MEMBER OF THE NYNOMIC GROUP

APPLICATION NOTE

# RAMAN VS INFRARED SPECTROSCOPY MEASUREMENT OF OCTASULFUR

## INTRO

# BACKGROUND OF APPLICATION

4Infrared and Raman are both categorized as vibrational spectroscopies, which broadly speaking, measure the same basic material properties. Namely, they provide a molecular fingerprint by determining the vibrational energy levels of a given material. The term fingerprint, in this case, is used to highlight the fact that for two materials to have the same vibrational spectra, they must have identical reduced mass, bond configuration, and steric effects. To put it more succinctly, the only way two samples can have the same vibrational spectra is that they must be the same material. Therefore, Raman and infrared are among the most used analytical techniques for unknown material identification and reaction monitoring.

Despite the surface-level similarities of the two techniques, in practice, there are many subtle (and not so subtle) differences, which have led many in the community to get the false impression that one technique is superior to the other. This fracturing is rather unfortunate since the two techniques are highly complementary, and most laboratories can benefit from owning both Raman and infrared setups. To illustrate this, we have decided to focus this application note on determining which vibrational modes are better suited for Raman analysis and which ones are better suited for infrared.

A detailed analysis of the selection rules governing infrared and Raman spectroscopy can be somewhat overwhelming to those unfamiliar with quantum mechanics and physical chemistry. But most spectroscopists are familiar with the primary takeaways – infrared absorbance is a linear process dependent on dipole moment, and Raman scattering is a nonlinear process dependent on polarizability. Armed with this basic understanding, we can utilize molecular symmetries to simplify the process. While this requires group theory, fortunately, only 32 different point (symmetry) groups are needed to characterize any possible molecular configuration, each having a well-defined character table, which includes all possible translational, rotational, and vibrational operations for that group. Furthermore, the point group has already been identified and cataloged for most molecules.

# HOW TO READ A CHARACTER TABLE

To illustrate the properties of a character table, we will use the relatively simple case of molecular octasulfur, which is the most commonly occurring sulfur found in nature. As shown in figure 1, octasulfur forms a crown-like ring of 8 atoms, each with equal bond lengths. From a simple visual inspection, it is apparent that this molecule is symmetric under several different possible transformations. For example, a rotation around the center of the ring by either $90^0$ or $180^0$ would leave the molecule completely unchanged. In group theory, these two symmetry operations are referred to as $C_4$ and $C_2$, where the general form $C_n$ operation refers to rotation about the axis by $360^0/n$. While these two operations are the most obvious, they are not the only symmetries associated with octasulfur; for example, the molecule can be reflected through a dihedral plan ($\sigma_d$), it can be rotated by $45^0$ and then reflected through the axis of symmetry ($S_8$), or it can simply not change at all (E).

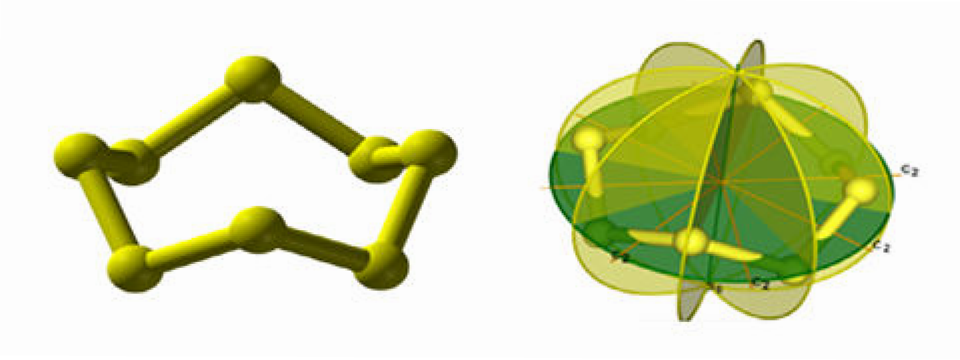
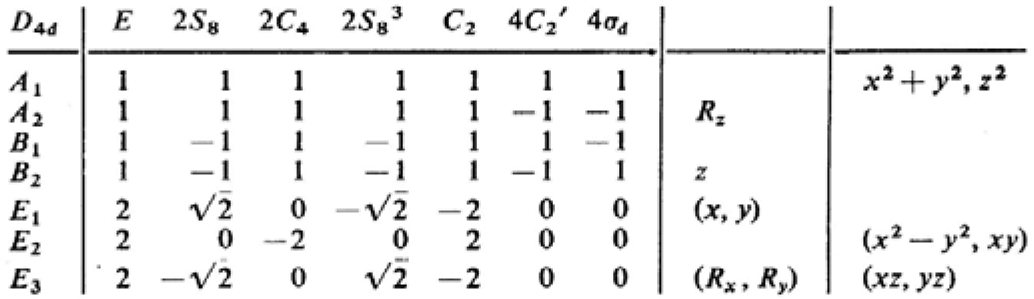


**FIGURE 1** Chemical structure of octasulfur; with some of the symmetry operations in the $D_{4d}$ point group

The 32-point groups, therefore, represent collections of all possible combinations of symmetry operations for a given geometry, and octasulfur falls into the $D_{4d}$ point group. The details of the naming conventions for the point groups are not particularly important, but in this case, $D_{4d}$ stands for a group containing a four-fold axis, four two-fold axes, and four dihedral mirror planes. Effectively this means that at least one $C_4$ is allowable, four $C_2'$, and four $\sigma_d$operations, where the prime indicates rotation perpendicular to the primary axis.There are 16 different possible symmetry operations for $D_{4d}$ point group, known collectively as the group's order.

While this may seem fairly complicated, character tables offer a simplified representation of all possible symmetry operations within the point group, which can be derived from the group multiplication table. Figure 2 shows the $D_{4d}$ character table, which is broken up into two main parts, the first showing the various irreducible representations of the group and the second showing the basis coordinates of each representation.



| $D_{4d}$ | $E$ | $2S_8$ | $2C_4$ | $2S_8^3$ | $C_2$ | $4C_2'$ | $4\sigma_d$ | | |
|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2+y^2, z^2$ |
| $A_2$ | 1 | 1 | 1 | 1 | 1 | −1 | −1 | $R_z$ | |
| $B_1$ | 1 | −1 | 1 | −1 | 1 | 1 | −1 | | |
| $B_2$ | 1 | −1 | 1 | −1 | 1 | −1 | 1 | $z$ | |
| $E_1$ | 2 | $\sqrt{2}$ | 0 | $-\sqrt{2}$ | −2 | 0 | 0 | $(x, y)$ | |
| $E_2$ | 2 | 0 | −2 | 0 | 2 | 0 | 0 | | $(x^2-y^2, xy)$ |
| $E_3$ | 2 | $-\sqrt{2}$ | 0 | $\sqrt{2}$ | −2 | 0 | 0 | $(R_x, R_y)$ | $(xz, yz)$ |

**FIGURE 2** $D_{4d}$ character table

The letters in the first column of the character table, known as the Mulliken symbols for the irreducible representations, where A & B are symmetric and anti-symmetric with respect to the principal rotational axis. E, T, G, and H are used to denote two-, three-, four- and five-dimensional irreducible representations, but it should be noted that most point groups do not require dimensionality greater than two. It is also essential to pay close attention to whether E is being used to denote the identity symmetry operation (top row) or the two-dimensional irreducible representation (first column).

While we will need to use all the information in the character table to eventually determine the allowed vibrational modes of our molecule, at this point, it is worth pointing out that a simple inspection of the basis coordinates can quickly determine if a mode can support infrared absorption or Raman scattering. Since, as stated previously, infrared is a linear process, only modes with a linear basis will be capable of supporting infrared absorption, which in our case corresponds to $B_2$ and $E_1$. By contrast, only $A_1$, $E_2$, and $E_3$ can support Raman scattering since they correspond to nonlinear basis coordinates. $B_2$, on the other hand, is known as a silent mode since it does not have a basis coordinate and therefore remains undetectable. While under certain circumstances, both Raman and infrared can be sensitive to rotational modes making $A_2$ potentially detectable, as with most introductory texts on this subject, we will ignore them since they do not correspond to molecular vibrations.

The last major takeaway that an initial inspection can make of this character table is that there are no infrared active symmetric modes or Raman active anti-symmetric modes. As it turns out, this trend is repeated across many point groups. While not a hard and fast rule, it is a reasonable first-order approximation to assume that symmetric vibrations are more Raman active and anti-symmetric vibrations are more infrared active.

# DETERMINATION OF ACTIVE MODES

Before we can determine the total number of vibrational modes, we must first calculate the character of the reducible representations for our specific molecule of interest, which is done through inspection to identify how many atoms in the molecule are unaffected by each symmetry operation. Since octasulfur is a ring molecule with no center atom, all of our rotation operations ($S_8$, $C_4$, $C_2$, $S_8^3$, & $C_2'$) will affect atoms, allowing us to set all of those terms equal to zero. We also know that, by definition, none of the atoms will be affected by the identity operation (E), so all eight will remain unaffected. The only tricky one to determine is the mirror operation ($\sigma_d$), but upon careful inspection, it can be determined to leave two atoms unaffected. Next, the character of each representation can be determined by multiplying the number of unaffected atoms by the total number of contributions per atom.

The trace of each transformation matrix determines the number of contributions per atom. This derivation is beyond the scope of this application note; however, the results are simple and easy to use. For the identity operation, the contributions per atom are always equal to 3, and for mirror operations, it is always equal to 1. To determine the number of contributions for a rotation operation ($C_n$) simply use the equation 1+2 cos (2π/n), and for an irregular rotation operation ($S_n$), use 2 cos(2π/n)-1. While there are no inversion operations (i) as part of the $D_{4d}$ point group, for the sake of completeness, we should note all inversion operations have a per atom contribution of -3. Therefore, we have a total reducible character of 24 for the identity operation, 2 for the mirror operation, and 0 for the rest (see table 1).

**TABLE 1:** Reducible Representation for Molecular Motion of Octasulfur.

| $D_{4d}$ | $E$ | $2S_8$ | $2C_4$ | $2S_8^3$ | $C_2$ | $4C_2'$ | $4\sigma_d$ |
|---|---|---|---|---|---|---|---|
| Unaffected Atoms | 8 | 0 | 0 | 0 | 0 | 0 | 2 |
| Contribution Per Atom | 3 | $\sqrt{2}-1$ | 1 | $\sqrt{2}-1$ | -1 | -1 | 1 |
| Character of Reducible Representation ($\Gamma_{red}$) | 24 | 0 | 0 | 0 | 0 | 0 | 2 |

**FIGURE 3:** Irreducible representation equation

$$\begin{pmatrix}\text{number of irreducible}\\ \text{representations of}\\ \text{a given type}\end{pmatrix} = \frac{1}{\text{order}}\sum\left[\begin{pmatrix}\text{number of}\\ \text{operations}\\ \text{in class}\end{pmatrix}\times\begin{pmatrix}\text{character}\\ \text{of reducible}\\ \text{representation}\end{pmatrix}\times\begin{pmatrix}\text{character of}\\ \text{irreducible}\\ \text{representation}\end{pmatrix}\right]$$

Using the equation shown in figure 3, we can determine the total number of irreducible representations for each type resulting in one representation of $A_2$ and $B_1$, two representations of $A_1$ and $B_2$, and three representations of $E_1$, $E_2$, and $E_3$. Finally, to find the total number of vibrational modes, we must subtract out the translational ($B_2$ & $E_1$) and rotational ($A_2$ & $E_3$) representations, which can be determined using the basis vectors in the character table. As shown in Table 2, this leaves us with two $A_1$, one $B_1$, one $B_2$, two $E_1$, three $E_2$, and two $E_3$ vibrational modes. Since the E modes each represent two orthogonal modes with the same energy, these leave us with 18 total vibrational modes, which is consistent with the fact that nonlinear molecules contain 3N-6 vibrational degrees of freedom. These modes can then be further subdivided into five infrared active modes, one $B_2$ & two $E_1$, since they have a linear basis, twelve Raman active modes, two $A_1$, three $E_2$, & two $E_3$, which have a nonlinear basis, and one silent mode, $B_1$, which is lacking any basis.

| $\Gamma_{total}$ | 2 $A_1$ | $A_2$ | $B_1$ | 2 $B_2$ | 3 $E_1$ | 3 $E_2$ | 3 $E_3$ |
|---|---|---|---|---|---|---|---|
| $-\Gamma_{trans}$ | | | | $B_2$ | $E_1$ | | |
| $-\Gamma_{rot}$ | | $A_2$ | | | | | $E_3$ |
| $=\Gamma_{vib}$ | 2 $A_1$ | | $B_1$ | $B_2$ | 2 $E_1$ | 3 $E_2$ | 2 $E_3$ |

**TABLE 3:** Classification of vibrational modes

# STRETCHING VS. BENDING

**TABLE 3:** Classification of vibrational modes

$$\begin{pmatrix}\text{number of irreducible}\\ \text{representations of}\\ \text{a given type}\end{pmatrix} = \frac{1}{\text{order}}\sum\left[\begin{pmatrix}\text{number of}\\ \text{operations}\\ \text{in class}\end{pmatrix}\times\begin{pmatrix}\text{character}\\ \text{of reducible}\\ \text{representation}\end{pmatrix}\times\begin{pmatrix}\text{character of}\\ \text{irreducible}\\ \text{representation}\end{pmatrix}\right]$$

In vibrational spectroscopy, we are primarily interested in two different types of vibrations– higher-frequency stretching and lower-frequency bending modes. The simplest way of differentiation between them is that stretching modes result from atoms moving back and forth along the bond axis. In contrast, bending modes result from deviations from the bond axis. Therefore, by transforming our coordinate system from a typical x-y-z cartesian system to a curvilinear coordinate system with motion restricted to the radial coordinate we can use group theory to identify the stretching modes. Since there will only be one degree of freedom this results in the contribution per atom from the identity operation reducing from 3 to 1. Using this new coordinate system, the reducible representation now becomes 8 for the identity operation, while remaining 2 for the mirror operation, and 0 for the rest. Following the same procedure as before, we now end up with eight stretching modes corresponding to $A_1$, $B_2$, $E_1$, $E_2$, and $E_3$. This means the ten remaining modes $A_1$, $B_1$, $E_1$, two $E_2$, and $E_3$ must all be bending modes.

To experimentally demonstrate these results, we used an AvaSpec-HSC 1024x58 TEC-EVO AKA our "HERO" configured to measure from 790nm to 1100nm with a 50µm slit and an *AvaLaser785* ultra-high-throughput Raman probe with an integrated 785nm wavelength stabilized laser source (see figure 4). A two second integration was used without any signal averaging. Based on the spectrum shown in figure 5, we are able to detect two distinct groupings of Raman bands. Based on our previous analysis, we can identify the lower-frequency cluster between 125cm$^{-1}$ - 275cm$^{-1}$ as the $A_1$, two E2, and E3 bending modes, and the higher frequency cluster between 400 cm-1 - 500cm-1 as the A1, E2, and E3 stretching modes. The peak visible below 100cm¬-1 is not a bending mode of the molecule. It is a structural vibration resulting from the fact that octasulfur forms an orthorhombic crystal at room temperature.

**FIGURE 4:** Set up of system with Raman 785 laser, AvaSpec-HSC, and sample holder

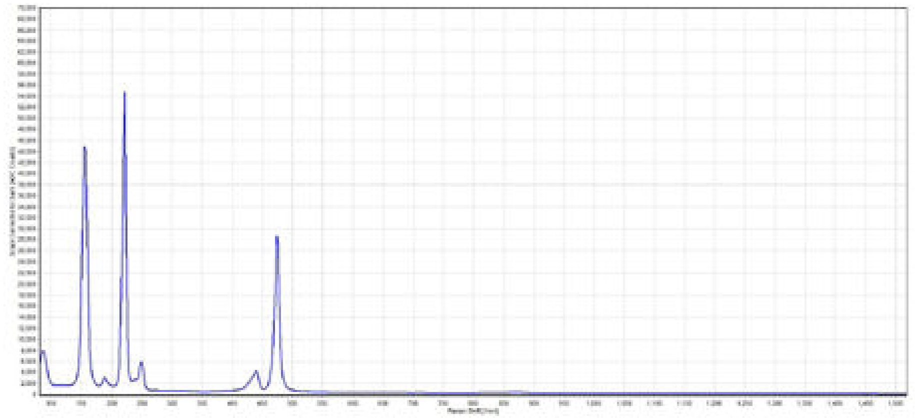


**FIGURE 5:** Raman spectrum of octasulfur

# FINAL THOUGHTS

This analysis is intended to provide insight into how physicists and chemists can determine the vibrational modes of a given molecule based on its geometry and highlight the importance of using both Raman and infrared spectroscopy as complementary tools. We specifically chose to look at octasulfur to highlight the power of symmetry and group theory for determining the spectra characteristics. Still, it is essential to remember that this approach can be applied to any molecule of interest. It is also important to note that while all the components used were standalone modules, they are also available as units OEM modules or can be integrated into multichannel rack mount systems. These units can communicate via USB, Ethernet, and the native digital & analog input/output capabilities of the Avantes AS5216 electronics board provides for a superior interface with other devices.   Additionally, the Avantes AS5216 DLL package, with sample programs in Delphi, Visual Basic, C#, C++, LabView, MatLab, and many other programming environments, enables users to develop their own code.

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