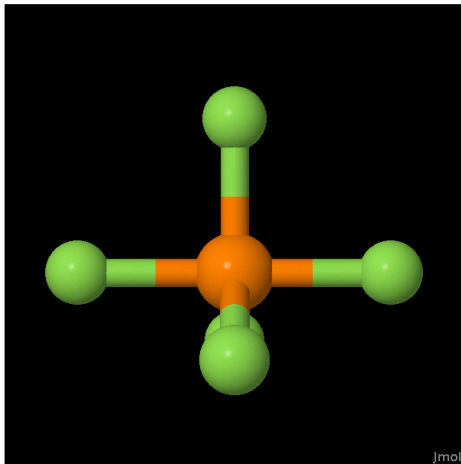


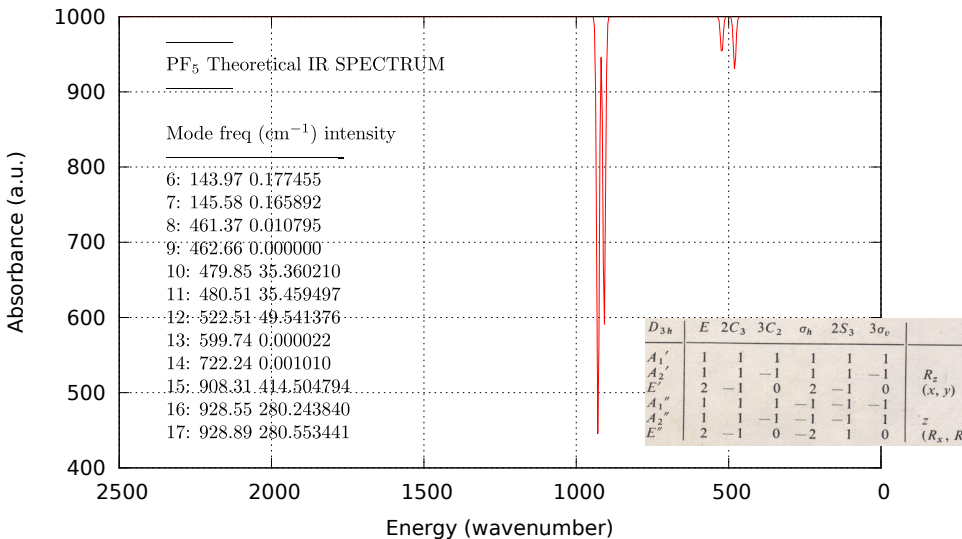
Connecting Symmetry, Vibrational Spectroscopy, and Inorganic Chemistry



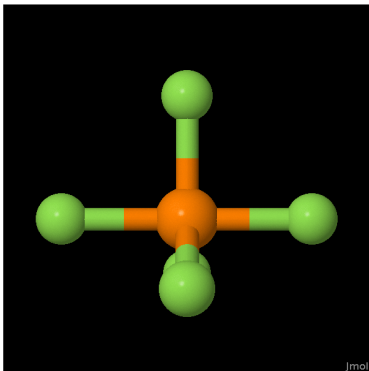
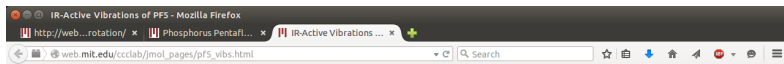
Menu to select vibration:

010: 480 cm⁻¹ ▾

spin



Animate the Normal Modes of PF₅



Menu to select vibration:

010: 480 cm⁻¹

spin



Massachusetts
Institute of
Technology



Selection Rule for Raman Spectroscopy

- The Raman selection rule is based upon changes in molecular polarizability during a vibration
- The molecular polarizability may undergo a change during a molecular vibration
- If the vibration or “normal mode” has the same symmetry as xz , yz , xy , x^2 , y^2 , or z^2 then it involves a change in the molecular quadrupole moment during the vibration, by symmetry, and otherwise not
- There is a mutual exclusion rule for point groups having an inversion center: no vibration may be both IR and Raman active

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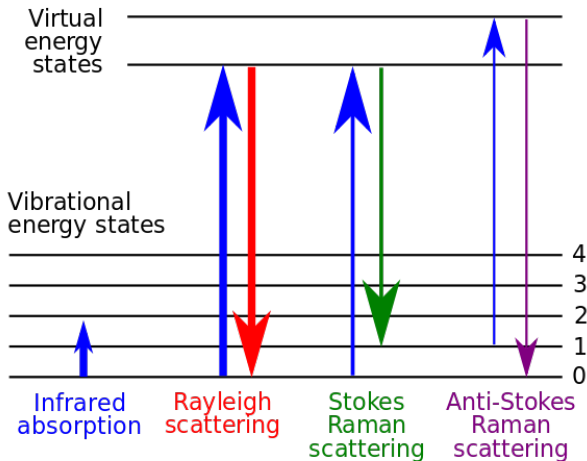
D_{6h} Illustrates the Rule of Mutual Exclusion

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	
1	Character Table																	
2																		
4		D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_6$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$				
5		A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$	
6		A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_x			
7		B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1				
8		B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1				
9		E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)		
10		E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$		
11		A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1				
12		A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	1	1	z		
13		B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	-1				
14		B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	1				
15		E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)			
16		E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0				
17																		
18		Representation																
19		Γ	15	-2	0	1	-1	1	-3	-2	0	7	1		3			
20																		
21		Reduced Representation																
22		1 A_{1g}																
23		0 A_{2g}																
24		0 B_{1g}																
25		1 B_{2g}																
26		0 E_{1g}																
27		2 E_{2g}																
28		0 A_{1u}																
29		1 A_{2u}																
30		1 B_{1u}																
31		1 B_{2u}																
32		2 E_{1u}																
33		1 E_{2u}																

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Technology

Raman is a Light Scattering Phenomenon



AsP₃ Characterization by Raman Spectroscopy

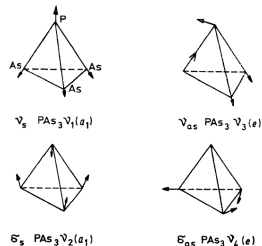
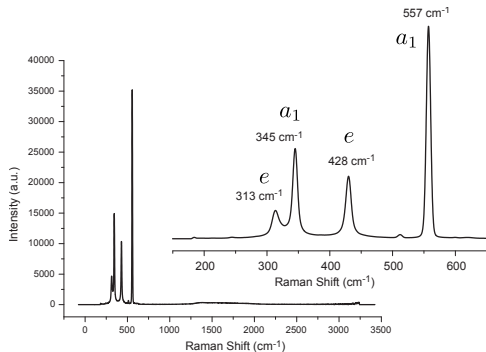
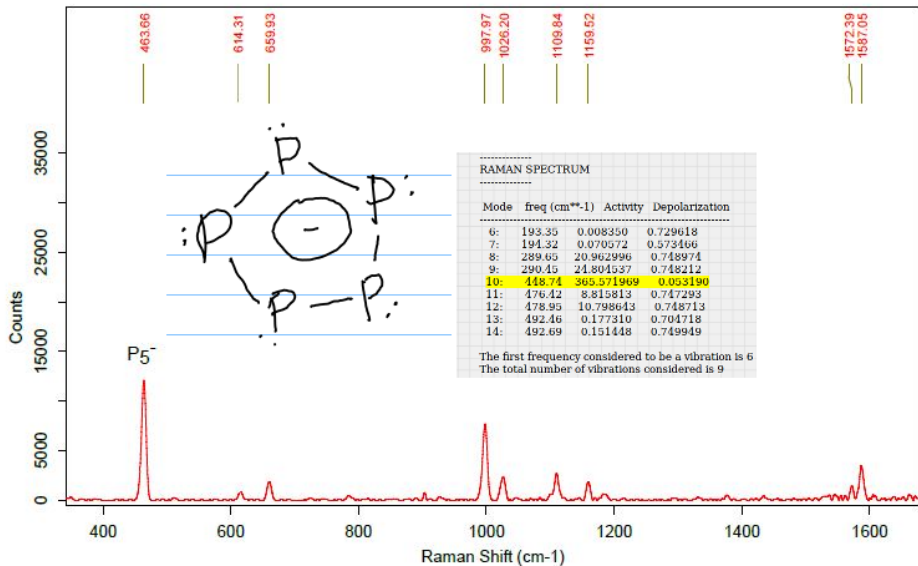


FIGURE 2 Approximate pictorial representation of the symmetry co-ordinates for the C_{3v}X₄Y₃; only one of the components of each degenerate mode (ν_3 and ν_4) is shown



Raman Spectrum of [PPN][P5]

Using REDUCE for Vibrational Analysis

The program only needs to know the # unshifted atoms for each class of operation

```
REDUCE - DOS in a BOX
Point groups available in this program are:
 1.Cs      10.D2      19.D6d
 2.Ci      11.D3      20.D2h
 3.C2      12.D4      21.D3h
 4.C2v     13.D5      22.D4h
 5.C3v     14.D6      23.D5h
 6.C4v     15.D2d   24.D6h
 7.C5v     16.D3d   25.S4
 8.C6v     17.D4d   26.Td
 9.C2h     18.D5d   27.Oh

and the infinite point groups:

28 .C**v
29 .D**h

Select the group by entering a number (1-29).
?
```

Using REDUCE for Vibrational Analysis

The program only needs to know the # unshifted atoms for each class of operation

```
REDUCE - DOS in a BOX
for each symmetry operator in the order shown below.
(Please hit enter after each number.)

E      2C5      2C5^2 5C2      Sigh 2S5      2S5^3 5Sigu
? 5
? 0
? 0
? 1
? 5
? 0
? 0
? 1

This summarizes your entries:

1      2      3      4      5      6      7      8
E      2C5      2C5^2 5C2      Sigh 2S5      2S5^3 5Sigu
5      0      0      1      5      0      0      1

Are all your entries correct? (Y or N)
?
```

Using REDUCE for Vibrational Analysis

The program only needs to know the # unshifted atoms for each class of operation

```
REDUCE - DOS in a BOX

The irreducible representation for vibrations is
1A1' + 1E1' + 2E2' + 1E2''

The IR active terms are
1E1'

The Raman active terms are
1A1' 2E2'

There is 1 polarized Raman band.

Do you wish to do another analysis? (Y or N)?
```

Connecting Vibrations
to Chemical Reactions
via the Potential Energy
Surface

IV. PENTAHALIDES OF PHOSPHORUS

The molecules PF_5 and PCl_5 have been the subject of a variety of studies which have suggested the possibility that they might exhibit internal motions. Both molecules are trigonal bipyramids so that, at any instant, the halogen atoms occupy two kinds of sites; three are assigned to equatorial positions, and the other two to polar positions. The F^{19} -resonance spectrum of PF_5 has been observed by Gutowsky, McCall, and Slichter.¹³ They report only a single fluorine resonance peak (split into a doublet due to P-F coupling), so that either the five fluorines are equivalent to a measurement as slow as NMR, or the chemical shifts and P-F couplings are accidentally identical for fluorines at both kinds of sites. The latter possibility is rather unlikely, particularly in light of the data to be cited regarding PCl_5 , so it will not be considered further.



Significance of the ^{19}F NMR Spectrum of PF_5

Excerpt from 1960 paper by R. Stephen Berry

The infrared spectrum of PF_5 has been observed by Gutowsky and Liehr,¹⁴ who find an apparently normal spectrum for a trigonal bipyramid. This suggests that the fluorine atoms may exchange at a rate slow compared with the time necessary to establish sharp vibrational levels, and fast compared with the inverse line widths associated with nuclear resonance measurements. Hence any exchange process which the fluorines undergo should occur at a frequency between about 10^{-8} and 10^{-2} sec.

- Definition of the term **fluxional process**: a low-energy, reversible rearrangement

Significance of the ^{19}F NMR Spectrum of PF_5

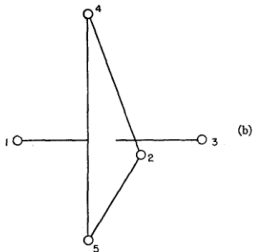
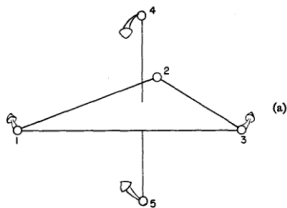
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Significance of the ^{19}F NMR Spectrum of PF_5

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Sort by
spin

Sort by
frequency

NMR Periodic Table

Sort by
receptivity

Sort by
abundance

PARAMETERS FOR:

^{19}F

Spin = 1/2

Natural abundance =
100%

*Frequency factor =
0.94094

†Magnetogyric ratio =
-25.1815

Receptivity vs. ^1H =
0.8328

Receptivity vs. ^{13}C =
 4.73×10^3

Shift range = -500 to +900
ppm

Shift reference: CFCl_3

*To find the resonant
frequency of this nuclide
on your system, multiply
its ^1H frequency by the
factor shown.

† $\times 10^{-7} \text{ radT}^{-1}\text{s}^{-1}$

RECEPTIVITY VS. ^{13}C

H				X	>10 ²	X	10 ⁻² -10 ⁰										He
Li	Be			X	10 ⁰ -10 ²	X	<10 ⁻²			B	C	N	O	F	Ne		
Na	Mg									Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The NMR Time Scale

Excerpt from 1983 paper by Robert G. Bryant, DOI: 10.1021/ed060p933

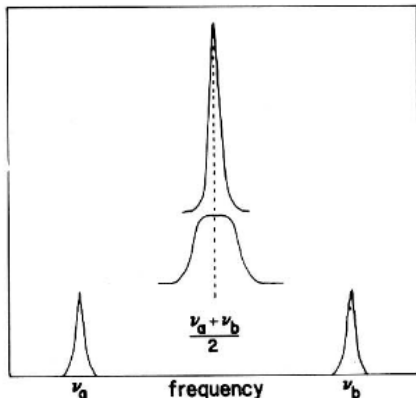


Figure 1. The idealized NMR spectra for a pair of exchanging resonances separated by a frequency $\Delta\nu = \nu_a - \nu_b$ shown schematically at the extremes of slow and fast exchange.

The NMR Time Scale

Excerpt from 1983 paper by Robert G. Bryant, DOI: 10.1021/ed060p933

Representative Chemical Shift Ranges, Coupling Constants, and Time Scales

Nucleus	Approximate Shift Range, ppm	Shifts at 1.4T Field or 60 MHz for ^1H , kHz	Time Scale Range ^a for 1.4T shifts	Shifts at 7T Field or 300 MHz for ^1H , kHz	Time Scale Range ^a for 7T shifts	Scalar Coupling Consts, Hz	Scalar Coupling Time Scale ^b
^1H	0– 10	0– 0.6	0.2 s–0.4 ms	0– 3	0.2 s–75 μs	$^2J_{\text{HH}} \sim 10$	~ 22 ms
^{13}C	0– 200	0– 3	0.2 s–75 μs	0– 15	0.2 s–15 μs	$^1J_{\text{CH}} \sim 150$	~ 1.5 ms
^{15}N	0– 900	0– 5.4	0.2 s–40 μs	0– 27	0.2 s– 8 μs	$^1J_{\text{NH}} \sim 50$	~ 4.5 ms
^{19}F	0– 300	0– 17	0.2 s–13 μs	0– 85	0.2 s– 3 μs	$^2J_{\text{HF}} \sim 50$	~ 4.5 ms
^{31}P	0– 700	0– 17	0.2 s–13 μs	0– 85	0.2 s– 3 μs	$^2J_{\text{P-F}} \sim 20$	~ 11 ms
^{59}Co	0–15,000	0–214	0.2 s–1 μs	0–1,070	0.2 s– 0.2 μs	$^1J_{\text{Co-N}} \sim 50$	~ 4.5 ms
^{199}Hg	0– 3,000	0– 32	0.2 s–7 μs	0– 160	0.2 s– 1.4 μs	$^1J_{^{13}\text{C}-^{199}\text{Hg}} \sim 2,500$	~ 90 μs

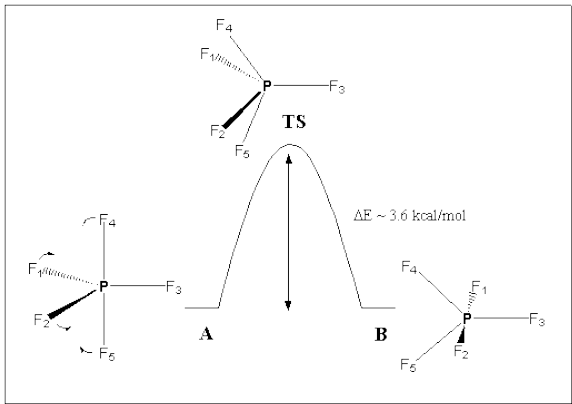
^a Taken as the coalescence lifetime given by eqn. 2 for a maximum shift; e.g., 10 ppm for ^1H , and a minimum resolvable shift of 1 Hz.

^b Taken as the coalescence lifetime obtained by substitution of J for $\Delta\nu$ in eqn. 2.



Berry Pseudorotation

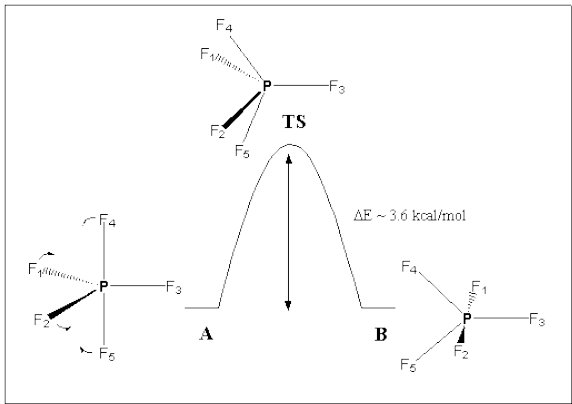
Cass et al. *J. Chem. Educ.*, 2006, 83, 336



- An *INTERMEDIATE* is at a local **minimum** on the free energy surface
- A *TRANSITION STATE* is at a local **maximum**

Berry Pseudorotation

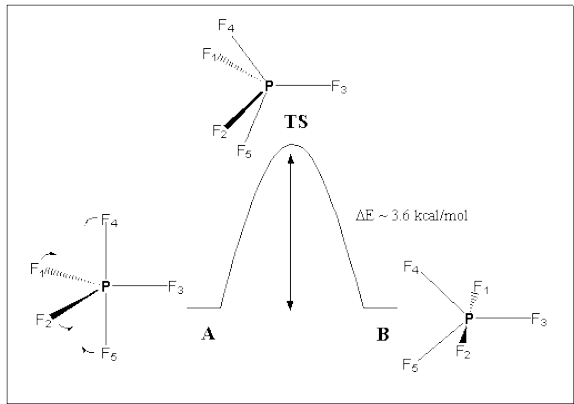
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Features of the Pseudorotation

- The point group of PF_5 is D_{3h} before and after the pseudorotation
- BPR involves pairwise exchange of axial and equatorial fluorines
- The transition state (TS) has C_{4v} symmetry
- A true TS has one negative root representing an imaginary frequency
- Animation of this normal mode provides a movie of the reaction coordinate

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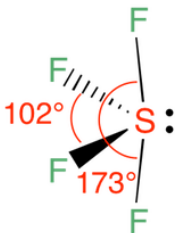
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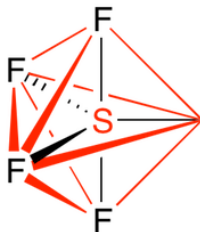
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Molecular Structure of SF₄, Another Fluxional Molecule



The F–S–F angle involving the axial F atoms is 173°



The red lines outline a **trigonal bipyramid**. Black lines show the electron pairs

Sulfur tetrafluoride has 10 electrons around the central sulfur atom. This means there are five electron pairs arranged in an trigonal bipyramidal shape with 102° F-S-F bond angles between the equatorial fluorine atoms and 173° between the axial fluorine atoms. The remaining lone pair is equatorial giving an overall see-saw shape.

NMR Investigation of Pseudorotation in SF₄

Excerpt from 1983 paper by Nancy S. True, DOI: 10.1021/ja00363a003

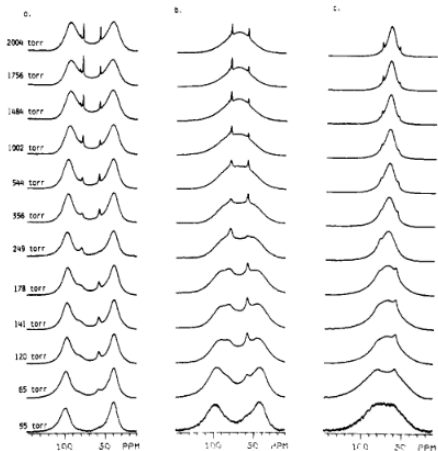


Figure 1. Pressure-dependent exchange-broadened ¹⁹F NMR spectra of SF₄ at (a) 308 K, (b) 328 K, and (c) 348 K. Limiting axial and equatorial resonances are at 97.73 and 37.03 ppm, respectively, referenced to CFC1₃. Sharp resonances at 56.21 and 77.19 ppm, apparent in the high-pressure samples, are due to SF₆ and SOF₂ impurities, respectively.

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Excerpt from 1983 paper by Nancy S. True, DOI: 10.1021/ja00363a003

Table II. Activation Energies for Pseudorotation in Sulfur Tetrafluoride

	E_{act} (kcal/mol)
gas at 2004 torr ^a	13.7 (0.5)
gas at 55 torr ^a	12.5 (0.5)
gas at ca. 3500 torr ^b	11.7 (1.5)
liquid ^b	11.2 (1.0)

^a This work. ^b Reference 25.

Table III. Normal Mode Assignment of SF₄

species	frequency (cm ⁻¹)	description ^a
A1 ν_1	891.5	ν sym, SF ₂ eq
ν_2	558.4	ν sym, SF ₂ ax.
ν_3	356 ^b	δ sciss SF ₂ eq and ax sym comb
ν_4	228 ^b	δ sciss SF ₂ eq and ax. asym comb
A2 ν_5	474	SF ₂ twist
B1 ν_6	730	ν asym SF ₂ ax.
ν_7	532	SF ₂ eq wagging
B2 ν_8	867	ν asym SF ₂ eq
ν_9	350	δ sciss SF ₂ ax. out of plane

^a Reference 37. ^b Pseudorotation modes.



Screenshot of our SF₄ TS Vibrations Applet

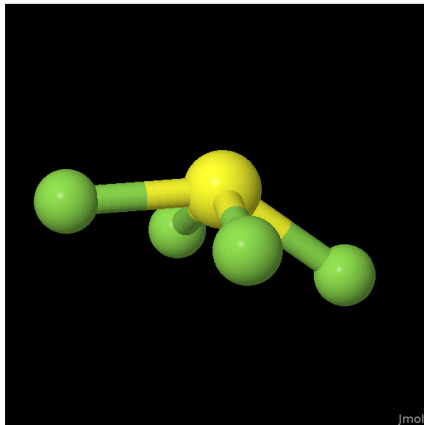
SF₄ Transition State Vibrations - Mozilla Firefox

SF₄ Transition State...

web.mit.edu/ccclab/jmol_pages/sf4_ts_vibs.html

Search

☆ 自 ↓ 家 ↗ 10 ▾ 9 三



Menu to select vibration:

001: -142 cm⁻¹

spin

setts
f
y



Summary of Some Key Points

- The reaction coordinate as a 2D slice of the potential energy surface (PES)
- Intermediates versus Transition States
- Intermediates are local minima, zero negative vibrational modes
- Transition state structures are characterized by a single negative vibrational mode
- Visualizing the imaginary mode of a TS is essentially a movie of the path from reactants to products
- BPR as an example of a fluxional process

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- Vibrational analysis, use REDUCE to check your work
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