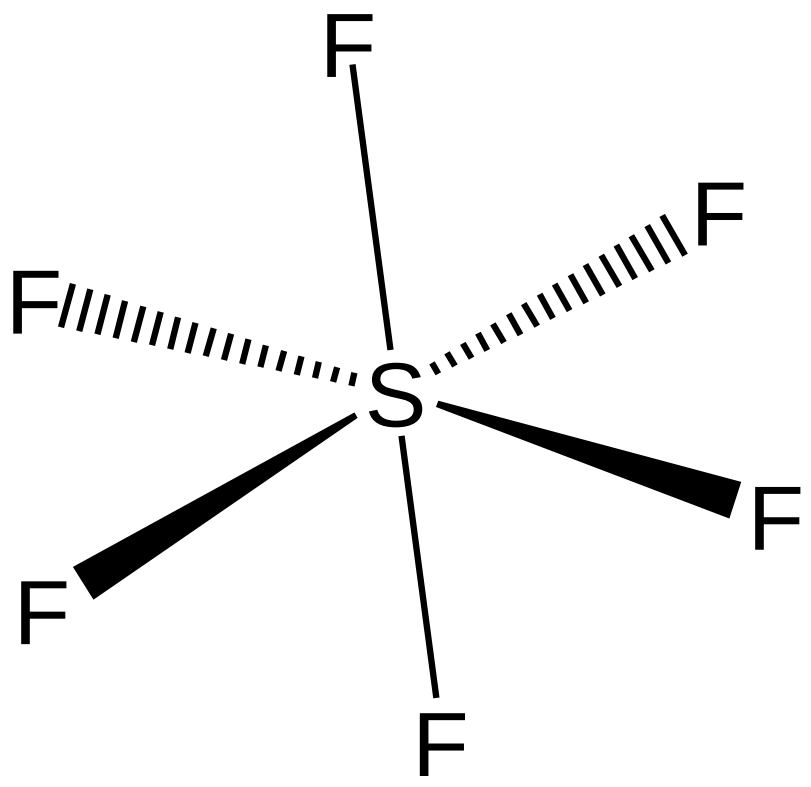
Predicting the vibrational spectra of SF_6

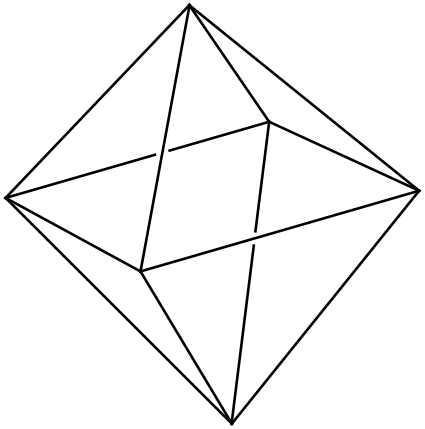


Using a Cartesian basis determine the irreducible Representations of the normal modes of vibration in SF_6.

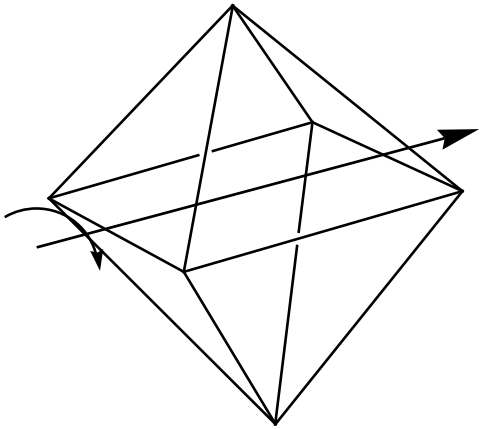
The O_h point group used for analysis

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		x^2-y^2
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

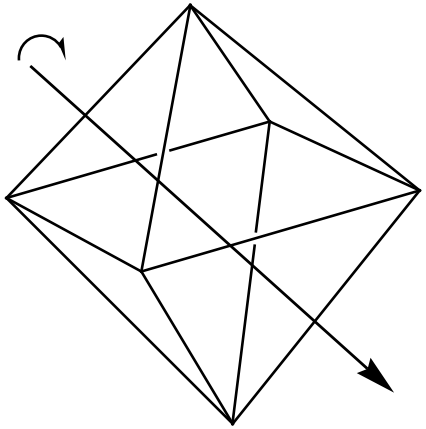
Rotations in the O_h point group



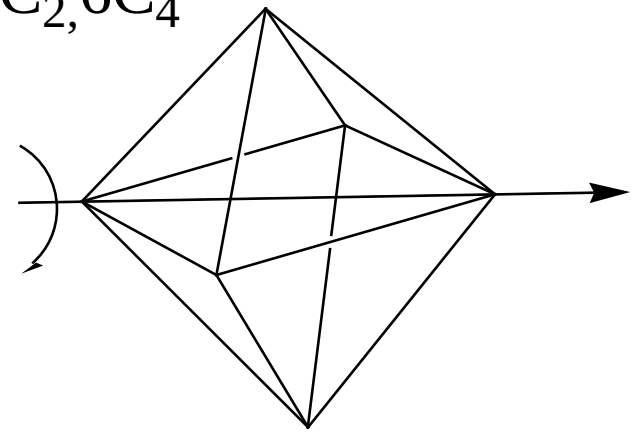
$6C_2$



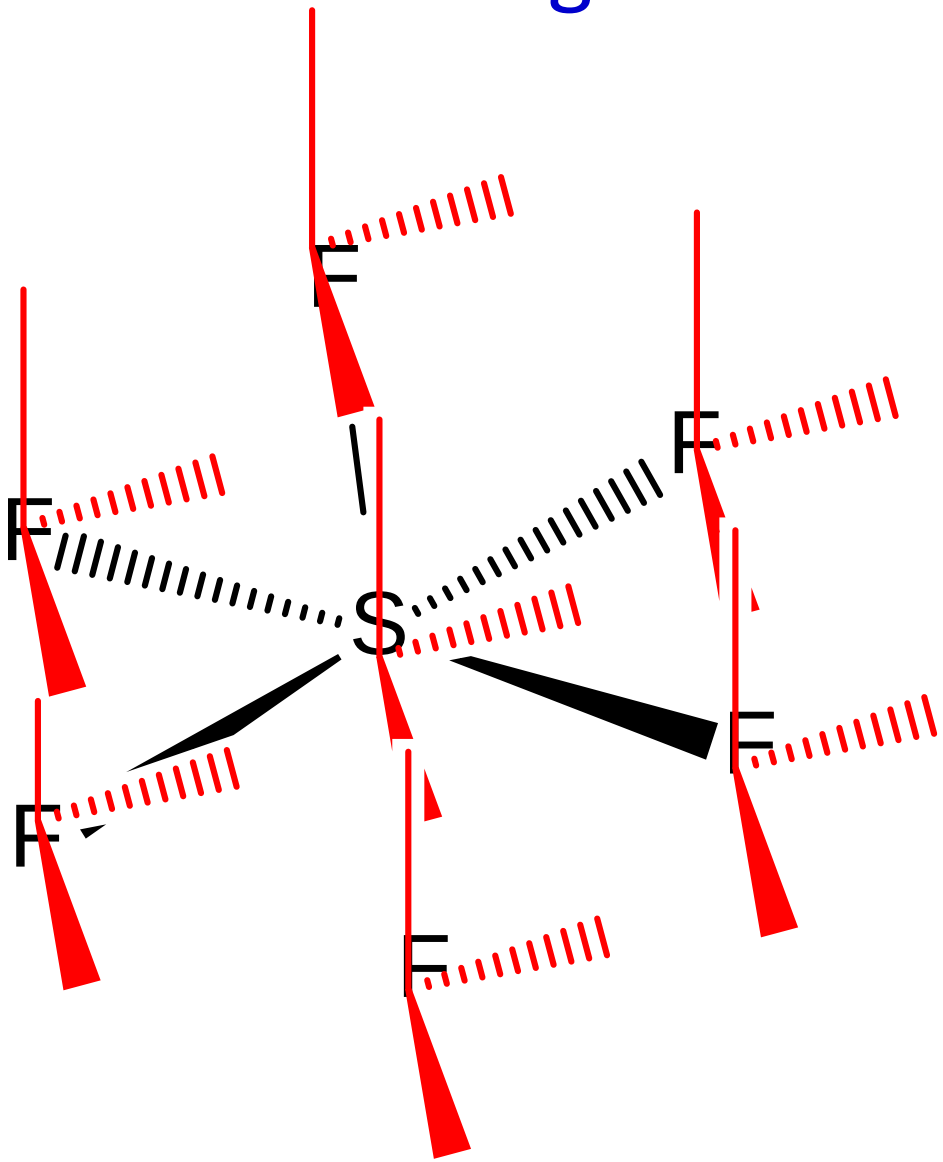
$8C_3$



$3C_2, 6C_4$



Cartesian basis has 3N degrees of freedom



Determine the reducible representation

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_{tot}	21	0	-1	3	-3	-3	-1	0	5	3
Γ_F	18	0	0	2	-2	0	0	0	4	2
Γ_S	3	0	-1	1	-1	-3	-1	0	1	1

$\Gamma_F = A_{1g} + E_g + T_{1g} + T_{2g} + 2T_{1u} + T_{2u}$

$\Gamma_S = T_{1u}$

Note that the dimension of the sums of the S and F atoms are 3 and 18, respectively, consistent with the starting Cartesian basis.

The O_h character table can be used to identify the translations (x,y,x) and rotations (R_x,R_y,R_z).

$\Gamma_{\mathbf{trans}} = T_{1u}$

$\Gamma_{\mathbf{rot}} = T_{1g}$

$\Gamma_{\mathbf{vib}} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$

There are only 5 normal modes because the symmetry of the octahedral geometry of the molecule.

Only the T_{1u} modes are infrared active.
The A_{1g} and T_{2g} modes are Raman active.
Only the A_{1g} mode is Franck-Condon active.