

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 BCl_3 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 | 995 $\cdot \text{cm}^{-1}$ | 480 $\cdot \text{cm}^{-1}$ | 471 $\cdot \text{cm}^{-1}$ | 244 $\cdot \text{cm}^{-1}$ |
| Activity | | | | |
| IR or Raman | IR, R | IR | R | IR, R |
| Symmetry | ■ | ■ | ■ | ■ |
| Stretch or Bend | ■ | ■ | ■ | ■ |

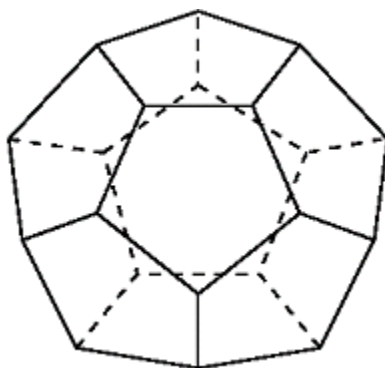
CH_3CN has 12 vibrational degrees of freedom, but 8 fundamental vibrational frequencies appear in the infrared at 2999, 2942, 2249, 1440, 1376, 1124, 918, and 380 cm^{-1} . Explain.

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_8H_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, $\text{C}_{20}\text{H}_{20}$, they measured its infrared and Raman spectra (*JACS* **1983**, 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} |
| <u>IR, R</u> Activity | R | R | R | R | R | R | R | R | IR | IR | IR |
| StretchOrBend | stretch | stretch | stretch | stretch | stretch | bend | bend | bend | stretch | stretch | ben |

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 Al₂H₆, 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 Al₂H₆ 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 C₆₀ is consistent with this data.

Do a symmetry analysis of the 60 π orbitals of C₆₀ and show that the results are in agreement with a Huckel calculation.

The following Raman and IR frequencies have been observed for the tetrahedral P₄ molecule. Is the assignment of tetrahedral geometry to this molecule in agreement with the spectroscopic data? Explain.

| | | |
|------------|------------|------------|
| R | R | R, IR |
| <u>614</u> | <u>372</u> | <u>466</u> |
| cm | cm | cm |

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

Tetrahydrane, C₄H₄, 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 tetrahydrane has not been synthesized.

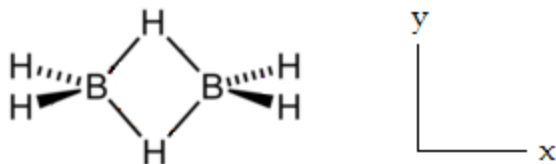
Do symmetry analyses on cis-difluoroethene (C_{2v}) and trans-difluoroethene (C_{2h}). Can spectroscopic methods (IR and Raman) be used to distinguish between these isomers. Explain.

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-MA₂B₂ has C_{2v} symmetry and trans-MA₂B₂ 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.

CH₃Cl has IR and Raman active modes at 3017, 2937, 1452, 1355, 1017, and 732 cm⁻¹. Is this data consistent with C_{3v} symmetry assignment for chloromethane?

Diborane, D_{2h} , 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.

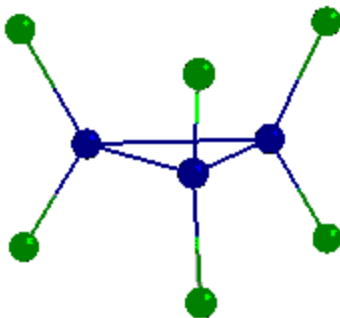


| | | | | | | | | | |
|--------------------|-------|----------|----------|----------|----------|----------|----------|----------|----------|
| D_{2h} | A_g | A_g | A_g | A_g | B_{1g} | B_{1g} | B_{2g} | B_{2g} | B_{3g} |
| <u>Raman</u> cm | 2524 | 2104 | 1180 | 794 | 1768 | 1035 | 2591 | 920 | 1012 |
| StretchOrBend | S | S | B | B | S | B | S | B | B |
| D_{2h} | A_u | B_{1u} | B_{1u} | B_{1u} | B_{2u} | B_{2u} | B_{3u} | B_{3u} | B_{3u} |
| <u>IR</u> cm | ia | 2612 | 950 | 368 | 1915 | 973 | 2525 | 1606 | 1177 |
| StretchOrBend | B | S | B | B | S | B | S | S | B |

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.

| | | | | | | | | | | | | |
|-------------------------------|------|------|------|------|------|------|------|------|-----|------|------|-----|
| <u>Frequency</u> cm^{-1} | 3038 | 1479 | 1188 | 3025 | 1438 | 1029 | 866 | 3103 | 854 | 3082 | 1188 | 734 |
| Activity | IR | IR | IR | R,IR | R,IR | R,IR | R,IR | IR | IR | R | R | R |
| Symmetry | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

| | | | | | | | | | | | | |
|-------------------------------|--------|--------|--------|------|------|------|------|---------|---------|-------|-------|-------|
| <u>Frequency</u> cm^{-1} | 3038 | 1479 | 1188 | 3025 | 1438 | 1029 | 866 | 3103 | 854 | 3082 | 1188 | 734 |
| Activity | R | R | R | R,IR | R,IR | R,IR | R,IR | IR | IR | R | R | R |
| Type | S | S | B | S | S | B | B | S | B | S | B | B |
| Symmetry | A_1' | A_1' | A_1' | E' | E' | E' | E' | A_2'' | A_2'' | E'' | E'' | E'' |



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.

| | | | | | | | | |
|---------------|----------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|
| Frequency | $816 \cdot \text{cm}^{-1}$ | $648 \cdot \text{cm}^{-1}$ | $947 \cdot \text{cm}^{-1}$ | $525 \cdot \text{cm}^{-1}$ | $1024 \cdot \text{cm}^{-1}$ | $533 \cdot \text{cm}^{-1}$ | $174 \cdot \text{cm}^{-1}$ | $520 \cdot \text{cm}^{-1}$ |
| Activity | R | R | IR | IR | R, IR | R, IR | R, IR | R |
| Symmetry | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

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

| | | | | | | | | |
|---------------|----------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|
| Frequency | $816 \cdot \text{cm}^{-1}$ | $648 \cdot \text{cm}^{-1}$ | $947 \cdot \text{cm}^{-1}$ | $525 \cdot \text{cm}^{-1}$ | $1024 \cdot \text{cm}^{-1}$ | $533 \cdot \text{cm}^{-1}$ | $174 \cdot \text{cm}^{-1}$ | $520 \cdot \text{cm}^{-1}$ |
| Activity | R | R | IR | IR | R, IR | R, IR | R, IR | R |
| Symmetry | A_1 | A_1 | A_2 | A_2 | E | E | E | E |
| StretchOrBend | S | S | S | B | S | B | B | B |

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.

| | | | | |
|---------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Frequency | $3019 \cdot \text{cm}^{-1}$ | $2717 \cdot \text{cm}^{-1}$ | $1534 \cdot \text{cm}^{-1}$ | $1306 \cdot \text{cm}^{-1}$ |
| Activity | IR, R | R | R | IR, R |
| Symmetry | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ |

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.

| | | | | | | | | | | | |
|------------------|-------|----------|-------|----------|----------|----------|-------|----------|----------|----------|----------|
| Frequency | 3108 | 3106 | 3019 | 2990 | 1623 | 1444 | 1342 | 1236 | 949 | 943 | 810 |
| cm^{-1} | | | | | | | | | | | |
| Activity | R | IR | R | IR | R | IR | R | R | R | IR | IR |
| StretchOrBend | S | S | S | S | S | B | B | B | B | B | B |
| Symmetry | A_g | B_{2u} | A_g | B_{3u} | B_{1g} | B_{1u} | A_g | B_{1g} | B_{2g} | B_{2u} | B_{3u} |

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

| | | | | | | | | | |
|----------------|-------|-------|-------|-------------------|-------------------|-------|-------|-------|-------|
| Frequency · cm | 926 | 576 | 286 | 232 | 220 | 527 | 609 | 364 | 161 |
| Activity | R, IR | R, IR | R, IR | R | R | R | R, IR | R, IR | R, IR |
| Symmetry | A_1 | A_1 | A_1 | $\frac{B_1}{B_2}$ | $\frac{B_1}{B_2}$ | B_1 | E | E | E |
| StretchOrBend | S | S | B | B | B | S | S | B | B |

IR and Raman data for $[\text{PtCl}_4]^{2-}$ which has D_{4h} symmetry. Establish that the symmetry assignment is correct.

| | | | | | | |
|---------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|
| Frequency | $332\cdot\text{cm}^{-1}$ | $320\cdot\text{cm}^{-1}$ | $314\cdot\text{cm}^{-1}$ | $183\cdot\text{cm}^{-1}$ | $170\cdot\text{cm}^{-1}$ | $93\cdot\text{cm}^{-1}$ |
| Activity | R | IR | R | IR | R | IR |
| Symmetry | A_{1g} | E_u | B_{1g} | E_u | B_{2g} | A_{2u} |
| StretchOrBend | S | S | S | B | B | B |

The vibrational modes of the ions $[\text{BrF}_2]^-$ and $[\text{BrF}_2]^+$ are given below. Identify which one is A and which one is B.

| | |
|---------|------------|
| A | B |
| 596(IR) | 715(IR, R) |
| 442(R) | 706(IR, R) |
| 198(IR) | 366(IR, R) |

The following spectroscopic data for $[\text{ClO}_4]^-$ is available. Show that it is consistent with T_d symmetry.

| | | | | |
|---------------|---------------------------|--------------------------|--------------------------|--------------------------|
| Frequency | $1102\cdot\text{cm}^{-1}$ | $935\cdot\text{cm}^{-1}$ | $628\cdot\text{cm}^{-1}$ | $462\cdot\text{cm}^{-1}$ |
| Activity | IR, R | R | IR, R | R |
| Symmetry | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ |

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.

| | | | | | | | | |
|---------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Frequency | $747\cdot\text{cm}^{-1}$ | $732\cdot\text{cm}^{-1}$ | $703\cdot\text{cm}^{-1}$ | $685\cdot\text{cm}^{-1}$ | $500\cdot\text{cm}^{-1}$ | $440\cdot\text{cm}^{-1}$ | $239\cdot\text{cm}^{-1}$ | $203\cdot\text{cm}^{-1}$ |
| Activity | R | IR, R | R | IR | IR | R | IR, R | IR, R |
| Symmetry | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

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})?

| | | | | | | |
|---------------|---------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Frequency | $1636\cdot\text{cm}^{-1}$ | $1010\cdot\text{cm}^{-1}$ | $989\cdot\text{cm}^{-1}$ | $592\cdot\text{cm}^{-1}$ | $412\cdot\text{cm}^{-1}$ | $360\cdot\text{cm}^{-1}$ |
| Activity | R | R | IR | R | IR | IR |
| Symmetry | ■ | ■ | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ | ■ | ■ |

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.

| | | | | | | | | | | | |
|------------------------|-------|-------|-------|-------|-------|-------|-------|------|-----|-----|-----|
| Frequency cm^{-1} | 3015 | 1443 | 1073 | 865 | 3007 | 1957 | 1398 | 3086 | 999 | 841 | 355 |
| Symmetry | A_1 | A_1 | A_1 | B_1 | B_2 | B_2 | B_2 | E | E | E | E |
| BendOrStretch | S | S | B | B | S | S | B | S | B | B | B |

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.

| C2H4 | C2D4 | Activity | $\frac{\text{Stretch}}{\text{Bend}}$ | Symmetry |
|------|------|----------|--------------------------------------|----------|
| 3108 | 2304 | R | ■ | ■ |
| 3106 | 2345 | IR | ■ | ■ |
| 3019 | 2251 | R | ■ | ■ |
| 2990 | 2200 | IR | ■ | ■ |
| 1623 | 1515 | R | ■ | ■ |
| 1444 | 1078 | IR | ■ | ■ |
| 1342 | 981 | R | ■ | ■ |
| 1236 | 1009 | R | ■ | ■ |
| 1007 | 726 | IA | ■ | ■ |
| 949 | 721 | R | ■ | ■ |
| 943 | 780 | IR | ■ | ■ |
| 810 | 586 | IR | ■ | ■ |

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 |
| $\frac{\text{IR}}{\text{Activity}}$ | yes | yes | yes | yes | yes | no | no | yes | yes | yes | yes | yes |
| $\frac{\text{Raman}}{\text{Activity}}$ | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes |
| Type | stretch | stretch | stretch | bend | bend | bend | bend | bend | stretch | bend | stretch | bend |

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

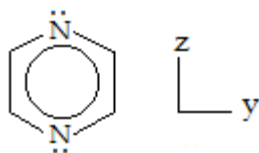
| | | | | | | | | | | | | |
|--------------------------|---------|---------|---------|-------|-------|-------|-------|-------|---------|-------|---------|-------|
| Frequency·cm | 3073 | 1578 | 1274 | 846 | 350 | 763 | 900 | 227 | 3090 | 1200 | 828 | 250 |
| Symmetry | A_g | A_g | A_g | A_g | A_g | B_g | A_u | A_u | B_u | B_u | B_u | B_u |
| <u>IR</u> Activity | no | no | no | no | no | no | yes | yes | yes | yes | yes | yes |
| <u>Raman</u> Activity | yes | yes | yes | yes | yes | yes | no | no | no | no | no | no |
| Type | stretch | stretch | stretch | bend | bend | bend | bend | bend | stretch | 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 | B_1 | B_1 | B_2 | B_2 | B_2 | B_2 |
| <u>IR</u> Activity | yes | yes | yes | yes | yes | no | yes | yes | yes | yes | yes | yes |
| <u>Raman</u> Activity | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes |
| Type | stretch | stretch | stretch | bend | bend | bend | bend | bend | stretch | 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 | Bend | Stretch | Stretch | Bend | Bend |
| <u>IR,R</u> Activity | R | R | R | R | R | R | R | R | R | R | R | R |
| o | o | o | o | o | o | o | o | o | o | o | o | o |
| 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 |
| <u>IR,R</u> 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 | $332 \cdot cm^{-1}$ | $314 \cdot cm^{-1}$ | $170 \cdot cm^{-1}$ | $320 \cdot cm^{-1}$ | $183 \cdot cm^{-1}$ | $93 \cdot cm^{-1}$ |
| Activity | R | R | R | IR | IR | IR |
| Symmetry | ■ | ■ | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ | ■ | ■ |

| | | | | | | |
|---------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|
| Frequency | $332 \cdot cm^{-1}$ | $314 \cdot cm^{-1}$ | $170 \cdot cm^{-1}$ | $320 \cdot cm^{-1}$ | $183 \cdot cm^{-1}$ | $93 \cdot cm^{-1}$ |
| Activity | R | R | R | IR | IR | IR |
| Symmetry | A_{1g} | B_{1g} | B_{2g} | E_u | A_{2u} | B_{2u} |
| StretchOrBend | S | S | B | S | B | B |

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

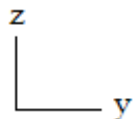
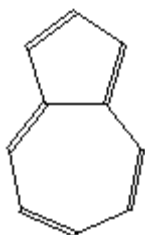
| | | | | | | | | | |
|---------------|------|-----|------|------|-----|-----|------|------|------|
| Frequency·cm | 294 | 287 | 283 | 274 | 193 | 165 | 143 | 140 | 108 |
| Activity | IR,R | R | IR,R | IR,R | R | R | IR,R | IR,R | IR,R |
| Symmetry | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| StretchOrBend | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

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

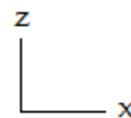
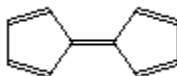
| | | | |
|----------|----|---|--------------|
| Activity | IR | R | Coincidences |
| Exp | 6 | 9 | 6 |
| C_{4v} | 6 | 9 | 6 |
| D_{3h} | 5 | 6 | 3 |

Do symmetry analyses on the three $C_{10}H_8$ isomers: azulene (C_{2v}), fulvalene (D_{2h}) and naphthalene (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.

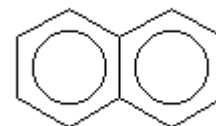
Azulene



Fulvalene

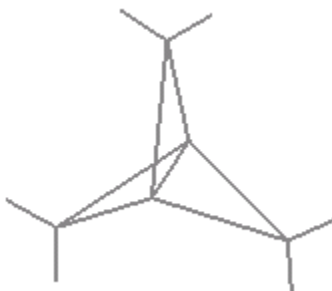


Naphthalene



| Molecule | IR Stretches | Raman Stretches | Coincidences | IR Bends | Raman Bends | Coincidences | InActive Modes |
|-------------|--------------|-----------------|--------------|----------|-------------|--------------|----------------|
| Azulene | 19 | 19 | 19 | 23 | 29 | 23 | 0 |
| Fulvalene | 9 | 10 | 0 | 11 | 14 | 0 | 4 |
| Naphthalene | 9 | 10 | 0 | 11 | 14 | 0 | 4 |

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.



| Propellane | IR | Raman | IR | Raman | InActive |
|------------|-----------|-----------|-------|-------|----------|
| | Stretches | Stretches | Bends | Bends | Modes |
| Bond | 4 | 9 | 4 | 6 | 3 |
| NoBond | 4 | 8 | 4 | 7 | 3 |

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.