



APPLICATION NOTE

RAMAN VS INFRARED SPECTROSCOPY MEASUREMENT OF OCTASULFUR



INTRO

APPLICATION BACKGROUND

Infrared and Raman spectroscopy 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 fingerprint 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 for them to be the same material. Therefore, Raman and infrared spectroscopy 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 believe 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 for 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 the 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. Although this requires knowledge of group theory, fortunately, only 32 different point (symmetry) groups are needed to characterize any possible molecular configuration, each having a well-defined character table that 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, the most commonly occurring sulfur in nature. Figure 1 shows 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° or 180° 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 $360^\circ/n$. 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 plane (σ_d), it can be rotated by 45° and then reflected through the axis of symmetry (S_8), or it can simply not change at all (E).

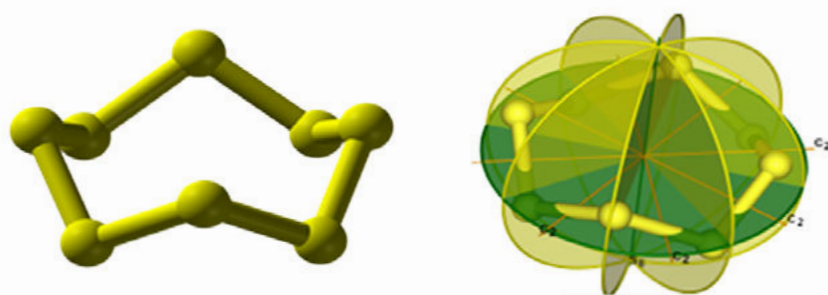


FIGURE 1 Chemical structure of octasulfur; with some of the symmetry operations in the D_{4d} point group

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 σ_d operations, where the prime indicates rotation perpendicular to the primary axis. There are 16 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 shows the various irreducible representations of the group and the second shows 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	R_z	$x^2 + y^2, z^2$
A_2	1	1	1	1	1	-1	-1		
B_1	1	-1	1	-1	1	1	-1	z	
B_2	1	-1	1	-1	1	-1	1		
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(x, y)	$(x^2 - y^2, xy)$
E_2	2	0	-2	0	2	0	0		
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 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 (σ_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 $1 + 2 \cos(2\pi/n)$, and for an irregular rotation operation (S_n), use $2 \cos(2\pi/n) - 1$. 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).

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 (Γ_{red})	24	0	0	0	0	0	2

TABLE 1: Reducible Representation for Molecular Motion of Octasulfur.

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

FIGURE 3: Irreducible representation equation

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.

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

TABLE 2: Total number of vibrational modes

STRETCHING VS. BENDING MODES

In vibrational spectroscopy, we are primarily interested in two 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.

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

TABLE 3: Classification of vibrational 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 50 μm 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 E_2 , and E_3 bending modes, and the higher frequency cluster between 400cm^{-1} - 500cm^{-1} as the A_1 , E_2 , and E_3 stretching modes. The peak visible below 100cm^{-1} is not a bending mode of the molecule, but a structural vibration resulting from octasulfur that forms an orthorhombic crystal at room temperature.



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

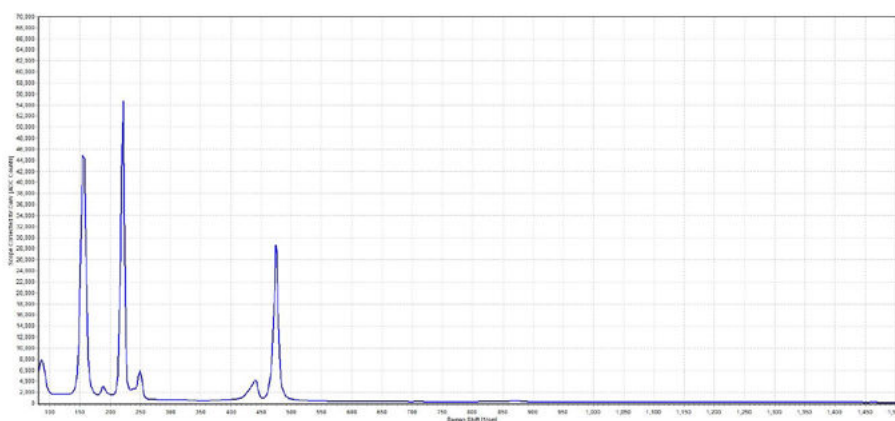


FIGURE 5: Raman spectrum of octasulfur

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.

For more information about the full range of spectrometer options available from Avantes for Raman spectroscopy, please feel free to visit the website at www.avantes.com or give us a call. We are happy to help!

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