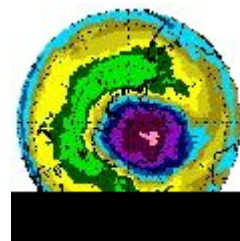


Cl₂O₄ in the Stratosphere

Group Theory and Vibrational Spectroscopy



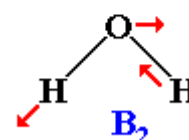
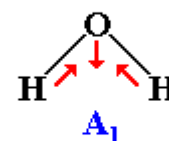
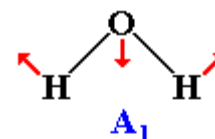
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Normal Modes of Vibration

The complex vibrations of a molecule are the superposition of relatively simple vibrations called the *normal modes of vibration*. Each normal mode of vibration has a fixed frequency. It is easy to calculate the expected number of normal modes for a molecule made up of N atoms.

Linear molecule of N atoms: # normal modes = $3N - 5$

Nonlinear molecule of N atoms: # normal modes = $3N - 6$



Bent (C_{2v})

The symmetries of the normal modes can be classified by group theory. (In this project we won't go into how this is done).

As an example, water has a symmetrical bent structure of C_{2v} symmetry. It has three atoms and three normal modes of vibration ($3 \times 3 - 6 = 3$). Pictures of the three normal modes are shown here along with their [symmetry types](#).

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Vibrational Spectroscopy

There are two types of spectroscopy that involve vibrational transitions. You should be very familiar with one of these from your Organic Chemistry course - **infrared spectroscopy**. During infrared spectroscopy experiments we observe transitions between vibrational energy levels of a molecule induced by the absorption of infrared (IR) radiation. The second type of vibrational spectroscopy is **Raman spectroscopy**. In Raman spectroscopy, vibrational transitions occur during the scattering of light by molecules.

At room temperature almost all molecules are in their lowest vibrational energy levels with quantum number $n = 0$. For each normal mode, the most probable vibrational transition is from this level to the next highest level ($n = 0 \rightarrow 1$). The strong IR or Raman bands resulting from these transitions are called **fundamental bands**. Other transitions to higher excited states ($n = 0 \rightarrow 2$, for instance) result in **overtone bands**. Overtone bands are much weaker than fundamental bands.

Not all fundamental vibrational transitions can be studied by both IR and Raman spectroscopy because they have different **selection rules**. Selection rules tell us if a transition is allowed or forbidden. An allowed transition has a high probability of occurring and will result in a strong band. Conversely a forbidden transition's probability is so low that the transition will not be observed. If a normal mode has an allowed IR transition, we say that it is **IR active**. Similarly if a normal mode has an allowed Raman transition, we say that it is **Raman active**.

If you know the point group of the molecule and the symmetry labels for the normal modes, then group theory makes it easy to predict which normal modes will be IR and/or Raman active. Look at the [character table](#) for the point group of the molecule.

If the symmetry label of a normal mode corresponds to x, y, or z, then the fundamental transition for this normal mode will be IR active.

If the symmetry label of a normal mode corresponds to products of x, y, or z (such as x^2 or yz) then the fundamental transition for this normal mode will be Raman active.

Consider the character table for the C_{2v} group shown at the right. We see that if a normal mode has A_1 , B_1 , or B_2 symmetry then it will be both IR and Raman active. If a normal mode has A_2 symmetry then it will be only Raman active.

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

In the example above, water has three normal modes: two of A_1 symmetry and one of B_2 symmetry. All of these are IR and Raman active. We would expect water to have three peaks corresponding to fundamental vibrations in the IR spectrum. There also would be three peaks in its Raman spectrum at the same frequencies as in the IR.

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Polarized and Depolarized Raman Bands ¹²

The assignment of Raman lines may be aided by measuring their intensity with a polarizing filter, first parallel and the perpendicular to the polarization of the incident radiation. If the polarization of the scattered beam is the same as that of the incident beam (intense only in the parallel direction), then the Raman line is said to be *polarized*. If the scattered light is intense in both the parallel and perpendicular direction, then the Raman line is *depolarized*.

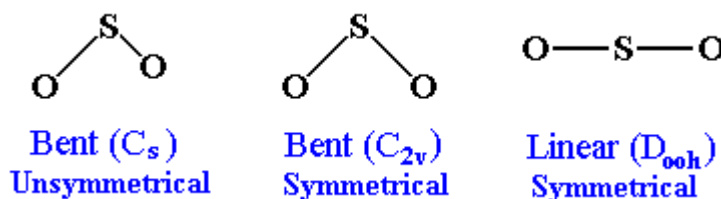
Only totally symmetric vibrations (a normal mode with all characters = 1 in the [character table](#)) give rise to polarized lines.

In the water example above, two of the Raman lines correspond to a totally symmetric vibration (A_1) and would be polarized. One would be depolarized.

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Example: The Geometry of the Sulfur Dioxide Molecule

Consider three possible geometries for the SO_2 molecule, linear and bent, shown at the right with their point groups.



The symmetry types for the normal modes of the three structures are shown here. For the C_s form 3 A' means that there are three different normal modes, all having the same symmetry (A'). Similarly, for the C_{2v} form two of the three normal modes have the same symmetry (A_1). *These modes are not identical and do not have the same energy - they just happen to have the same symmetry.*

Structure	Normal Modes
C_s	3 A'
C_{2v}	2 A_1 , B_2
$D_{\infty h}$	Σ_g^+ , Σ_u^+ , Π_u

Now we need to look at the character tables to see which normal modes one would expect to be observed in the IR and Raman for each structure. The character tables for the three point groups are shown below.

C_s structure: 3 normal modes, all having A' symmetry

The C_s structure should have 3 IR active fundamental transitions. These three fundamental transitions also should be Raman active. We would expect to observe three strong peaks in the IR and three

	C_s	E	σ_h		
IR Raman A'	1	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	-1	z, R_x, R_y	yz, xz

strong peaks in the Raman at the same frequency as in the IR.

All of the Raman lines would be polarized because they are totally symmetric (A' symmetry).

C_{2v} structure: 3 normal modes, two with A_1 symmetry, one with B_2

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

The C_{2v} structure should have 3 IR active fundamental transitions. These three fundamental transitions also should be Raman active. We would expect to observe three strong peaks in the IR and three strong peaks in the Raman at the same frequency as in the IR.

Two of the Raman lines are totally symmetric (A_1 symmetry) and would be polarized. One Raman line would be depolarized.

$D_{\infty h}$ Structure: 3 normal modes with Σ_g^+ , Σ_u^+ , Π_u symmetries

	$D_{\infty h}$	E	$2C_{\infty}^{\Phi}$		
Raman Σ_g^+	1	1		$x^2 + y^2, z^2$
Σ_g^-	1	1	R_z	
Π_g	2	$2 \cos \Phi$	(R_x, R_y)	(xz, yz)
Δ_g	2	$2 \cos 2\Phi$		$(x^2 - y^2, xy)$
...					
IR Σ_u^+	1	1	z	
Σ_u^-	1	1		
IR Π_u	2	$2 \cos \Phi$	(x, y)	
Δ_u	2	$2 \cos 2\Phi$		

The $D_{\infty h}$ structure should have two IR active fundamental transitions. It will have one Raman active fundamental transition at a different frequency than either of the IR peaks..

The Raman line will be polarized.

The experimental infrared and Raman bands of liquid and gaseous sulfur dioxide have been reported in a book by Herzberg⁷. Only the strong bands corresponding to fundamental transitions are shown below. The polarized Raman bands are in red.

Fundamental	2	1	3
IR (cm⁻¹)	519	1151	1336
Raman (cm⁻¹)	524	1151	1336

Conclusion:

The existence of three experimental bands in the IR and Raman corresponding to fundamental transitions weighs strongly against the symmetrical linear (D_{ooH}) structure. We usually do not expect more strong bands to exist than are predicted by symmetry.

Group theory predicts that both bent structures would have three fundamental transitions that are active in both the IR and Raman. However all three of the Raman lines would be polarized if the structure were unsymmetrical (C_s symmetry). The fact that one Raman line is depolarized indicates that the structure must be bent and symmetrical (C_{2v} symmetry).

The sulfur dioxide molecule has C_{2v} symmetry.

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Group Theory

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