Introduction

The purpose of today's lecture is to give you some familiarity with how the symmetry properties of a molecule can be reflected in two kinds of vibrational spectroscopy. Indeed, you will see that much can be learned about the symmetry of the molecule from the study of its vibrational spectra!

We start out by recognizing that a nonlinear molecule possesses 3 degrees of freedom for every atom in the molecule. That means, for example, that the water molecule with its three atoms has a total of 9 degrees of freedom. Of those 9 degrees of freedom for the water molecule, three are translational, and three are rotational. When the molecule undergoes translation, none of the internal distances or angles are changing. Similarly, when a molecule undergoes rotation, it can be understood to maintain its equilibrium geometry. On the other hand, when a molecule is vibrating then its atoms are moving with respect to one another. In the case of a nonlinear molecule there are a total of $3N - 6$ vibrations, since we subtract three translations and three rotations from the total number of degrees of freedom. In the case of a linear molecule, the formula becomes $3N - 5$, because while we can subtract three translations, we can only subtract two rotations, because a linear molecule effectively cannot rotate about its axis.

Vibrations of the Water Molecule

In the case of the water molecule, we know that the correct point group is C_{2v}, and it is easy to write down the number of atoms that remain unshifted upon application of the group operations. Here, the result is the following list: 3, 1, 1, 3. This information can be used as input to the program REDUCE.exe to execute a vibrational analysis. The vibrational analysis reveals that the three normal modes (fundamental molecular vibrations) of the water molecule can serve as bases for $2A_1 + B_2$ irreducible representations. Looking at the character table for the C_{2v} point group, we can see that vibrations of both of these symmetry types will be IR active, since the selection rule for IR activity is that the mode must result in a dipole moment change for the molecule. An irreducible representation corresponding to a mode involving a dipole moment change will have x, y, or z listed at the right hand side of the character table. This is because the symmetry of the electric dipole operator is the same as that for x, y, or z vectors. Accordingly, all three of the normal modes for the water molecule are expected to show up as bands in this molecule's infrared spectrum. Indeed, the three normal modes can be understood pictorially as follows: there is a symmetric stretch (A_1) and an asymmetric stretch (B_2) and there is a single H-O-H bend (A_1). Because it takes more energy to stretch a chemical bond than it does to change a bond angle, the A_1 and B_2 stretches will occur at high energy relative to the A_1 bend.

The criterion for Raman activity is different from that for infrared activity. In particular, for a normal mode to exhibit Raman activity, there has to occur a change in the molecular polarizability during the course of the vibration. In the character table, this corresponds to the listing of quadratic terms such as xy and xz at the right-hand side of the table.

Structure of Sulfur Hexafluoride

Let us now consider the sulfur hexafluoride molecule. There are various conceivable symmetrical geometries for this molecule, and we can consider the effect of the molecular symmetry with respect to our expectations for the corresponding vibrational spectra.

One conceivable geometry for SF_6 would be a planar hexagon shape, with sulfur at the center, and this would correspond to D_{6h} symmetry. Now, we can apply the group operations and see for

each one how many atoms are not moved, and this results in the following list:

$$7,\ 1,\ 1,\ 1,\ 3,\ 1,\ 1,\ 1,\ 1,\ 7,\ 1,\ 3$$

Using this information as input to the program REDUCE.exe we obtain a vibrational analysis such that the $3N - 6$ normal modes are predicted to transform as $A_{1g} + B_{2g} + 2E_{2g} + A_{2u} + B_{1u} + B_{2u} + 2E_{1u} + E_{2u}$. Notice that, from the character table for D_{6h}, we can see immediately that none of the IR active bands will be Raman active, and vice versa. And in particular, in the present case, the prediction is for three IR active bands ($A_{2u} + 2E_{1u}$), and three Raman active bands ($A_{1g} + 2E_{2g}$).

A different conceivable geometry for SF_6 is one in which the sulfur atom resides at the center of a trigonal prism. Once again, we apply the group operations in order to discover for each one how many atoms remain in position. The resulting list in this case is:

$$7,\ 1,\ 1,\ 1,\ 1,\ 3$$

which reduces to $2A_1' + 3E' + A_1'' + 2A_2'' + 2E''$. As in the previous geometry, this result is consistent with $3N - 6 = 15$ normal modes. However, you will notice from inspection of the character table that the IR and Raman spectra are no longer mutually exclusive. In particular, the three bands of E' symmetry should be active in both the IR and Raman spectra. The overall prediction, which you should verify, is for 5 bands in the IR, and a total of seven bands in the Raman.

Finally, let's consider SF_6 in the octahedral geometry. In this case once again we examine the effect of carrying out the group operations on the molecule, to generate a list of the items that are not shifted by the operation. In this case, the list is as follows:

$$7,\ 1,\ 1,\ 3,\ 3,\ 1,\ 1,\ 1,\ 5,\ 3$$

Stemming from these input data, we find the following symmetry species for the 15 normal modes of octahedral SF_6: $A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$. Like the case of D_{6h} symmetry, the O_h point group is one in which there is present an inversion center; in such cases the IR and Raman spectra are always mutually exclusive. The prediction based on octahedral symmetry for SF_6 is that there will be only two bands in the IR spectrum, while there will be three in the Raman spectrum.

Which of the three geometries we have considered for SF_6 is in fact consistent with the experimental data?

What is REDUCE.exe Doing?

Take the example of the water molecule. There are nine total degrees of freedom, and we can assign three vectors (x, y, z) to each nucleus in the water molecule and use these as the basis for a *reducible representation*. Since any atoms that are shifted by the symmetry operation do not contribute to the corresponding character in the reducible representation, our first job is to figure out how many atoms remain unshifted with each group operation. For water, this list is: 3, 1, 1, 3, with the molecule lying in the yz plane. Then, these characters are multiplied by those for the (x, y, z) vectors, namely 3, -1, 1, 1 (this is the sum of the characters of the rows in which x, y, z appear in the C_{2v} character table, to give the reducible representation, Γ_{tot}, for all nine degrees of freedom:

$$\Gamma_{tot} = 9\ -1\ 1\ 3$$

This reducible representation reduces to: $3A_1 + A_2 + 2B_1 + 3B_2$. From this we subtract the translations $(A_1 + B_1 + B_2)$ and rotations $(A_2 + B_1 + B_2)$ leaving finally the vibrations:

$$\Gamma_{vib} = 2A_1 + B_2$$