

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· cm^{-1}	480· cm^{-1}	471· cm^{-1}	244· cm^{-1}
<u>Activity</u>	IR, R	IR	R	IR, R
IRorRaman	IR, R	IR	R	IR, R
Symmetry	■	■	■	■
StretchOrBend	■	■	■	■

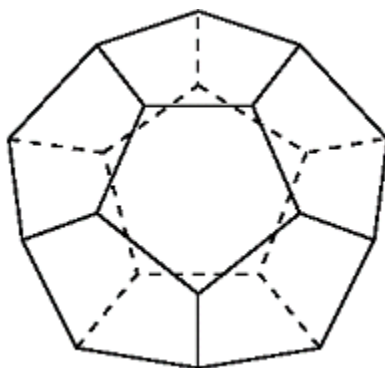
CH_3CN has 12 vibrational degrees of freedom, but 8 fundamental vibrational frequencies appear in the infrared at 2999, 2942, 2249, 1440, 1376, 1124, 918, and 380 cm^{-1} . Explain.

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.

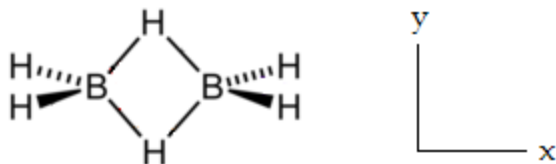
Do symmetry analyses on cis-difluoroethene (C_{2v}) and trans-difluoroethene (C_{2h}). Can spectroscopic methods (IR and Raman) be used to distinguish between these isomers. Explain.

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.

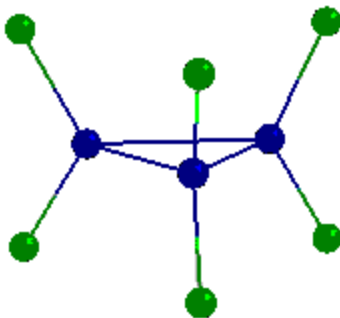


D_{2h}	A_g	A_g	A_g	A_g	B_{1g}	B_{1g}	B_{2g}	B_{2g}	B_{3g}
<u>Raman</u> cm	2524	2104	1180	794	1768	1035	2591	920	1012
StretchOrBend	S	S	B	B	S	B	S	B	B
D_{2h}	A_u	B_{1u}	B_{1u}	B_{1u}	B_{2u}	B_{2u}	B_{3u}	B_{3u}	B_{3u}
<u>IR</u> cm	ia	2612	950	368	1915	973	2525	1606	1177
StretchOrBend	B	S	B	B	S	B	S	S	B

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 cm^{-1}	3108	3106	3019	2990	1623	1444	1342	1236	949	943	810
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.

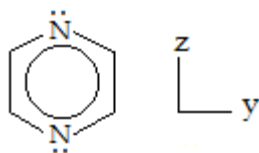
Frequency·cm	3073	1578	1274	846	350	763	900	227	3090	1200	828	250
Symmetry	A_g	A_g	A_g	A_g	A_g	B_g	A_u	A_u	B_u	B_u	B_u	B_u
<u>IR</u> Activity	no	no	no	no	no	no	yes	yes	yes	yes	yes	yes
<u>Raman</u> Activity	yes	yes	yes	yes	yes	yes	no	no	no	no	no	no
Type	stretch	stretch	stretch	bend	bend	bend	bend	bend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

Frequency	$332 \cdot \text{cm}^{-1}$	$314 \cdot \text{cm}^{-1}$	$170 \cdot \text{cm}^{-1}$	$320 \cdot \text{cm}^{-1}$	$183 \cdot \text{cm}^{-1}$	$93 \cdot \text{cm}^{-1}$
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.

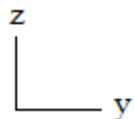
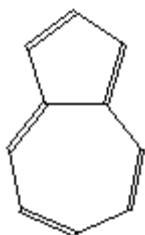
Frequency·cm	294	287	283	274	193	165	143	140	108
Activity	IR,R	R	IR,R	IR,R	R	R	IR,R	IR,R	IR,R
Symmetry	■	■	■	■	■	■	■	■	■
StretchOrBend	■	■	■	■	■	■	■	■	■

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

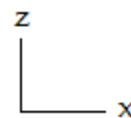
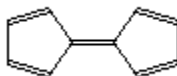
Activity	IR	R	Coincidences
Exp	6	9	6
C_{4v}	6	9	6
D_{3h}	5	6	3

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.

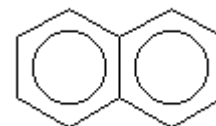
Azulene



Fulvalene

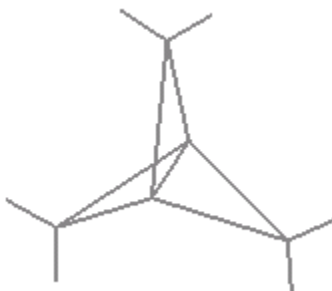


Naphthalene



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.