6.13: An Extensive Set of Group Theory Problems for Chemists

The following table shows the vibrational frequencies of CH_4. Assuming CH_4 belongs to the T_d point group, fill in the gaps in the table. Use S for stretch and B for bend to designate type of vibration.

Frequency	$2917cm^{-1}$	$1534cm^{-1}$	$3019cm^{-1}$	$1306cm^{-1}$
Stretch or Bend	■	■	■	■
Symmetry	■	■	■	■
Activity IR or Raman	■	■	■	■

The following table shows the vibrational frequencies of CD_4. Assuming CD_4 belongs to the T_d point group, fill in the gaps in the table. Use S for stretch and B for bend to designate type of vibration.

Frequency	$2109cm^{-1}$	$1092cm^{-1}$	$2259cm^{-1}$	$966cm^{-1}$
Stretch or Bend	■	■	■	■
Symmetry	■	■	■	■
Activity IR or Raman	■	■	■	■

The following table summarizes the infrared activity CH_2D_2. Assuming it belongs to the C_{2v} point group, complete the table. Use S for stretch and B for bend to designate the type of vibration.

Frequency	2974	2202	1436	1033	1333	3013	1090	2234	1155
Stretch or Bend	■	■	■	■	■	■	■	■	■
Symmetry	■	■	■	■	■	■	■	■	■
Activity IR or Raman	■	■	■	■	■	■	■	■	■

The following table summarizes the infrared activity of CH_3D. Assuming CH_3D belongs to the C_{3v} point group, fill in the gaps in the table. Use S for stretch and B for bend to designate type of vibration.

Frequency	$2945cm^{-1}$	$2200cm^{-1}$	$1300cm^{-1}$	$3017cm^{-1}$	$1471cm^{-1}$	$1155cm^{-1}$
Stretch or Bend	■	■	■	■	■	■
Symmetry	■	■	■	■	■	■
Activity IR or Raman	■	■	■	■	■	■

Formaldehde has vibrational frequencies at 2843, 2776, 1501, 1251, 1746, and 1167 cm^{-1}. How many are IR active and how many are Raman active. Separate them into bends and stretches.

Frequency	2843	2776	1501	1251	1746	1167
Stretch or Bend	A_1	A_1	A_1	B_1	B_2	B_2
Symmetry	Stretch	Stretch	Bend	Bend	Stretch	Bend
Activity IR or Raman	IR, R	IR, R	IR, R	IR, R	IR, R	IR, R

PH_3 (C_{3v}) has IR and Raman active vibrations at 2421, 2327, 1121, and 991 cm^{-1}. PD_3 has IR and Raman active vibrations at 1698, 1694, 806 and 730 cm^{-1}. Make assignments in terms of stretches and bends.

The infrared spectrum of BCl3 shows vibrational bands at 995, 480, and 244 cm^{-1}, while Raman bands appear at 995, 471, and 244 cm^{-1}. Is the geometry of the molecule trigonal pyramid (C_{3v}) or trigonal planar (D_{3h})? Is your answer to this question consistent with chemical bonding principles? Assign symmetry labels to the vibrational bands and identify the stretches and bends.

| Frequency	$995cm^{-1}$	$480cm^{-1}$	$471cm^{-1}$	$224cm^{-1}$
Activity IR or Raman	IR, R	IR	R	IR, R
Symmetry	■	■	■	■
Stretch or Bend	■	■	■	■

CH_3CN has 12 vibrational degrees of freedom, but 8 fundamental vibrational frequencies appear in the infrared at 2999, 2942, 2249, 1440, 1376, 1124, 918, and 380 cm^{-1}. Explain.

The infrared spectrum of methane shows two absorptions: a bend at 1306 cm^{-1} and a stretch at 3019 cm^{-1}. Demonstrate that a symmetry analysis assuming tetrahedral symmetry for methane is consistent with this spectroscopic data. Also predict how many Raman active modes methane should have.

The infrared spectrum of XeF$_4$ has absorptions at 161, 291, and 586 cm^{-1} (two bends, one stretch), while the Raman spectrum has peaks at 218, 524, and 554 cm^{-1} (one bend, two stretches). Is its molecular structure tetrahedral or square planar? References: *J. Am. Chem. Soc.* **1963**, 85, 1927; *J. Phys. Chem.* **1971**, 54, 5247.

Cubane, C$_8$H$_8$, has 42 vibrational degrees of freedom, but only three IR active modes. Cubane belongs to the octahedral point group. Show that group theory predicts three IR active modes. Determine how many vibrational modes will be Raman active. Will there be any coincidences between the IR and Raman active modes? The synthesis and characterization of cubane was reported in 1964 by Philip Eaton and Thomas Cole in JACS **1964**, 86, 3157-3158. They reported three IR bands at 3000, 1231, and 851 cm^{-1}.

When Paquette's group synthesized dodecahedrane, C$_{20}$H$_{20}$, they measured its infrared and Raman spectra (JACS 1**983**, 105, 5446-5450). They found three IR active bands at 2945, 1298, and 728 cm^{-1} and eight Raman frequencies at 2924, 2938, 1324, 1164, 1092, 840, 676, and 480 cm^{-1}. Use group theory to show that these data are consistent with the fact that dodecahedrane has icosahedral symmetry.
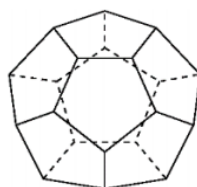
Frequency cm	2938	2924	1324	1164	1092	840	676	480	2945	1298	728
Symmetry	A_g	A_g	H_g	H_g	H_g	H_g	H_g	H_g	T_{1u}	T_{1u}	T_{1u}
$\frac{\text{IR, R}}{\text{Activity}}$	R	R	R	R	R	R	R	R	IR	IR	IR
Stretch or Bend	stretch	stretch	stretch	stretch	stretch	bend	bend	bend	stretch	stretch	bend

Sulfur tetrafluoride represents a difficult case which can't be resolved to complete satisfaction on the basis of IR and Raman data alone. The experimental spectra show eight (five certain and three likely) IR bands and eight (five certain and three likely) Raman bands, and eight (five certain and three likely) coincidences between the two. This information plus nmr spectra lead to the conclusion that the symmetry is C$_{2v}$ or the see-saw structure predicted by VSEPR.

The March 28, 2003 issue of Science reported the synthesis and characterization of Al$_2$H$_6$, the aluminum analog of diborane (therefore, dialane). The researchers reported the following experimental IR frequencies in cm^{-1}: B$_{1u}$ (1932, 836); B$_{2u}$ (1268, 632); B$_{3u}$ (1915, 1408,702). Do a symmetry analysis of Al$_2$H$_6$ which belongs to the D$_{2h}$ point group. How many vibrational modes are there? Which ones are IR active and what are their symmetry designations. The researchers reported that one of the expected low frequency vibrations (~200 cm^{-1}) was not observed. What is the symmetry of this vibrational mode?

Buckminsterfullerene (C60) has four IR active vibrational modes (528, 577, 1180, 1430 cm^{-1}) and ten Raman active modes (273, 436, 496, 710, 773, 110, 1250, 1435, 1470, 1570 cm^{-1}). Demonstrate that the assumption of icosahedral symmetry for C$_{60}$ is consistent with this data.

Do a symmetry analysis of the 60π orbitals of C$_{60}$ and show that the results are in agreement with a Huckel calculation.

The following Raman and IR frequencies have been observed for the tetrahedral P$_4$ molecule. Is the assignment of tetrahedral geometry to this molecule in agreement with the spectroscopic data? Explain.

$$\begin{pmatrix} R & R & R, IR \\ \frac{614}{cm} & \frac{372}{cm} & \frac{466}{cm} \end{pmatrix}$$

Isotopic subsitution for one of the ^{31}P atoms with a ^{32}P atom reduces the symmetry to C_{3v}. Redo the symmetry analysis and predict the number of IR and Raman active vibrational modes.

Tetrahedrane, C_4H_4, belongs to the T_d point group. Use group theory to predict the number of IR and Raman active vibrational modes it has. Predict also the number of stretches and bends will appear in each type of spectroscopy. To date tetrahedrane has not been synthesized.

Do symmetry analyses on cis-difluoroethene (C_{2v}) and trans-difluoroethene (C_{2h}). Can spectroscopic methods (IR and Raman) be used to distinquish between these isomers. Explain. What about 1,1 difluoroethene? What point group does it belong to? Can spectroscopic methods distinguish it from the cis and trans isomers examined above? Cis-MA_2B_2 has C_{2v} symmetry and trans-MA_2B_2 has D_{2h} symmetry. Determine the IR and Raman active modes for each molecule and discuss how such spectroscopic evidence can be used to distinguish the two isomers.

CH_3Cl has IR and Raman active modes at 3017, 2937, 1452, 1355, 1017, and 732 cm^{-1}. Is this data consistent with C3v symmetry assignment for chloromethane?

Diborane, D2h, has 18 vibrational degrees of freedom. Nine modes are Raman active and nine are IR active. There are no coincidences. Do a symmetry analysis of diborane to confirm the assignments made in the table below. Identify stretches and bends. The xy plane is the plane of the paper. The four terminal H atoms of diborane lie in the xz plane and the two bridging atoms lie in the xy plane.
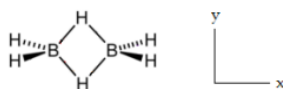

$$
\begin{pmatrix}
\text{D}_{2h} & A_g & A_g & A_g & A_g & B_{1g} & B_{1g} & B_{2g} & B_{2g} & B_{3g} \\
\frac{\text{Raman}}{\text{cm}} & 2524 & 2104 & 1180 & 794 & 1768 & 1035 & 2591 & 920 & 1012 \\
\text{Stretch or Bend} & S & S & B & B & S & B & S & B & B \\
\text{D}_{2h} & A_u & B_{1u} & B_{1u} & B_{1u} & B_{2u} & B_{2u} & B_{3u} & B_{3u} & B_{3u} \\
\frac{\text{IR}}{\text{cm}} & ia & 2612 & 950 & 368 & 1915 & 973 & 2525 & 1606 & 1177 \\
\text{Stretch or Bend} & B & S & B & B & S & B & S & S & B
\end{pmatrix}
$$

The following IR and Raman spectroscopic data is available for cyclopropane, C_3H_6. Demonstrate that this data is consistent with a D_{3h} symmetry assignment for cyclopropane. In addition complete the table below.

$$
\begin{pmatrix}
\frac{\text{Frequency}}{\text{cm}^{-1}} & 3038 & 1479 & 1188 & 3025 & 1438 & 1029 & 866 & 3103 & 854 & 3082 & 188 & 734 \\
\text{Activity} & IR & IR & IR & R,IR & R,IR & R,IR & R,IR & IR & IR & R & R & R \\
\text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\
\text{Stretch or Bend} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare
\end{pmatrix}
$$

$$
\begin{pmatrix}
\frac{\text{Frequency}}{\text{cm}^{-1}} & 3038 & 1479 & 1188 & 3025 & 1438 & 1029 & 866 & 3103 & 854 & 3082 & 188 & 734 \\
\text{Activity} & IR & IR & IR & R,IR & R,IR & R,IR & R,IR & IR & IR & R & R & R \\
\text{Symmetry} & S & S & B & S & S & B & B & \S & B & S & B & B \\
\text{Stretch or Bend} & A1' & A1' & A1' & E' & E' & E' & E' & A2'' & A2'' & E'' & E'' & E''
\end{pmatrix}
$$
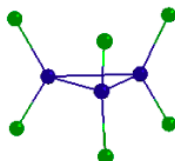
PX_5 has trigonal bipyramidal geometry and therefore belongs to the D_{3h} point group. Use the model provided to do a symmetry analysis of PX_5 by determining Γ_{uma} and Γ_{bonds}.

The following spectroscopic information is available.

$$\begin{pmatrix} \text{Frequency} & 816cm^{-1} & 648cm^{-1} & 947cm^{-1} & 525cm^{-1} & 1024cm^{-1} & 533cm^{-1} & 174cm^{-1} & 520cm^{-1} \\ \text{Activity} & R & R & IR & IR & R,IR & R,IR & R,IR & R \\ \text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{Stretch or Bend} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

Is the symmetry analysis consistent with the spectroscopic data? Explain in detail.

$$\begin{pmatrix} \text{Frequency} & 816cm^{-1} & 648cm^{-1} & 947cm^{-1} & 525cm^{-1} & 1024cm^{-1} & 533cm^{-1} & 174cm^{-1} & 520cm^{-1} \\ \text{Activity} & R & R & IR & IR & R,IR & R,IR & R,IR & R \\ \text{Symmetry} & A_1 & A_1 & A_2 & A_2 & E & E & E & E \\ \text{Stretch or Bend} & S & S & S & B & S & B & B & B \end{pmatrix}$$

The following IR and Raman vibrational data is available for tetrahedral methane. Complete the table. Also show that vibrational data is not consistent with a square planar (D_{4h}) or square pyramid (C_{4v}) geometry.

$$\begin{pmatrix} \text{Frequency} & 3019cm^{-1} & 2717cm^{-1} & 1534cm^{-1} & 1306cm^{-1} \\ \text{Activity} & IR,R & R & R & IR,R \\ \text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{Stretch or Bend} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

The following IR and Raman spectroscopic data is available for ethene, C_2H_4. Demonstrate that this data is consistent with a D_{2h} symmetry assignment for ethene. In addition complete the table below.

$$\begin{pmatrix} \text{Frequency} & 3018 & 3106 & 3019 & 2990 & 1623 & 1444 & 1342 & 1236 & 949 & 943 & 810 \\ \text{Activity} & R & IR & R & IR & R & IR & R & R & R & IR & IR \\ \text{Stretch or Bend} & S & S & S & S & S & B & B & B & B & B & B \\ \text{Symmetry} & Ag & B2u & Ag & B3u & B1g & B1u & Ag & B1g & B2g & B2u & B3u \end{pmatrix}$$

IR and Raman data for $XeOF_4$, which has C_{4v} symmetry. Establish that the symmetry assignment is correct.

$$\begin{pmatrix} \text{Frequency cm} & 926 & 576 & 286 & 232 & 220 & 527 & 609 & 364 & 161 \\ \text{Activity} & R,IR & R,IR & R,IR & R & R & R & R,IR & R,IR & R,IR \\ \text{Symmetry} & A_1 & A_1 & A_1 & \frac{B_1}{B_2} & \frac{B_1}{B_2} & B_1 & E & E & E \\ \text{Stretch or Bend} & S & S & B & B & B & S & S & B & B \end{pmatrix}$$

IR and Raman data for $[PtCl_4]^{2-}$ which has D_{4h} symmetry. Establish that the symmetry assignment is correct.

$$\begin{pmatrix} \text{Frequency} & 332cm^{-1} & 320cm^{-1} & 314cm^{-1} & 183cm^{-1} & 170cm^{-1} & 93cm^{-1} \\ \text{Activity} & R & IR & R & IR & R & IR \\ \text{Symmetry} & A_{1g} & E_u & B_{1g} & E_u & B_{2g} & A_{2u} \\ \text{Stretch or Bend} & S & S & S & B & B & B \end{pmatrix}$$

The vibrational modes of the ions $[BrF_2]^-$ and $[BrF_2]^+$ are given below. Identify which one is A and which one is B.

$$\begin{bmatrix} A & B \\ 596(IR) & 715(IR,R) \\ 442(R) & 706(IR,R) \\ 198(IR) & 366(IR,R) \end{bmatrix}$$

The following spectroscopic data for $[ClO_4]^-$ is available. Show that it is consistent with T_d symmetry.

$$\begin{pmatrix} \text{Frequency} & 1102cm^{-1} & 935cm^{-1} & 628cm^{-1} & 462cm^{-1} \\ \text{Activity} & IR,R & R & IR,R & R \\ \text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{Stretch or Bend} & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

MoF_5 has trigonal bipyramidal geometry and therefore belongs to the D_{3h} point group. Use the model provided to do a symmetry analysis of MoF_5 by determining Γ_{uma} and Γ_{bonds}. The following spectroscopic information is available.

$$\begin{pmatrix} \text{Frequency} & 747cm^{-1} & 732cm^{-1} & 703cm^{-1} & 685cm^{-1} & 500cm^{-1} & 440cm^{-1} & 239cm^{-1} & 203cm^{-1} \\ \text{Activity} & R & IR,R & R & IR & IR & R & IR,R & IR,R \\ \text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{Stretch or Bend} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

The Raman and IR spectra of a sample of N_2F_2 are measured and the results are shown below. Is the sample cis-difluordiazine (C_{2v}) or trans-difluordiazine (C_{2h})?

$$\begin{pmatrix} \text{Frequency} & 1636cm^{-1} & 1010cm^{-1} & 989cm^{-1} & 592cm^{-1} & 412cm^{-1} & 360cm^{-1} \\ \text{Activity} & R & R & IR & R & IR & IR \\ \text{Symmetry} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \\ \text{Stretch or Bend} & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare & \blacksquare \end{pmatrix}$$

Benzene has IR active modes at 675, 1035, 1479, and 3036 cm^{-1}. Demonstrate that this is consistent with D_{6h} symmetry. Separate the vibrations into stretches and bends.

Do a symmetry analysis of the π orbitals of benzene and show that it is consistent with the results of a Huckel calculation on benzene.

Allene, C_3H_4, belongs to the D_{2d} point group.

$$\begin{pmatrix} \frac{\text{Frequency}}{cm^{-1}} & 3015 & 1443 & 1073 & 865 & 3007 & 1957 & 1398 & 3086 & 999 & 841 & 355 \\ \text{Symmetry} & A_1 & A_1 & A_1 & B_1 & B_2 & B_2 & B_2 & E & E & E & E \\ \text{Bend or Stretch} & S & S & B & B & S & S & B & S & B & B & B \end{pmatrix}$$

The following data is available for ethene and deuterated ethene which have D_{2h} symmetry. To each of the vibrational modes determine whether it is a stretch or a bend and its symmetry.

C_2H_4	C_2D_4	Activity	Stretch / Bend	Symmetry
3108	2304	R	$\blacksquare$	$\blacksquare$
3106	2345	IR	$\blacksquare$	$\blacksquare$
3018	2251	R	$\blacksquare$	$\blacksquare$
2990	2200	IR	$\blacksquare$	$\blacksquare$
1623	1515	R	$\blacksquare$	$\blacksquare$
1444	1078	IR	$\blacksquare$	$\blacksquare$
1342	981	R	$\blacksquare$	$\blacksquare$
1236	1009	R	$\blacksquare$	$\blacksquare$
1007	726	IA	$\blacksquare$	$\blacksquare$
949	721	R	$\blacksquare$	$\blacksquare$
943	780	IR	$\blacksquare$	$\blacksquare$
810	586	IR	$\blacksquare$	$\blacksquare$

BH_3 has D_{3h} symmetry. Determine the reducible representation for the hydrogen 1s orbitals (collectively). What linear combination of boron valence orbitals has the same symmetry.

CH_4 has T_d symmetry. Determine the reducible representation for the hydrogen 1s orbitals (collectively). What linear combination of carbon valence orbitals has the same symmetry.

The following vibrational frequencies are available for cis-dichloroethene. Complete the table assuming that the molecule has C_{2v} symmetry.

Frequency cm	3077	1587	1179	711	173	876	406	697	3072	1303	857	571
Symmetry	A_1	A_1	A_1	A_1	A_1	A_2	A_2	B_1	B_2	B_2	B_2	B_2
IR Activity	yes	yes	yes	yes	yes	no	no	yes	yes	yes	yes	yes
Raman Activity	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Type	stretch	stretch	stretch	bend	bend	bend	bend	bend	bend	bend	stretch	bend

The following vibrational frequencies are available for trans-dichloroethene. Complete the table assuming that the molecule has C_{2h} symmetry.

Frequency cm	3073	1578	1274	846	350	763	900	227	3090	1200	828	250
Symmetry	A_g	A_g	A_g	A_g	A_g	B_g	A_u	A_u	B_u	B_u	B_u	B_u
IR Activity	no	no	no	no	no	no	yes	yes	yes	yes	yes	yes
Raman Activity	yes	yes	yes	yes	yes	yes	no	no	no	no	no	no
Type	stretch	stretch	stretch	bend	bend	bend	bend	bend	bend	bend	stretch	bend

The following vibrational frequencies are available for 1,1-dichloroethene. Complete the table assuming that the molecule has C_{2v} symmetry.

Frequency cm	3035	1627	1400	603	299	686	875	460	3130	1095	800	372
Symmetry	A_1	A_1	A_1	A_1	A_1	A_2	A_2	B_1	B_2	B_2	B_2	B_2
IR Activity	yes	yes	yes	yes	yes	no	no	yes	yes	yes	yes	yes
Raman Activity	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Type	stretch	stretch	stretch	bend	bend	bend	bend	bend	bend	bend	stretch	bend

Pyrazine has D_{2h} symmetry. Confirm the entries in the following table.

Symmetry	A_g	A_g	A_g	A_g	A_g	B_{1g}	B_{2g}	B_{2g}	B_{3g}	B_{3g}	B_{3g}	B_{3g}
Frequency cm	3054	1578	1230	1015	596	757	919	703	3041	1524	1118	641
Type	Stretch	Stretch	Stretch	Bend	Bend	Bend	Bend	Stretch	Stretch	Bend	Bend	
$\frac{Ir, R}{Activity} R$	R	R	R	R	R	R	R	R	R	R	R	
○	○	○	○	○	○	○	○	○	○	○	○	○
Symmetry	A_u	A_u	B_{1u}	B_{1u}	B_{1u}	B_{1u}	B_{2u}	B_{2u}	B_{2u}	B_{2u}	B_{3u}	B_{3u}
Frequency cm	na	363	3066	1484	1135	1021	3066	1418	1346	1063	804	416
Type	Bend	Bend	Stretch	Stretch	Bend	Bend	Stretch	Stretch	Stretch	Bend	Bend	Bend
$\frac{IR,R}{Activity}$	IR	IR	IR	IR	IR	IR	IR	IR	IR	IR	IR	IR
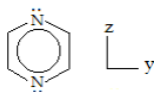
Is the following spectroscopic data consistent with the assignment of D_{4h} symmetry to tetrachloroplatinate, $PtCl_4^{2-}$?

Frequency	$332 cm^{-1}$	$314 cm^{-1}$	$170 cm^{-1}$	$320 cm^{-1}$	$183 cm^{-1}$	$93 cm^{-1}$
Activity	R	R	R	IR	IR	IR
Symmetry	■	■	■	■	■	■
Stretch or Bend	■	■	■	■	■	■

Frequency	$332 cm^{-1}$	$314 cm^{-1}$	$170 cm^{-1}$	$320 cm^{-1}$	$183 cm^{-1}$	$93 cm^{-1}$
Activity	R	R	R	IR	IR	IR
Symmetry	A_{1g}	B_{1g}	B_{2g}	E_u	A_{2u}	B_{2u}
Stretch or Bend	S	S	B	S	B	B

Given the following spectroscopic data determine the whether $InCl_5^{2-}$ has C_{4v} or D_{3h} symmetry.

Frequency cm	294	287	283	274	193	165	143	140	108
Activity	IR, R	R	IR, R	IR, R	R	R	IR, R	IR, R	IR, R
Symmetry	■	■	■	■	■	■	■	■	■
Stretch or Bend	■	■	■	■	■	■	■	■	■

Symmetry analysis supports C_{4v} symmetry as indicated below.

Activity	IR	R	Coincidences
Exp	6	9	6
C_{4v}	6	9	6
D_{3h}	5	6	3

Do symmetry analyses on the three $C_{10}H_8$ isomers: azulene (C_{2v}), fulvalene (D_{2h}) and napthalene (D_{2h}). Determine whether IR and Raman spectroscopy can be used to distinguish between the isomers. Completing the table below should facilitate answering the question.
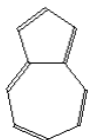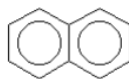
Azulene   Fulvalene   Napthalene
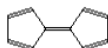
$$
\begin{pmatrix}
\text{Molecule} & \frac{\text{IR}}{\text{Stretches}} & \frac{\text{Raman}}{\text{Stretches}} & \text{Coincidences} & \frac{\text{IR}}{\text{bends}} & \frac{\text{Raman}}{\text{Bends}} & \text{Coincidences} & \frac{\text{InActive}}{\text{Modes}} \\
\text{Azulene} & 19 & 19 & 19 & 23 & 29 & 23 & 0 \\
\text{Fulvalene} & 9 & 10 & 0 & 11 & 14 & 0 & 4 \\
\text{Napthalene} & 9 & 10 & 0 & 11 & 14 & 0 & 4
\end{pmatrix}
$$

Propellane has, as shown below, has D$_{3h}$ symmetry. To date it hasn't been synthesized, but theoreticians debate whether or not it has a bridging carbon-carbon bond as shown in the figure. Do a symmetry analysis with and without the bridging bond to determine whether vibrational spectroscopy could decide the issue if the molecule ever became available.
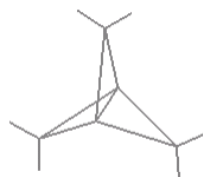
$$
\begin{pmatrix}
\text{Propellane} & \frac{\text{IR}}{\text{Stretches}} & \frac{\text{Raman}}{\text{Stretches}} & \frac{\text{IR}}{\text{Bends}} & \frac{\text{Raman}}{\text{Bends}} & \frac{\text{InActive}}{\text{Modes}} \\
\text{Bond} & 4 & 9 & 4 & 6 & 3 \\
\text{No Bond} & 4 & 8 & 4 & 7 & 3
\end{pmatrix}
$$

Raman spectroscopy would be required to answer this question, because it indicates one less stretch and one more bend in the vibrational spectroscopy. This makes sense since the number of vibrational degrees of freedom must be conserved. If there is one less bond, there must be one less stretch and therefore one more bend. In this case, the change is observable (hypothetically) in Raman spectroscopy.

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