $\checkmark$ | $\checkmark$ | $\checkmark$ |  |  |  |
|  |  |  |  | $\checkmark$ | $\checkmark$ | $\checkmark$ |
|  | no peaks in common, total 6 peaks |  |  |  |  |  |

The data clearly shows that a molecule with a centre of symmetry, the IR spectrum and Raman spectrum have no peaks in common.

## CIS ISOMER

The theoretical and experimental data for the cis- $\mathrm{N}_{2} \mathrm{~F}_{2}$ are given in Tables 12 and 13.


Fig. 7: The geometry of cis- $\mathrm{N}_{2} \mathrm{~F}_{2}$

Table 12: Derivation of Reducible Representation for generating vibrational symmetries for Cis- $\mathrm{N}_{2} \mathrm{~F}_{2}$

| $\mathrm{C}_{2 \mathrm{v}}$ | E | $\mathrm{C}_{2}$ | $\sigma_{x z}$ | $\sigma_{\mathrm{Yz}}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| US ${ }_{\text {a }}$ | 4 | 0 | 0 | 4 |  |
| $\mathrm{X}_{\text {so }}$ | 3 | -1 | 1 | 1 |  |
| $\Gamma_{3 N}$ | 12 | 0 | 0 | 4 |  |
| $\Gamma_{3 N}$ | 4A | $2 \mathrm{~A}_{2}$ | $2 \mathrm{~B}_{1}$ | $4 \mathrm{~B}_{2}$ |  |
| $\Gamma_{\text {trans }}$ | $\mathrm{A}_{1}$ |  | $\mathrm{B}_{1}$ | $\mathrm{B}_{2}$ |  |
| $\Gamma_{\text {ROT }}$ |  | $\mathrm{A}_{2}$ | $B_{1}$ | $\mathrm{B}_{2}$ |  |
| $\Gamma_{\text {VIB }}$ | $3 \mathrm{~A}_{1}$ | $\mathrm{A}_{2}$ |  | $2 \mathrm{~B}_{2}$ |  |
| $\mathrm{IR}_{\text {A }}$ | $\checkmark$ |  |  | $\checkmark$ | 5 peaks |
| $\mathrm{RM}_{\text {A }}$ |  |  |  | $\checkmark$ | 6 peaks |
| 5 peaks in common |  |  |  |  |  |

Table 13: IR and Raman Spectral data ${ }^{2}$ of $\mathrm{Cis}-\mathrm{N}_{2} \mathrm{~F}_{2}$


It is also interesting to note that the less symmetrical a molecule is, the more peaks are observed.

## The A-X stretchng frequencies

The vibrational stretching frequencies are extremely useful in characterizing molecular structures. The stretching modes refer to the stretch between two atoms (A-X). A-X can refer to two atoms such as $\mathrm{C}-\mathrm{H}, \mathrm{C}=\mathrm{O}, \mathrm{C}-\mathrm{Cl}, \mathrm{N}-\mathrm{H}$ and $\mathrm{C}-\mathrm{S}$.

Let us take $\mathrm{H}_{2} \mathrm{CO}$ molecule as an illustration. It has a $\mathrm{C}_{2 \mathrm{v}}$ geometry as shown below.

Using the 'unshifted atom method', it is predicted that 6 peaks to be observed. Furthermore, two C-H stretching frequencies and one CO stretching frequency are expected. This is in agreement with the experimental data. This is summed up in Table 14.


Fig. 8: The geometry of $\mathrm{H}_{2} \mathrm{CO}$

Table 14: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{H}_{2} \mathrm{CO}$ as well the spectral data of $\mathrm{H}_{2} \mathrm{CO}$

| $\mathrm{C}_{2 v}$ | E | $\mathrm{C}_{2}$ | $\Gamma_{\mathrm{xz}}$ | $\Gamma_{\mathrm{YZ}}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| US ${ }_{\text {a }}$ | 4 | 2 | 4 | 2 |  |  |
| $\mathrm{X}_{\text {so }}$ | 3 | -1 | 1 | 1 |  |  |
| $\Gamma_{3 N}$ | 12 | -2 | 4 | 2 |  |  |
| $\Gamma_{3 N}$ | $4 \mathrm{~A}_{1}$ | $\mathrm{A}_{2}$ | $4 \mathrm{~B}_{1}$ | $3 \mathrm{~B}_{2}$ |  |  |
| $\Gamma_{\text {trans }}$ | $\mathrm{A}_{1}$ |  | $\mathrm{B}_{1}$ | $\mathrm{B}_{2}$ |  |  |
| $\Gamma_{\text {ROT }}$ |  | $\mathrm{A}_{2}$ | B | $\mathrm{B}_{2}$ |  |  |
| $\Gamma_{\text {VIB }}$ | $3 A_{1}$ |  | $2 \mathrm{~B}_{1}$ | $\mathrm{B}_{2}$ |  |  |
| $\mathrm{IR}_{\text {A }}$ | $\checkmark$ |  | $\checkmark$ | $\checkmark$ | 6 peaks |  |
| $\mathrm{RM}_{\text {A }}$ | $\checkmark$ |  | $\checkmark$ | $\checkmark$ | 6 peaks |  |
| C-H | 2 | 0 | 2 | 0 |  |  |
| $\Gamma_{\text {CH }}$ | $\mathrm{A}_{1}$ |  | $\mathrm{B}_{1}$ |  | 2 peaks |  |
| $\mathrm{C}=0$ | 1 | 1 | 1 | 1 |  |  |
| $\Gamma_{\text {co }}$ | $\mathrm{A}_{1}$ |  |  |  | 1 peak |  |
| $\mathrm{H}_{2} \mathrm{CO}^{3}$ | 2783 | 1746 | 1500 | 2843 | 1249 | 1167 |
| $\mathrm{C}-\mathrm{H}$ | $\mathrm{A}_{1}$ | $\mathrm{A}_{1}$ | $\mathrm{A}_{1}$ | $\mathrm{B}_{1}$ | $\mathrm{B}_{1}$ | $\mathrm{B}_{2}$ |
| $\mathrm{C}=\mathrm{O}$ |  | $\checkmark$ |  |  |  |  |

## Metal carbonyls

Consider the $\mathrm{C} \equiv \mathrm{O}$ stretching frequencies. Hence use $\mathrm{C} \equiv \mathrm{O}$ bonds as the as the BASIS SET.

The $\mathrm{C} \equiv \mathrm{O}$ stretching frequency can be used for structural analysis of carbonyls. This is illustrated by the examples of $\mathrm{Ni}(\mathrm{CO})_{4}$, and the distinction of the isomers of $\mathrm{MX}_{2}(\mathrm{CO})_{4}$. The results are given in Tables 15-17.


Fig. 9: The geometry of $\mathrm{Ni}(\mathrm{CO})_{4}$

Table 15: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{C} \equiv \mathrm{O}$ stretching frequencies of $\mathrm{Ni}(\mathrm{CO})_{4}$

| $\mathbf{T}_{\mathrm{d}}$ | $\mathbf{E}$ | $\mathbf{8 C}$ | $\mathbf{3 C}$ | $\mathbf{C S}_{\mathbf{2}}$ | $\mathbf{6} \boldsymbol{\sigma}_{\mathrm{d}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| CO | 4 | 1 | 0 | 0 | 2 |
| $\Gamma_{\mathrm{CO}}$ | 4 | 8 | 0 | 0 | 12 |
| $\Gamma_{\mathrm{CO}}$ | $\mathrm{A}_{1}$ | $\mathrm{~T}_{2}$ |  |  |  |
| $\mathrm{IR}_{\mathrm{A}}$ | $\sqrt{ }$ | $\sqrt{2}$ |  |  | 1 peak |
| $\mathrm{RM}_{\mathrm{A}}$ | $\sqrt{2}$ | $\sqrt{2}$ |  |  | 2 peaks |



Fig. 10: The geometry of trans- $\mathrm{MX}_{2}(\mathrm{CO})_{4}$
Table 16: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{C} \equiv \mathrm{O}$ stretching symmetries of Trans-MX ${ }_{2}(\mathrm{CO})_{4}$

| $\mathrm{D}_{4}$ | E | $2 \mathrm{C}_{4}$ | $\mathrm{C}_{2}$ | $2 \mathrm{C}_{2}{ }^{\text {D }}$ | $2 \mathrm{C}_{2}{ }^{\text {D D }}$ | i | $2 S_{4}$ | $\sigma_{\text {h }}$ | $2 \sigma_{v}$ | $2 \sigma_{d}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CO | 4 | 0 | 0 | 2 | 0 | 0 | 0 | 4 | 2 | 0 |
| $\Gamma_{\text {co }}$ | 4 | 0 | 0 | 4 | 0 | 0 | 0 | 4 | 4 | 0 |
| $\begin{aligned} & \Gamma_{\mathrm{co}} \\ & \mathrm{IR}_{\mathrm{A}} \end{aligned}$ | $\mathrm{A}_{19}$ | $\mathrm{B}_{19}$ | $\begin{aligned} & \mathrm{E}_{\mathrm{u}} \end{aligned}$ |  |  |  |  |  |  | 1 peak |
| $R M_{A}$ |  | s in |  |  |  |  |  |  |  | 2 peaks |



## $C_{2 v}$

## $\mathrm{Cis}-\mathrm{MX}_{2}(\mathrm{CO})_{4}$



Fig. 11: The geometry of cis- $\mathrm{MX}_{2}(\mathrm{CO})_{4}$

Table 17: Derivation of Reducible Representation for generating vibrational symmetries for $\mathrm{C} \equiv \mathrm{O}$ stretching symmetries of $\mathrm{Cis}-\mathrm{MX}_{2}(\mathrm{CO})_{4}$

| $\mathrm{C}_{2 \mathrm{v}}$ | E | $\mathrm{C}_{2}$ | $\boldsymbol{\sigma}_{\mathrm{xz}}$ | $\boldsymbol{\sigma}_{\mathrm{yz}}$ |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| CO | 4 | 0 | 2 | 2 |  |
| $\tilde{\mathrm{~A}}_{\mathrm{CO}}$ | $2 \mathrm{~A}_{1}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ |  |  |
| $\mathrm{IR}_{\mathrm{A}}$ | $\sqrt{ }$ | $\sqrt{2}$ | $\sqrt{2}$ |  | 4 peaks |
| $\mathrm{RM}_{\mathrm{A}}$ | $\sqrt{ }$ | $\sqrt{2}$ | $\sqrt{2}$ |  | 4peaks |
|  | all in common |  |  |  |  |

It should be noted that when considering stretching frequencies, the filtration of $\Gamma_{\text {TRANS }}$ and $\Gamma_{\mathrm{ROT}}$ is not involved. on

## CONCLUSION

This paper aims to appeal to many readers of science so as to greatly appreciate the correlation
between the symmetry and point group of a molecule/ion on one hand and its infrared/Raman spectrum on the other. The molecule could be as simple as $\mathrm{C}_{2} \mathrm{H}_{4}$ or $\mathrm{P}_{4}$ to more complex ones such as $\mathrm{C}_{6} \mathrm{H}_{6}$ or $\mathrm{C}_{60}$. It is hoped that from various backgrounds such biology, biochemistry, chemistry, physics, mathematics and geology among others will enjoy reading this article.

## ACKNOWLEDGEMENTS

I would like to extend my sincere thanks to Professor Friedrick Grein of the University of New Brunswick, Canada who first introduced me to the concepts of symmetry and point groups of molecules.

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