

## Problem Set PS04

ISSUED: 1/27/99 Due: 2/10/00

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Name \_\_\_\_\_

**Instructions.** Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

### Mathematical Exercises

1. What is the result of operating on the following functions with the inversion operator:  $\hat{i}f(x, y, z) = f(-x, -y, -z)$ ? Is the function an eigenfunction of the operator? If so, what is the eigenvalue? Label the function as gerade or ungerade when appropriate.

(a)  $f = \frac{x^2+y^2+z^2}{x+y+z}$

(b)  $f = xyz$

(c)  $f = xy - z$

2. What is the result of operating on the following functions with the vertical mirror operator:  $\hat{\sigma}_v f(x, y, z) = f(-x, -y, z)$ ? Is the function an eigenfunction of the operator? If so, what is the eigenvalue?

(a)  $f = \frac{x^2+y^2+z^2}{x+y+z}$

(b)  $f = xyz$

(c)  $f = xy - z$

3. What is the result of operating on the following functions with the rotation operator:  $\hat{C}_4 f(x, y, z) = f(y, -x, z)$ ? Is the function an eigenfunction of the operator? If so, what is the eigenvalue?

(a)  $f = \frac{x^2+y^2+z^2}{x+y+z}$

(b)  $f = xyz$

(c)  $f = xy - z$

4. Are the counting numbers a group under multiplication? under division? under addition? under subtraction?
5. List all the symmetry element for the  $C_{3v}$  group. (Hint there are six symmetry elements in the group)
6. Write out the multiplication table for the  $C_{3v}$  group.

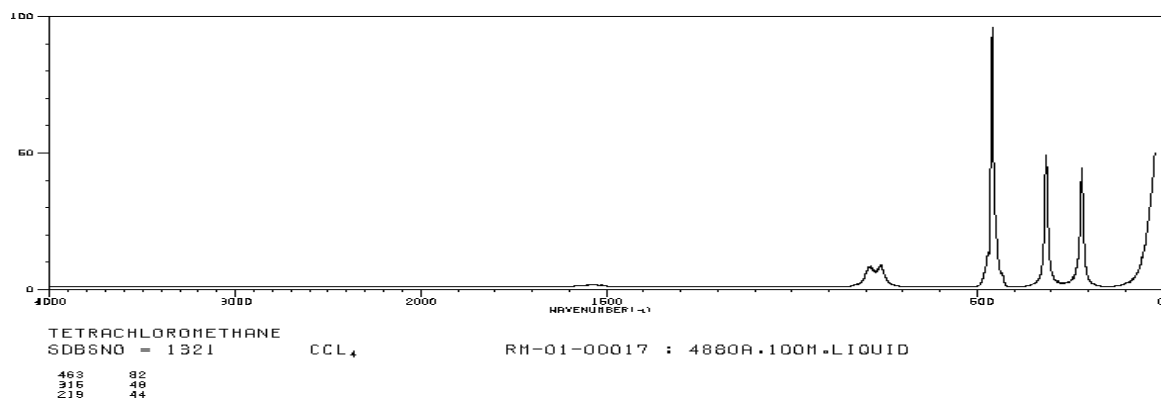
7. Write out the different sets of eigenvalues (the vectors) for the  $C_{3v}$  group. Construct the character table for the  $C_{3v}$  group from these vectors. Combine the columns that are identical. This should take you from six to three columns. Compare your table to the  $C_{3v}$  table given in the handout. (It is helpful to download the MATHEMATICA notebook called *allvects* from the PChem site.)
8. Evaluate all the possible two component direct products for the  $C_{3v}$  group.

## Exercises

9. Use your flow chart to determine the point groups for
  - HCl
  - $\text{PH}_3$
  - *cis*- $\text{Fe}(\text{CO})_4\text{IBr}$  (octahedral)
  - $\text{PtCl}_4$  (square planar configuration)
  - *trans*- $\text{PtCl}_2(\text{CO})_2$ . (square planar configuration)
  - $\text{Fe}(\text{CO})_5$  (trigonal bipyramidal)
  - $\text{H}_2\text{O}_2$  (hydrogen peroxide)
  - $\text{Cr}(\text{en})_3^{3+}$ ,  $\text{en} \equiv \text{H}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2$  a bidentate ligand (Ask Kaia and Erica or the TA's what this ion looks like)
10. What is the VSEPR arrangement (molecular geometry) for carbon tetrachloride, chloroform, and dichloromethane? Do these molecules belong to the same point group?
11. How the normal modes are there for ammonia, chloroform, and benzene.

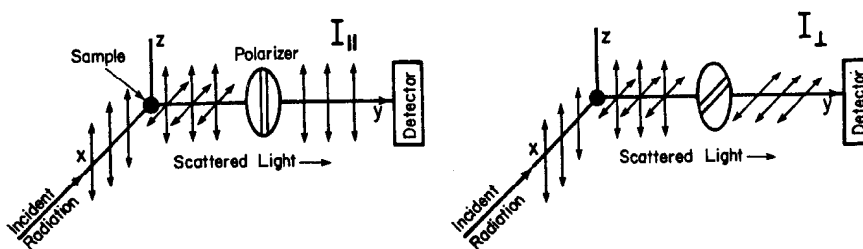
## Conceptual Problems

12. Use your normal modes and character table handouts to assign labels to the peaks in Raman spectra shown below (Note: ignore the broad weak double peak around  $780\text{ cm}^{-1}$ . It is not due to a simple vibrational mode.)

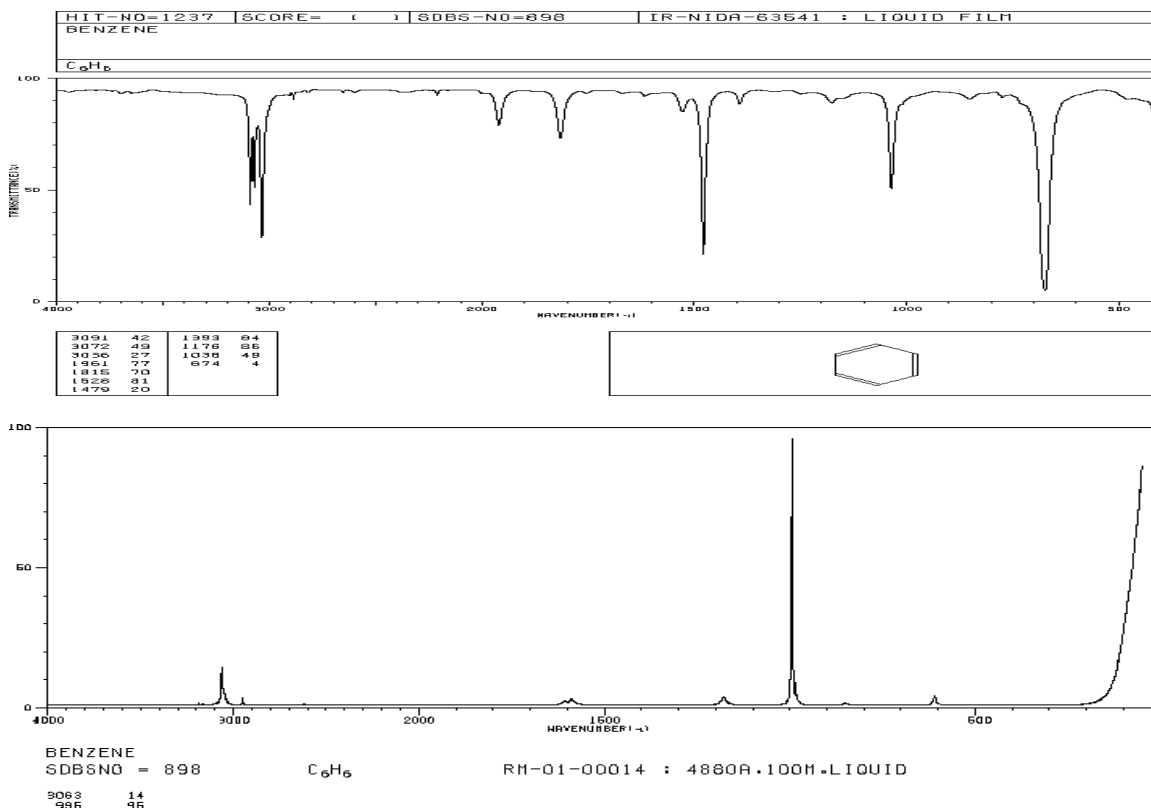


13. Study the schematic of a typical Raman experiment shown in the figure below. Comparison of the  $I_{\parallel}$  and  $I_{\perp}$  spectra given information on the symmetry of the modes corresponding to each peak. As it turns out, totally symmetric modes (those of whose vectors consist of all +1's, e.g.,  $A_1$  or  $A_g$  modes) appear only in the  $I_{\parallel}$  spectra and are completely absent in the  $I_{\perp}$  spectra. Non-totally symmetric modes appear for both configurations. The Raman spectrum of  $\text{CCl}_4$  shown in the previous problem was obtained in the  $I_{\parallel}$  configuration. Based on your peak assignments in that problem draw the  $I_{\perp}$  spectrum for  $\text{CCl}_4$ .

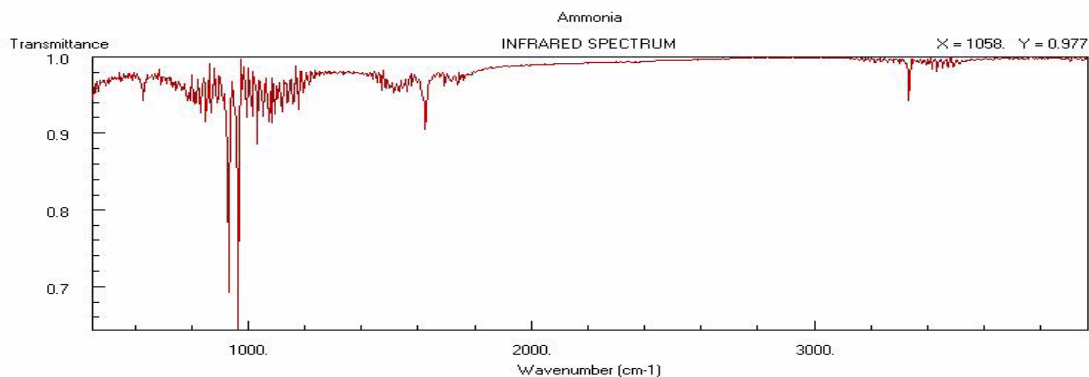
**Fig. 3-43.** To measure the polarization of Raman scattered radiation, a solution is placed at the origin of the coordinate system and  $xz$  plane polarized light is shined on it.  $I_{\parallel}$  is the intensity of the  $yz$ -polarized scattered light.  $I_{\perp}$  is the intensity of the  $xy$ -polarized scattered light. The polarizer is essentially transparent to light in one polarization and opaque to light in any other polarization.



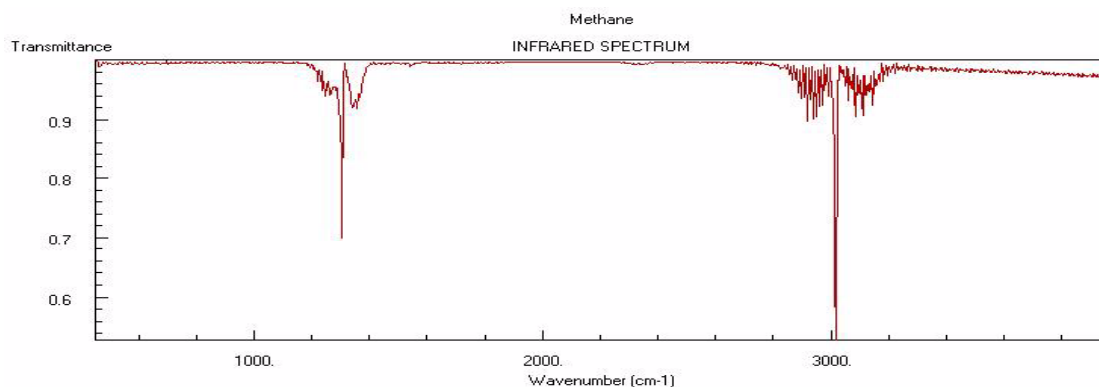
14. Based on the IR and Raman spectra shown below comment on how well the mutual exclusion principle holds even for these liquid phase spectra (careful, the scales are different).



15. Use your normal modes and character table hand out to assign vibrations to the following IR spectrum of ammonia



16. Use your normal modes and character table hand out to assign vibrations to the following IR spectrum of methane

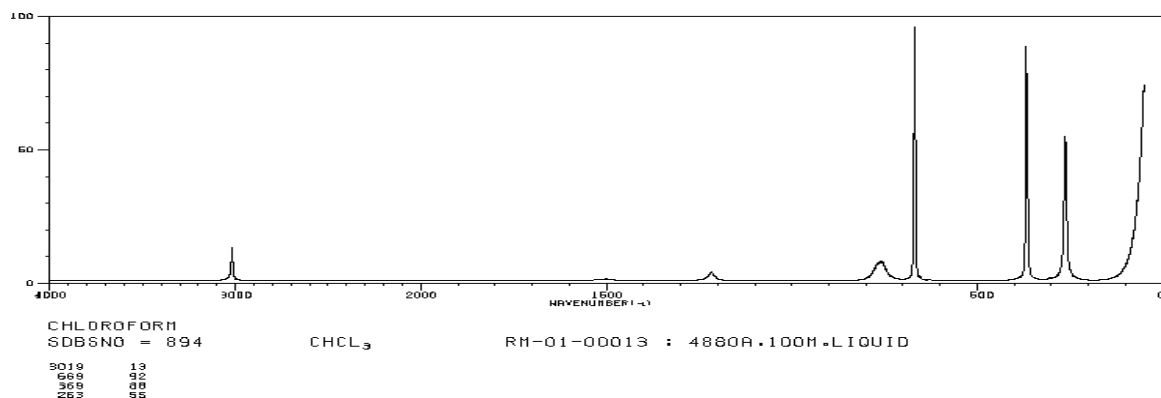


17. The following data for formaldehyde is from the NIST web book database. Construct the IR and Raman spectra for formaldehyde

Symmetry:  $C_{2v}$  Symmetry Number  $\sigma = 2$

Sym. Species	No	Approximate type of mode	Selected Freq. Value	Rating	Infrared Value	Phase	Raman Value	Phase	Comments
$a_1$	1	CH2 s-str	2783	<a href="#">A</a>	2782.5	<a href="#">S</a> gas	2781.6	<a href="#">S</a> liq.	
$a_1$	2	CO str	1746	<a href="#">A</a>	1746.1	<a href="#">VS</a> gas	1742.3	<a href="#">W</a> liq.	
$a_1$	3	CH2 scis	1500	<a href="#">A</a>	1500.1	<a href="#">S</a> gas	1499.7	<a href="#">M</a> liq.	
$b_1$	4	CH2 a-str	2843	<a href="#">A</a>	2843.1	<a href="#">VS</a> gas	2866	<a href="#">W</a> liq.	
$b_1$	5	CH2 rock	1249	<a href="#">A</a>	1249.1	<a href="#">S</a> gas			
$b_2$	6	CH2 wag	1167	<a href="#">A</a>	1167.3	<a href="#">S</a> gas			

18. Normal modes often involve the entire molecule and multiple bonds. The normal modes are also often the most convenient way to describe complicated vibrational motion of polyatomic molecules. Any vibrational motion can be written as a superposition of normal mode vibrations in much the same way any wavefunction can be written as a superposition of eigenfunction. For molecules in which a large discrepancy in weight exists between atoms (or regions), a ‘local’ mode picture is often useful. A local mode is the vibration of one particular bond. Consider chloroform  $\text{HCCl}_3$ . Here one of the normal modes can be well approximated by a local mode describing the C–H stretch. Identify this local mode in the Raman spectrum of chloroform shown below. Also Using the local mode picture draw the Raman spectra of deuterated chloroform,  $\text{DCCl}_3$ . Be as quantitatively correct on your peak positions as possible. (Hint: Treat the local mode as a harmonic oscillator and consider how the frequency scales with mass.)



19. Draw pictures of a ‘local’ mode basis set for carbon dioxide. (You should have four pictures two of which are two-fold degenerate). Draw pictures illustrating the appropriate linear combination of normal modes and rotations required to give the local mode motion. Likewise draw pictures to illustrate the appropriate linear combination of local modes required to give the normal mode motion.

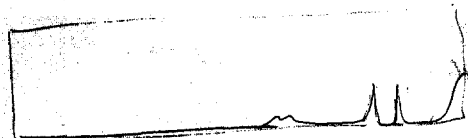


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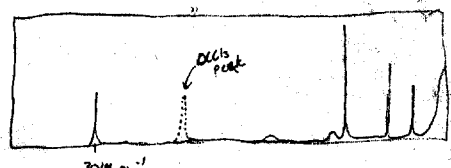
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Benzene has sharp IR modes at 874 cm⁻¹, 1038 cm⁻¹, 1479 cm⁻¹, 3058 cm⁻¹, 3072 cm⁻¹, 3087 cm⁻¹

Benzene has strong Raman modes at 986 cm⁻¹ and 5063 cm⁻¹ (really 992 cm⁻¹)

These modes are different. mutual exclusion holds.

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The mode at 3014 cm⁻¹ is well approximated by the H-C stretch: H-C(H)(H)(H)

The frequency (energy) scales as  $\frac{1}{\sqrt{m}}$  so as we double the mass of H going to D the D-C stretch should be  $\frac{1}{\sqrt{2}}(3014) = 2134 \text{ cm}^{-1}$

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Local mode basis

$$\leftarrow O=C=O, \quad O=C=\vec{O}, \quad \uparrow O=C=O, \quad O=C=O \uparrow$$

2x degenerate      2x degenerate

Normal mode basis

$$\leftarrow O=C=O, \quad \leftarrow O=C=\vec{O}, \quad \uparrow O=C=O \uparrow$$

2x degenerate

$$\leftarrow O=C=O = \leftarrow O=C=O + \leftarrow O=C=\vec{O}$$

$$O=C=\vec{O} = \leftarrow O=C=O - \leftarrow O=C=\vec{O}$$

$$\uparrow O=C=O = \uparrow O=C=O \uparrow + \uparrow O=C=O \downarrow$$

(rotation)

$$O=C=O \uparrow = \uparrow O=C=O \uparrow + \downarrow O=C=O \uparrow$$

(rotation)

$$\leftarrow O=C=O = \leftarrow O=C=O + O=C=\vec{O}$$

$$\leftarrow O=C=\vec{O} = \leftarrow O=C=O - O=C=\vec{O}$$

$$\uparrow O=C=O \uparrow = \uparrow O=C=O + O=C=O \uparrow$$