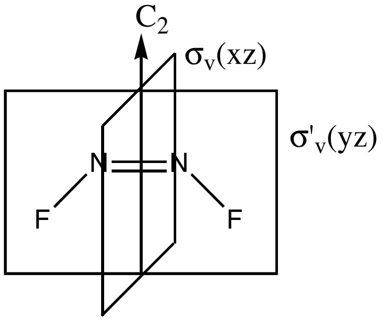
Calculation on the NH_3 molecule

- use the department computers and carry out an optimisation and then frequency analysis of the NH_3 molecule. Animate the vibrations.
    - animation of the normal modes can be found on my web-site at
    - http://www.huntresearchgroup.org.uk/teaching.html

Bench-top analysis of cis-N_2F_2

- determine the symmetry and activity of the vibrational modes of cis N_2F_2 and then derive the stretching vibrations using the projector method.



C_{2v}	E	C_2	σ_v	σ'_v
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

- determine the reducible representation:

C_{2v}	E	C_2	σ_v	σ'_v
unshifted atoms	4	0	0	4
$\chi(per\ atom)$	3	−1	1	1
$\Gamma_{3N}(N_2F_2)$	12	0	0	4

- reduce using the reduction formula:

C_{2v}	E	C_2	σ_v	σ'_v	
$\Gamma_{3N}(N_2F_2)$	12	0	0	4	
A_1	1	1	1	1	$\Rightarrow \frac{1}{4}\left[(1\bullet 12\bullet 1)+0+(1\bullet 4\bullet 1)\right]=\frac{16}{4}=4$
A_2	1	1	−1	−1	$\Rightarrow \frac{1}{4}\left[(2\bullet 15\bullet 1)+0+(1\bullet 4\bullet -1)\right]=\frac{8}{4}=2$
B_1	1	−1	1	−1	$\Rightarrow \frac{1}{4}\left[(1\bullet 12\bullet 1)+0+(1\bullet 4\bullet -1)\right]=\frac{8}{4}=2$
B_2	1	−1	−1	1	$\Rightarrow \frac{1}{4}\left[(2\bullet 15\bullet 1)+0+(1\bullet 4\bullet 1)\right]=\frac{16}{4}=4$

$$\Gamma_{3N}(N_2F_2)=4A_1+2A_2+2B_1+4B_4$$

- confirm the number of vibrations =3N=3•4=12 and 4+2+2+4=12
- remove the translational and rotational motion of the center of mass

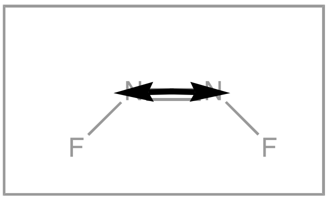
$$\begin{aligned}\Gamma(T) &= A_1 + B_1 + B_2 \\ \Gamma(R) &= A_2 + B_1 + B_2 \\ \Gamma(T+R) &= A_1 + A_2 + 2B_1 + 2B_2\end{aligned}$$

$$\begin{aligned}\Gamma_{vib}(N_2F_2) &= \Gamma_{3N} - \Gamma(T+R) \\ &= \left(4A_1 + 2A_2 + 2B_1 + 4B_2\right) - \left(A_1 + A_2 + 2B_1 + 2B_2\right) \\ &= 3A_1 + A_2 + 2B_2\end{aligned}$$

- determine the infrared and Raman activity

$$\begin{aligned}&\textit{IR active } \Gamma(T) = A_1 + B_1 + B_2 \\ &\textit{Raman active } \Gamma(f) = A_1 + A_2 + B_1 + B_2 \\ &\Gamma_{vib}(N_2F_2) = 3A_1(IR,pol) + A_2(depol) + 2B_2(IR,depol)\end{aligned}$$

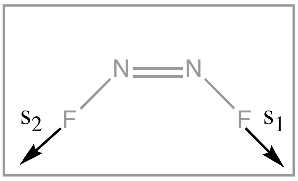
- Consider the stretches first
  - the N=N stretch, the vector under C_2 may appear to reverse onto itself, **in the case of stretching vectors reversals of this kind are NOT counted as -1**.



N=N stretch will be A_1

C_{2v}	E	C_2	σ_v	σ'_v
$\Gamma(s_{N=N})$	1	1	1	1

  - for the N-F stretches, take a vector for each motion, determine the reducible representation, and reduce it to the irreducible representation components



C_{2v}	E	C_2	σ_v	σ'_v	
$\Gamma(s_{N-F})$	2	0	0	2	
A_1	1	1	1	1	$\Rightarrow \frac{1}{4}\left[(1\bullet 2\bullet 1)+0+(1\bullet 2\bullet 1)\right] = \frac{4}{4} = 1$
$\Gamma(s_{N-F}) - A_1$	1	-1	-1	1	$\Rightarrow B_2$

$\Gamma(s_{N-F}) = A_1 + B_2$

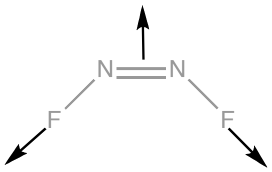
  - thus we determine $\Gamma_{stretches} = 2A_1 + B_2$
  - use the projection operator, then draw out the vibrational modes adding vectors to eliminate the CoM motion

C_{2v}	E	C_2	σ_v	σ'_v
$Q[s_1]$	s_1	s_2	s_2	s_1
A_1	1	1	1	1
B_2	1	-1	-1	1

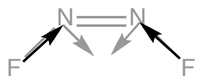
$$\psi^{A_1} = \frac{1}{4}\left[s_1 + s_2 + s_2 + s_1\right] = \frac{1}{2}\left[s_1 + s_2\right]$$

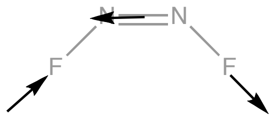
$$\psi^{B_2} = \frac{1}{2}\left[s_1 - s_2\right]$$

  - two equivalent representations of the final motions:

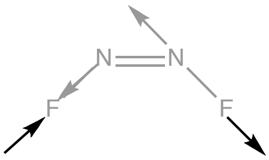


N-F
symmetric stretch
A$_1$

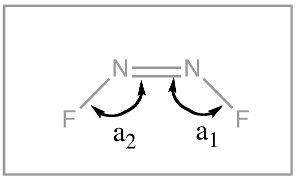




N-F
asymmetric stretch
B$_2$



- Consider the in-plane motions



C_{2v}	E	C_2	σ_v	σ'_v
$\Gamma(a_{N-N-F})$	2	0	0	2

same as stretches

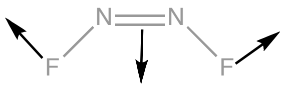
$\Gamma(a_{N-N-F}) = A_1 + B_2$

C_{2v}	E	C_2	σ_v	σ'_v
$Q[a_1]$	a_1	a_2	a_2	a_1
A_1	1	1	1	1
B_2	1	-1	-1	1

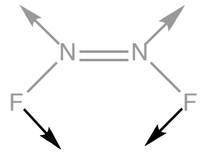
$$\psi^{A_1} = \frac{1}{2}[a_1 + a_2]$$

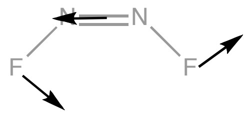
$$\psi^{B_2} = \frac{1}{2}[a_1 - a_2]$$

  - it is clear the in-plane modes have the same reducible representation as the stretches, and hence will span the same IR $\Gamma_{in-plane} = A_1 + B_2$
  - two equivalent representations of the final motions:

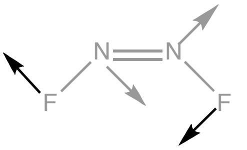


N=N-F
symmetric bend
A$_1$





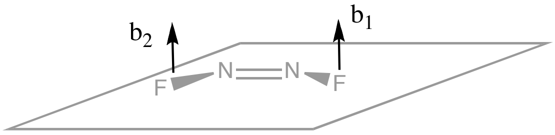
N=N-F
asymmetric bend
B$_2$



- calculate the out-of-plane motions
  - as the first step determine the remaining IRs

$$\begin{aligned}
\Gamma_{vib}(N_2F_2) &= 3A_1(IR,pol) + A_2(depol) + 2B_2(IR,depol) \\
\Gamma_{N=N\ stretch} &= A_1 \\
\Gamma_{N-F\ stretch} &= A_1 + B_2 \\
\Gamma_{in-plane} &= A_1 + B_2 \\
\Gamma_{out-of-plane} &= \Gamma_{vib}(N_2F_2) - \Gamma_{N=N\ stretch} - \Gamma_{N-F\ stretch} - \Gamma_{in-plane} \\
&= A_2
\end{aligned}$$

  - **out-of-plane vector reversals ARE counted as -1**.



$$\begin{array}{l|cccc} C_{2v} & E & C_2 & \sigma_v & \sigma_v' \\ \hline \Gamma(b_{N-N-F}) & 2 & 0 & 0 & -2 \\ & & & & \\ A_2 & 1 & 1 & -1 & -1 \\ \hdashline \Gamma(b_{N-N-F})-A_2 & 1 & -1 & 1 & -1 \end{array}$$

$$A_2 \Rightarrow \frac{1}{4}\left[(1\bullet 2\bullet 1)+0+(1\bullet -2\bullet -1)\right]=\frac{4}{4}=1$$

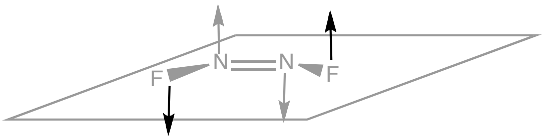
$$\Gamma(b_{N-N-F})-A_2 \Rightarrow B_1$$

$$\Gamma(b_{N-N-F})=A_2+B_1$$

eliminate B$_1$ mode

$$\begin{array}{c|cccc} C_{2v} & E & C_2 & \sigma_v & \sigma_v' \\ \hline Q[b_1] & b_1 & -b_2 & b_2 & -b_1 \\ A_2 & 1 & 1 & -1 & -1 \end{array}$$

$$\psi^{A_2}=\frac{1}{4}\left[b_1-b_2-b_2+b_1\right]=\frac{1}{2}\left[b_1-b_2\right]$$



F-N=N-F
asymmetric bend A$_2$

- lighter grey arrows introduced to stop CoM motion of whole molecule.

Complete the Assignment

- thus we have found the form of all the vibrational modes of cis-N$_2$F$_2$

$$\Gamma_{vib}(N_2F_2)=3A_1(IR,pol)+A_2(depol)+2B_2(IR,depol)$$

$$\Gamma_{N=N\ stretch}=A_1$$

$$\Gamma_{N-F\ stretch}=A_1+B_2$$

$$\Gamma_{in-plane}=A_1+B_2$$

$$\Gamma_{out-of-plane}=A_2$$

- we can add further detail to our interpretation of an experimental spectrum or prediction of a spectrum yet to be obtained
- generally when assigning a spectrum:
  - stretches in general occur at higher wavenumbers than bends
  - the stronger the bond the higher the wavenumber
  - asymmetric modes generally occur at higher energies than symmetric modes (but not always!)
- all of the information obtained can be summarised in a table

Infrared (gas; cm^{-1})	Raman (gas; cm^{-1})	Symmetry	Normal mode
IR	(pol)	A$_1$	N=N stretch
IR	(depol)	B$_1$	N-F asym stretch
IR	(pol)	A$_1$	N-F sym stretch
IR	(pol)	A$_1$	in-plane sym bend
IR	(depol)	B$_2$	in-plane asym bend
	(depol)	A$_2$	out-of-plane asym bend

$Pd(NH_3)_2Cl_2$ Spectrum

- The example from lecture one stated that we could determine which isomer (cis or trans) of $Pd(NH_3)_2Cl_2$ was present from the IR spectrum. The trans isomer has D_{2h} symmetry and exhibits a single Pd-Cl stretching vibration ν(Pd-Cl) around 350 cm^{-1} while the cis isomer, which has C_{2v} symmetry, exhibits two stretching modes, **Table 1** and **Figure 1**.

	M-X vibrations	
	IR	Raman
trans-isomer D_{2h}	b_{3u}	a_g
cis-isomer C_{2v}	a_1, b_2	a_1, b_2

Table 1 Active M-X stretching modes for ML_2X_2 complexes

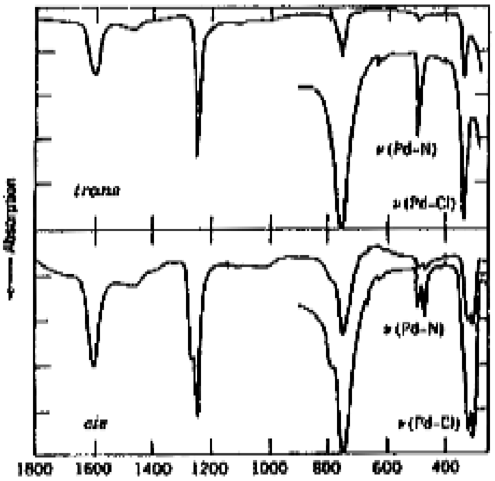
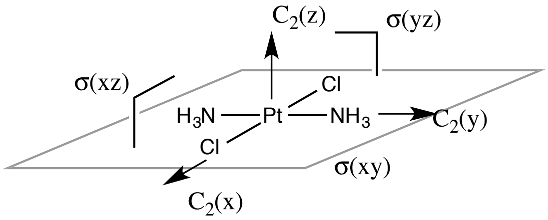
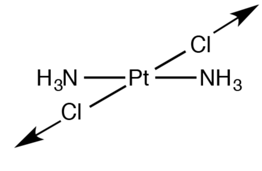


Figure 1 IR spectra of cis and trans $[Pd(NH_3)_2Cl_2)]$ Spectrum[i]

- Prove this by determining the contribution to the spectrum for the Pd-Cl stretching modes for both the cis and trans complexes.
- First identify the point group of the molecule and identify all of the symmetry elements



- depict the Pd-Cl stretching vibrations to be examined and determine the reducible contribution

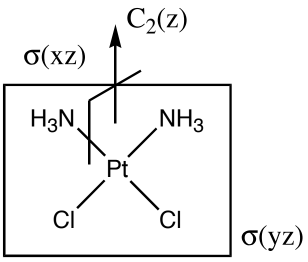


D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma(Pd-Cl)$	2	0	0	2	0	2	2	0

- reduce the reducible contribution, as this is a stretch we start by checking and eliminating the totally symmetric vibration

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma(Pd-Cl)$	2	0	0	2	0	2	2	0	
$-A_g$	1	1	1	1	1	1	1	1	
$\Gamma(Pd-Cl)-A_g$	1	-1	-1	1	-1	1	1	-1	$\Rightarrow B_{3u}$

  - in this case we have A_g and B_{3u} symmetry as the possible modes
  - thus $\Gamma_{vib}(Pd-Cl) = A_g + B_{3u}$
- identify the infrared and Raman active modes
  - IR active modes have the same symmetry as the translational vectors, thus $\Gamma(IR) \Rightarrow \{B_{1u}, B_{2u}, B_{3u}\}$ and the Raman modes have the same symmetry as the binary functions, thus $\Gamma(Raman) \Rightarrow \{A_g, B_{1g}, B_{2g}, B_{3g}\}$
  - in addition this molecule has a center of symmetry, and therefore by the rule of mutual exclusion we expect that no modes will be present in both the Raman and IR spectra
- assign Γ_{vib}(Pd-Cl)
  - hence $\Gamma_{vib}(Pd-Cl) = A_g(pol) + B_{3u}(IR)$
  - thus we expect 1 infrared active mode, and 1 active Raman mode which will be polarized
- determine the contribution on Pd-Cl stretching modes to the cis complex



C_{2v}	E	C_2	$\sigma(xz)$	$\sigma'(yz)$	
$\Gamma(Pd-Cl)$	2	0	0	2	
A_1	1	1	1	1	
$\Gamma(Pd-Cl)-A_1$	1	-1	-1	1	$\Rightarrow B_2$

  - thus $\Gamma_{vib}(Pd-Cl) = A_1 + B_2$
  - IR active modes have the same symmetry as the translational vectors, thus $\Gamma(IR) \Rightarrow \{A_1, B_1, B_2\}$ and the Raman modes have the same symmetry as the binary functions, thus $\Gamma(Raman) \Rightarrow \{A_1, A_2, B_1, B_2\}$
  - hence $\Gamma_{vib}(Pd-Cl) = A_1(IR, pol) + B_2(IR, depol)$
  - we expect 2 infrared active modes, and 2 active Raman modes one of which will be polarized, both modes will be present in both the Raman and IR spectra.
- Thus for the higher symmetry trans-complex a single mode due to the Pd-Cl stretching vibration is expected in the IR spectrum, and for the lower symmetry cis-complex two modes are expected in the IR spectrum.

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[i] from Nakamoto *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edition (1997), John Wiley & Sons, New York, PartB, p10, Fig III-5.