Applications: IR and Raman

# Information

You should remember from physical chemistry that a molecular vibration is infrared active (has a visible infrared absorption peak) only if it results in a change in the dipole moment of the molecule. In group theory terms, a vibrational mode is active in the infrared if it corresponds to an irreducible representation that has the same symmetry (or transforms) as the Cartesian coordinates x, y, or z because a vibrational motion that shifts the center of charge of the molecule in any of the x, y, or z directions results in a change In dipole moment. Otherwise, the vibrational mode is not infrared active.

# Model I

Consider ammonia. Analysis of the x, y , and z coordinates of each atom in NH3 gives the following representation:

|  |  |  |  |
| --- | --- | --- | --- |
| C3v | E | 2C3 | 3v |
|  | 12 | 0 | 2 |

# Critical Thinking Questions

1. Explain why the reducible representation in the model is correct. Use pictures and explain how I got 12, 0, and 2.
2. Reduce  to its irreducible representations.

# Information

Once you have the irreducible representations, they must be classified as translations, rotations, or vibrations.

**Translational motion** is motion through space with x, y, and z components. If an irreducible representation label has an x, y, or z in the right column it transforms like a translation.

**Rotational motion** can be separated into rotation about the orthogonal x, y, and z axes.   
These are labeled Rx, Ry, and Rz in the table.

**Vibrational motions** are the remaining motions. For non-linear motions there should be 3N-6 vibrational motions.

# Critical Thinking Questions

1. How many translations should exist in the representation given in Model I?
2. How many translations should exist for any system?

# Model II

Imagine the motion of XeF4 (square planar). It is a D4h molecule which has a representation that reduces to A1g + A2g + B1g + B2g + Eg + 2A2u + B2u + 3Eu. Looking at the character table, the A2u and **one** of the Eu are translations, A2g and Eg are rotations. There are 9 vibrations (3\*5-6=9). They are A1g, B1g, B2g, A2u, B2u and the remaining 2Eu.

# Critical Thinking Questions

1. Explain why the translations for XeF4 are A2u and Eu.
2. Does this agree with your answer to CTQ 4?
3. How do you know that Eg is not a vibration in the D4h group?
4. Why can A2u be both a vibration and a translation?

1. Xenon tetrafluoride has 9 vibrations (3N-6). The remaining representations are A1g, B1g, B2g, A2u, B2u and the remaining 2Eu. Explain how these count as 9 vibrations.
2. Now, go back to your ammonia representation.
   1. How many vibrations should ammonia have?
   2. Classify the irreducible representations into translational, rotational, and vibrational modes.

# Information

**If a vibrational mode corresponds to an irreducible representation that has the same symmetry (or transforms) as the Cartesian coordinates x, y, or z it is infrared active.** This is because these types of vibrational motion shifts the center of charge of the molecule and causes a change in the dipole moment. If the motion does not correspond to an x, y, or z label in the character table, it is infrared inactive.

For Raman spectroscopy, a change in the polarizability is required. This corresponds to transforming in the same manner as any of the quadratic functions (xy, x2, z2, yz, y2, etc or any linear combination of these).

1. For XeF4, which vibrational modes are infrared active?
2. For ammonia, which vibrational modes are infrared active?
3. For ammonia, which vibrational modes are Raman active?

# Summary Sheet

Using the x, y, and z coordinates for each atom in SF6,

1. Determine the reducible representation.
2. Reduce it.
3. Classify the irreducible representations into translational, rotational, and vibrational modes.
4. Which vibrational modes are infrared active?
5. Which vibrational modes are Raman active?

# Information

Instead of looking at all a molecule’s vibrations, it is often useful to look at a particular type of vibrational mode for a compound. For example, consider *ci*s- and *trans*-dicarbonyl square planar metal complexes. Here, the IR can distinguish whether a sample is *cis*- or *trans*-ML2(CO)2.

# Critical Thinking Questions

1. Draw *cis*-ML2(CO)2.
2. Label the CO bonds as 1 and 2.
3. Using the C2v point group (why did I choose this one?), draw pictures of what happens to these two bonds under the 4 operations. Make the principal axis (C2) the z axis with the xz plane assigned as the plane of the molecule.
4. What is the character of the reducible representation for these two bonds? Note: I have supplied the value for E. Why is it 2 and not a larger number?

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| C2v | E | C2 | xz | yz |
|  | 2 |  |  |  |

1. Reduce it.
2. How many vibrations are there? (Hint, how many bonds did you start with?)
3. How many are vibrationally active?
4. Now, draw *trans*-ML2(CO)2. Note that the principal axis, C2 is again chosen as the z-axis, but this time the plane of the molecule is the xy plane. Your C2 axis will be the one perpendicular to the plane of the molecule.
5. What point group is trans-ML2(CO)2? (HINT: It is different than the *cis*)
6. Repeat steps 3-5.
7. How many vibrations are there?
8. How many are IR active?
9. Explain, in grammatically correct sentences, how the IR can distinguish between *cis*- and *trans*-ML2(CO)2.

# Summary Sheet

1. Determine the number of IR-active CO stretching modes for *fac*-Mo(CO)3(NCCH3)3. Show all work (don’t just go look up the spectrum).
2. Determine the number of IR-active CO stretching modes for Mn(CO)5Cl.