Assigning Symmetries of Vibrational Modes

C. David Sherrill
School of Chemistry and Biochemistry
Georgia Institute of Technology

June 2000; Revised July 2010

1 Introduction

Group theory is a very powerful tool in quantum chemistry. By analyzing the symmetry properties of molecules, we can easily make predictions such as whether a given electronic transition should be allowed or forbidden, whether a molecule should have dipole moment, whether a given vibrational mode should be visible in the infrared or not, etc. Here we will assume a basic familiarity with point groups and discuss how group theory can be used to determine the symmetry properties of molecular vibrations.

2 O_4^+ Has D_{2h} Symmetry

Our example will the O_4^+ cation, which has D_{2h} point group symmetry, as shown in Figure 1. The Cartesian coordinates of this molecule are given in Table 1, and the character table for D_{2h} is given in Table 2. From the table, we can see that there are eight distinct symmetry operations for this point group: the identity (E), three different C_2 rotation axes, a center of inversion (i), and three mirror planes (σ). You can easily verify that O_4^+ possesses all of these symmetry properties. These symmetry operations form the columns of the table. There are also eight rows, or *irreducible representations*, labeled A_g, B_{1g}, …, B_{3u}. The 1's and -1's in the table indicate whether the irreducible representation (or irrep, for short) is symmetric or antisymmetric for that symmetry operation.

3 How Many Vibrational Modes Belong To Each Irrep?

From the sketch of the molecular geometry and the character table, we can fairly easily determine how many vibrational modes there will be of each symmetry type (i.e., each irreducible representation).

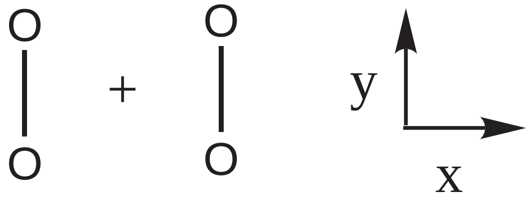


Figure 1: O_4^+ Cation

Table 1: O_4^+ Cartesian Coordinates

```
-----------------------------------------------------
     Standard Nuclear Orientation (Angstroms)
   I     Atom         X             Y             Z
-----------------------------------------------------
   1      O       1.320000     -0.582500     0.000000
   2      O       1.320000      0.582500     0.000000
   3      O      -1.320000      0.582500     0.000000
   4      O      -1.320000     -0.582500     0.000000
-----------------------------------------------------
```

Table 2: Character Table for Point Group D_{2h}

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Table 3: Character Contributions of Some Common Symmetry Operations

E	3
σ	1
C_2	-1
i	-3
C_3	0

Table 4: Symmetry Decomposition of Atomic Motions

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Stationary Atoms	4	0	0	0	0	4	0	0
Char contrib	3	-1	-1	-1	-3	1	1	1
Γ_{red}	12	0	0	0	0	4	0	0

The process is as follows. Apply each of the symmetry operations of the point group (E, $C_2(z)$, etc.) to the molecule, and determine *how many atoms are not moved by the operation.* Then, multiply this number by the so-called *character contribution* of that symmetry operation. This will yeild a series of h numbers, where h is the number of distinct symmetry operations in the point group (8 for D_{2h}).

What is this mysterious character contribution? Technically speaking, it is the trace of the matrix representation in xyz Cartesian coordinates of that operation. However, it is usually easier just to memorize the character contributions of the most commonly used symmetry operations. A partial table of character contributions is given in Table 3.

Using these rules, we can obtain an 8-member array of integers usually denoted Γ_{red}, a *reducible* array. This is done in Table 3. The next step is to decompose the reducible array into a unique linear combination of irreducible representations (irreps). This is easily accomplished using dot products. For example, to get the number of a_g modes, we take the dot product of Γ_{red} with the row of the character table for a_g, and divide by the number of operations in the group (8 for D_{2h}). So, $\Gamma_{red} \cdot \Gamma_{a_g}/h = (12 + 4)/8 = 2$. In a similar manner, we can determine the contributions from the other irreps, to obtain a decomposition of Γ_{red} as 2 a_g + 2 b_{1g} + b_{2g} + b_{3g} + a_u + b_{1u} + 2 b_{2u} + 2 b_{3u}.

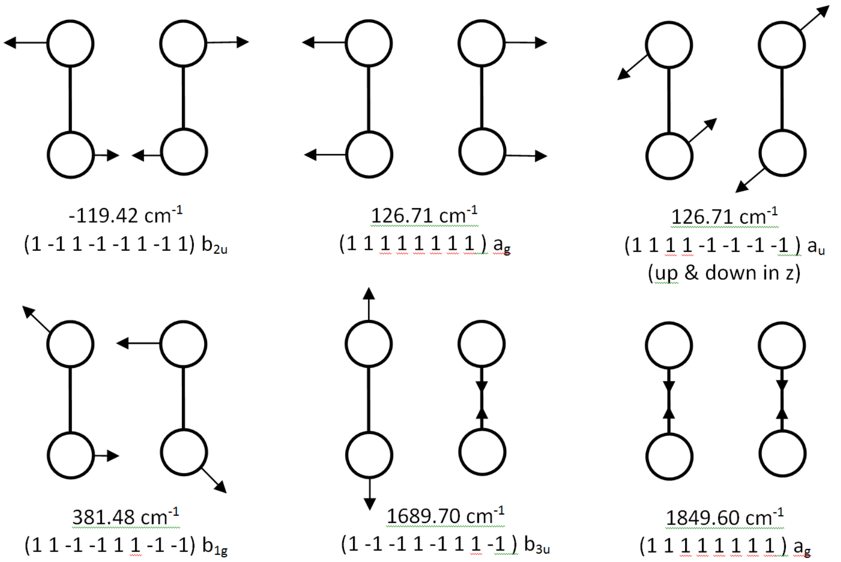
Next, we need to subtract out the translations and rotations. The irreps of the translations can be found in most character tables by looking for which row contains x, y, and z on the right-hand side of the table. Here, this gives b_{1u}, b_{2u}, and b_{3u}. Likewise, rotations are denoted in the table by R_x, R_y, R_z, which correspond to b_{1g}, b_{2g}, and b_{3g}. So, subtracting these out from Γ_{red}, we find that the vibrations are described by: 2 a_g, b_{1g}, a_u, b_{2u}, and b_{3u}. There are a total of six vibrations, which is correct according to the $3N - 6$ rule.

Below is the output from a Q-Chem calculation. These normal modes are sketched in Figure 2, along with the irreducible representations of each.

```
**********************************************************************
**                                                                  **
**                       VIBRATIONAL ANALYSIS                       **
**                       --------------------                       **
**                                                                  **
**        VIBRATIONAL FREQUENCIES (CM**-1) AND NORMAL MODES         **
**                  INFRARED INTENSITIES (KM/MOL)                   **
**                                                                  **
**********************************************************************


Frequency:      -119.42                 126.71                 131.78
IR Active:          YES                    YES                    YES
IR Intens:        0.466                  0.000                  0.000
Raman Active:       YES                    YES                    YES
              X      Y      Z        X      Y      Z        X      Y      Z
O        -0.500  0.000  0.000    0.500 -0.001  0.000    0.000  0.000 -0.500
O         0.500  0.000  0.000    0.500  0.001  0.000    0.000  0.000  0.500
O        -0.500  0.000  0.000   -0.500  0.001  0.000    0.000  0.000 -0.500
O         0.500  0.000  0.000   -0.500 -0.001  0.000    0.000  0.000  0.500

Frequency:       281.48                1689.70                1849.60
IR Active:          YES                    YES                    YES
IR Intens:        0.000                *******                  0.000
Raman Active:       YES                    YES                    YES
              X      Y      Z        X      Y      Z        X      Y      Z
O         0.457 -0.202  0.000    0.000  0.500  0.000    0.001  0.500  0.000
O        -0.457 -0.202  0.000    0.000 -0.500  0.000    0.001 -0.500  0.000
O        -0.457  0.202  0.000    0.000  0.500  0.000   -0.001 -0.500  0.000
O         0.457  0.202  0.000    0.000 -0.500  0.000   -0.001  0.500  0.000
```



-119.42 cm^{-1}
(1 -1 1 -1 -1 1 -1 1) b_{2u}

126.71 cm^{-1}
(1 1 1 1 1 1 1 1) a_g

126.71 cm^{-1}
(1 1 1 1 -1 -1 -1 -1) a_u
(up & down in z)

381.48 cm^{-1}
(1 1 -1 -1 1 1 -1 -1) b_{1g}

1689.70 cm^{-1}
(1 -1 -1 1 -1 1 1 -1) b_{3u}

1849.60 cm^{-1}
(1 1 1 1 1 1 1 1) a_g

Figure 2: Sketches of Normal Modes of O_4^+

4 Symmetry-Adapted Linear Combinations

Now, how would we have come up with these vibrational normal modes if we *hadn't* had the program? Group theory isn't sufficient to give us normal modes in general, but in this case, it woudl almost get us there, because other than a_g, no irrep has more than one vibration. In such cases, the normal mode is *symmetry-determined*. In the case of irreps with more than one vibration, group theory can at least give us a symmetry-adapted set of vectors (basis); these vectors are mixed to form the normal modes. It is important to point out that we could say similar things about molecular orbitals. Some MO's may be symmetry-determined (in a sufficiently small basis set), and others may be linear combinations of the symmetry-adapted AO's belonging to some irrep. Thus, we need to know how to form *symmetry-adapted linear combinations* (SALC's) of basis functions like atomic orbitals or vibrational displacement vectors. To explore this, we will stick with our O_4^+ vibrational example for now.

Let us use *displacement vectors* in the x, y, and z directions on each atom as our basis functions, and then we will form SALC's from these to see what the vibrations *should* look like (without the need for computations). We do this using the technique of *projection operators*.

Our job is somewhat easier for this example because each atom is symmetry-equivalent to all the others. Hence, it will suffice to apply projection operators to only the x, y, and z displacements on *one* of the atoms. Let's label the displacements as x_i, y_i, or z_i, where i is the number of the atom displaced. See Figure 3 for the displacements of atom 1. First, we must determine what

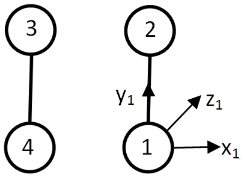


Figure 3: Displacement Vectors for Atom 1 in O_4^+

Table 5: Result of Symmetry Operations on Atomic Displacements

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
x_1	x_1	$-x_3$	$-x_4$	x_2	$-x_3$	x_1	x_2	$-x_4$
y_1	y_1	$-y_3$	y_4	$-y_2$	$-y_3$	y_1	$-y_2$	y_4
z_1	z_1	z_3	$-z_4$	$-z_2$	$-z_3$	$-z_1$	z_2	z_4

each symmetry operator does to each of our basis vectors. Referring to Fig. 3, we can construct Table 5, which provides the results of each symmetry operation on x_1, y_1, and z_1.

To apply a projection operator, we dot each of the rows in Table 5 with the rows of the character table — there will be a separate projection operator for each irrep. Because the totally symmetric irrep contains all 1's in its row, the rows in the Table are already the result of applying $\hat{P}_{A_g}$ to x_1, y_1, and z_1. Hence, $\hat{P}_{A_g}(x_1) = 2x_1 + 2x_2 - 2x_3 - 2x_4$, or $x_1 + x_2 - x_3 - x_4$ (we aren't usually too concerned about normalization). Referring to Figure 2, this is the 126.71 cm^{-1} a_g normal mode! Similarly, $\hat{P}_{A_g}(y_1) = y_1 - y_2 - y_3 + y_4$. This is the 1849.60 cm^{-1} normal mode. Finally, $\hat{P}_{A_g}(z_1) = 0$ (all the z displacements cancel). There is no third a_g mode.

We can apply projection operators to x_1, y_1, and z_1 for each irrep to build up a complete basis of SALC's. As another example,

$$\begin{aligned}
\hat{P}_{A_u}(x_1) &= x_1 - x_3 - x_4 + x_2 + x_3 - x_1 - x_2 + x_4 = 0, \\
\hat{P}_{A_u}(y_1) &= y_1 - y_3 + y_4 - y_2 + y_3 - y_1 + y_2 - y_4 = 0, \\
\hat{P}_{A_u}(z_1) &= z_1 + z_3 - z_4 - z_2 + z_3 + z_1 - z_2 - z_4 = z_1 - z_2 + z_3 - z_4.
\end{aligned}$$

Consulting Fig. 2, we see that $\hat{P}_{A_u}(z_1)$ is the 131.73 cm^{-1} normal mode.

Finally, let's try the B_{1u} irrep:

$$\begin{aligned}
\hat{P}_{B_{1u}}(x_1) &= x_1 - x_3 + x_4 - x_2 + x_3 - x_1 + x_2 - x_4 = 0, \\
\hat{P}_{B_{1u}}(y_1) &= y_1 - y_3 - y_4 + y_2 + y_3 - y_1 - y_2 + y_4 = 0, \\
\hat{P}_{B_{1u}}(z_1) &= z_1 + z_3 + z_4 + z_2 + z_3 + z_1 + z_2 + z_4 = z_1 + z_2 + z_3 + z_4.
\end{aligned}$$

Table 6: Result of Symmetry Operations on σ_1

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
σ_1	σ_1	σ_3	σ_4	σ_2	σ_3	σ_1	σ_2	σ_4

Now note that there is not a b_{1u} normal mode of vibration! Why is this? If we examine the result of $\hat{P}_{B_{1u}}(z_1)$, we see that it displaces *all* of the atoms in the z direction. This is just a *translation* of the entire molecule in the z direction. Creating SALC's out of Cartesian displacements will, in general, create not only vibrations but also translations and rotations. We already discussed above how to identify the irreps of translations and rotations.

5 Symmetry-Adapted Orbitals

As a last example, we will see that we can create SALC's of atomic orbitals in exactly the same way. Consider the case of ethylene (which is still point-group D_{2h}, see Figure 4). The 4 C–H σ bonds are symmetry-equivalent, so we can make 4 C–H bonding SALC's.

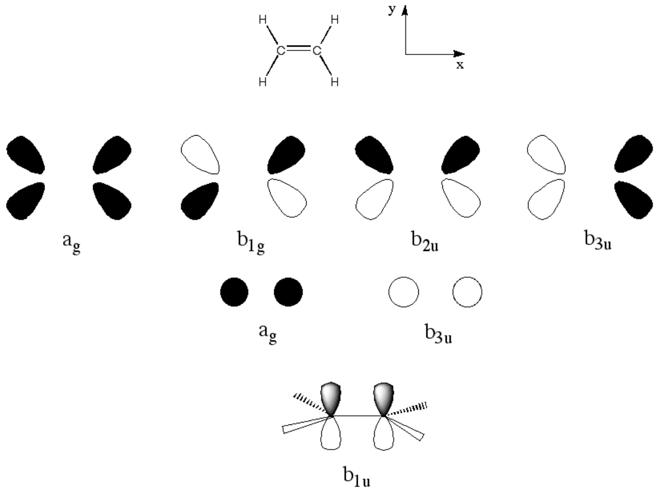


Figure 4: Ethylene Molecular Orbitals

The four non-zero SALC's are:

$$\hat{P}_{A_g}(\sigma_1) = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$$

$$\begin{aligned}\hat{P}_{B_{1g}}(\sigma_1) &= \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 \\ \hat{P}_{B_{2u}}(\sigma_1) &= \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4 \\ \hat{P}_{B_{3u}}(\sigma_1) &= \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4\end{aligned}$$

These are pictured in Figure 4. Note that four C–H bonds go in to the symmetry-adaptation, and four C–H SALC's come out. We could use similar procedures to construct the remaining four occupied orbitals, which are the symmetric (a_g) combination of the two C 1s core orbitals, the antisymmetric (b_{3u}) combination of the two C 1s core orbitals, the a_g C–C σ bonding orbital, and the b_{1u} C–C π bonding orbital (see Fig. 4).

Finally, it is worth commenting that we can often come up with the SALC's by intuition more easily than we can work out the projection operators (especially with a little experience and practice). This is certainly true for the ethylene symmetry-adapted orbitals.

Acknowledgments. The author thanks Dr. Sahan Thanthiriwatte for providing the figures.