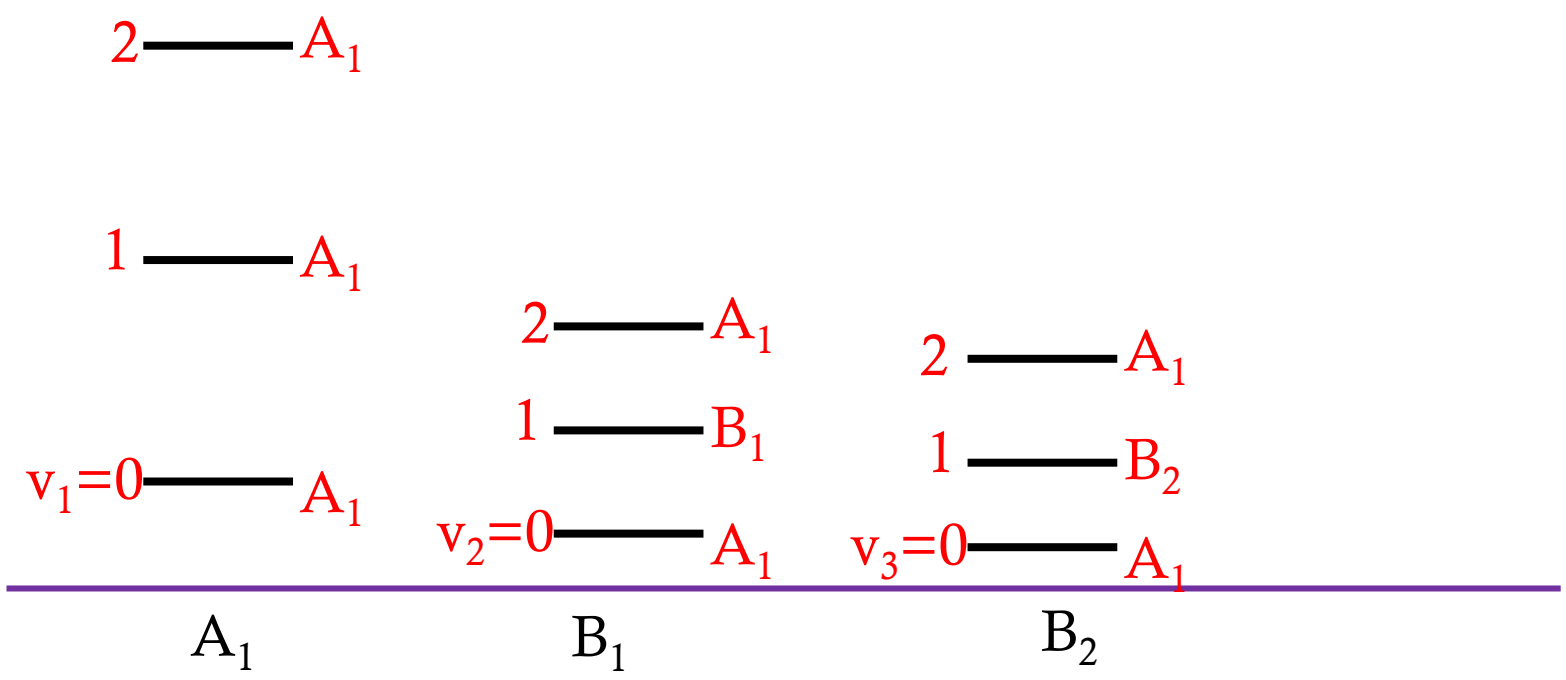
Symmetry & Bonding

Answers to the Questions 34-39

34,

In methanal (formaldehyde) three of the normal modes are found to have the following wavenumber: 2783 cm^{-1} (mode 1, symmetry A_1), 1249 cm^{-1} (mode 2, symmetry B_1), 1167 cm^{-1} (mode 3, symmetry B_2). You may assume that for any normal modes not mentioned specifically the molecule is in the ground state.

a) Draw a diagram, roughly to scale, showing the energy of the ground, first and second excited states for each normal mode (i.e. the states with $v = 0, 1, 2$). Label each state with the irreducible representation to which it belongs.



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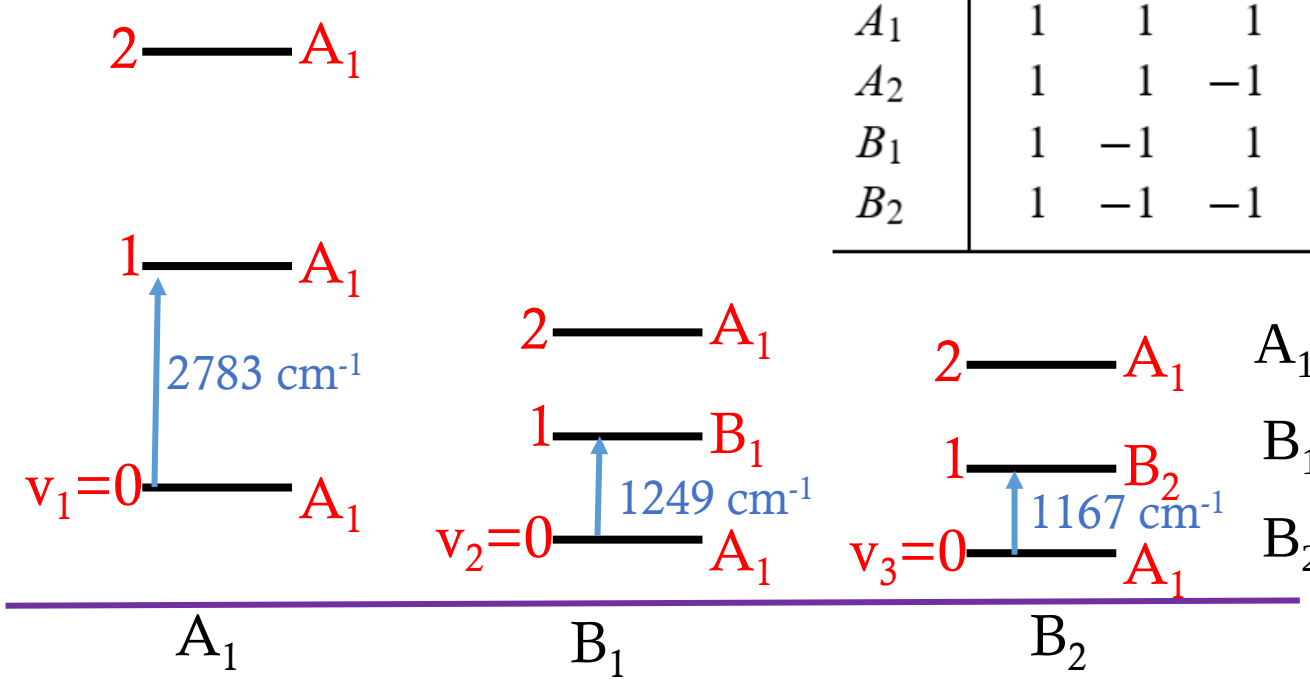
b) By computing the appropriate triple direct products, determine whether or not the $v = 0 \rightarrow 1$ transition is allowed in the infra-red for each normal mode. State the frequency of any allowed transitions, and mark the transitions on your diagram.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2;y^2;z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz



A_1 v_1 =0→1: $A_1 \otimes \Gamma_\mu \otimes A_1 = A_1$ if $\Gamma_\mu = A_1$, allowed

B_1 v_2 =0→1: $A_1 \otimes \Gamma_\mu \otimes B_1 = A_1$ if $\Gamma_\mu = B_1$, allowed

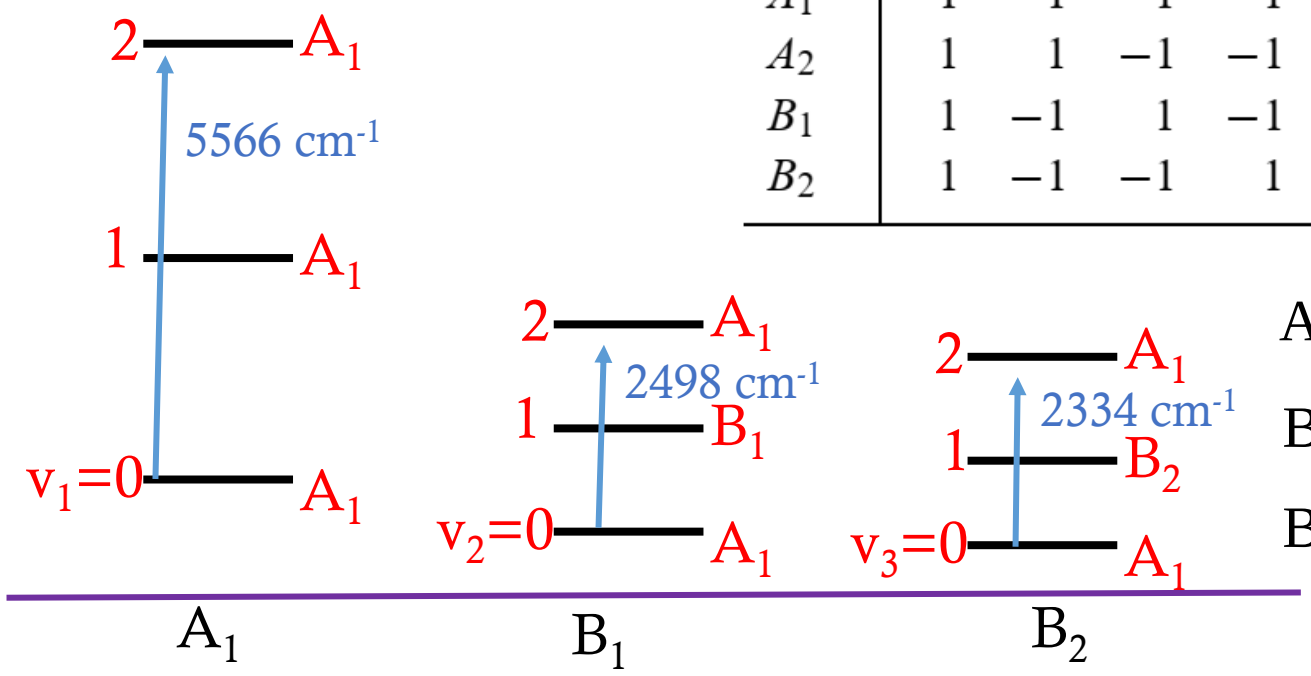
B_2 v_3 =0→1: $A_1 \otimes \Gamma_\mu \otimes B_2 = A_1$ if $\Gamma_\mu = A_2$, allowed

34,

In methanal (formaldehyde) three of the normal modes are found to have the following wavenumber: 2783 cm^{-1} (mode 1, symmetry A_1), 1249 cm^{-1} (mode 2, symmetry B_1), 1167 cm^{-1} (mode 3, symmetry B_2). You may assume that for any normal modes not mentioned specifically the molecule is in the ground state.

c) For each normal mode, determine whether or not the $\nu = 0 \rightarrow 2$ transition (i.e. the first overtone) is symmetry allowed in the infra-red. Compute the frequency of any allowed transitions, and mark the transitions on your diagram.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2;y^2;z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz



A_1 v_1 =0→2: $A_1 \otimes \Gamma_\mu \otimes A_1 = A_1$ if $\Gamma_\mu = A_1$, allowed!

B_1 v_2 =0→2: $A_1 \otimes \Gamma_\mu \otimes A_1 = A_1$ if $\Gamma_\mu = A_1$, allowed

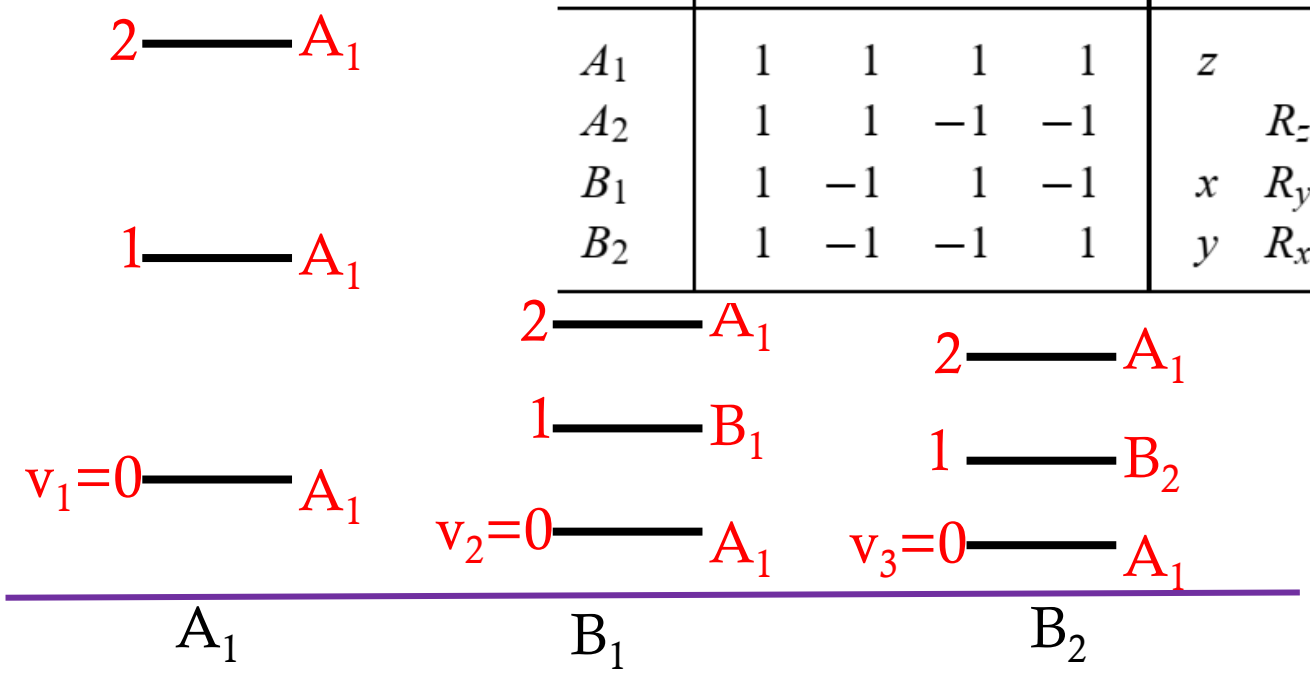
B_2 v_3 =0→2: $A_1 \otimes \Gamma_\mu \otimes A_1 = A_1$ if $\Gamma_\mu = A_1$, allowed

34,

In methanal (formaldehyde) three of the normal modes are found to have the following wavenumber: 2783 cm^{-1} (mode 1, symmetry A_1), 1249 cm^{-1} (mode 2, symmetry B_1), 1167 cm^{-1} (mode 3, symmetry B_2). You may assume that for any normal modes not mentioned specifically the molecule is in the ground state.

d) Determine whether or not the following combination lines are symmetry allowed in the infra-red: (i) mode 1 $\nu_1 = 0 \rightarrow 1$ together with mode 2 $\nu_2 = 0 \rightarrow 1$; (ii) mode 1 $\nu_1 = 0 \rightarrow 1$ together with mode 3 $\nu_3 = 0 \rightarrow 1$; (iii) mode 2 $\nu_2 = 0 \rightarrow 1$ together with mode 3 $\nu_3 = 0 \rightarrow 1$. Compute the frequency of any allowed transitions.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2;y^2;z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz



i) $A_1 \otimes A_1 = A_1 \rightarrow A_1 \otimes B_1 = B_1$

$A_1 \otimes \Gamma_\mu \otimes B_1 = A_1$ if $\Gamma_\mu = B_1$, allowed

$\nu = \nu_1 + \nu_2 = 2783 + 1249 = 4032\ cm^{-1}$

ii) $A_1 \otimes A_1 = A_1 \rightarrow A_1 \otimes B_2 = B_2$

$A_1 \otimes \Gamma_\mu \otimes B_2 = A_1$ if $\Gamma_\mu = B_2$, allowed

$\nu = \nu_1 + \nu_3 = 2783 + 1167 = 3950\ cm^{-1}$

iii) $A_1 \otimes A_1 = A_1 \rightarrow B_1 \otimes B_2 = A_2$

$A_1 \otimes \Gamma_\mu \otimes A_2 \neq A_1$ as $\Gamma_\mu \neq A_2$, not allowed

NH_3

(a) Point group: ?

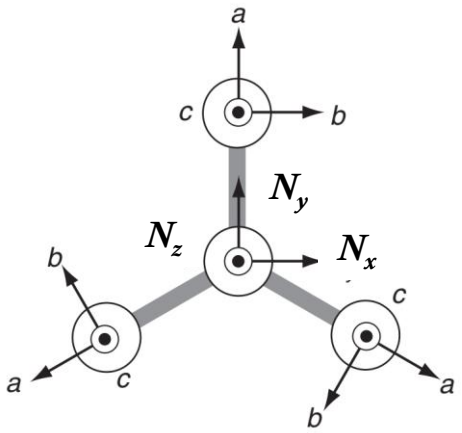
S&B Ex.36

(b) Determine the symmetries of the normal modes. (You may find it convenient to use a set of displacement vectors analogous to those uses in Ex. 33 for BH_3 in which the *a* set of vectors are along the line of the N–H bonds.)

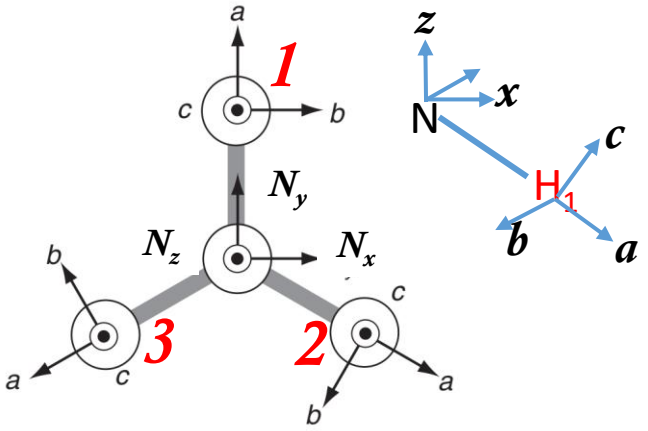
(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman.

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there i.e. how many of these features occur at the same frequency in the infra-red and Raman spectra?

(e) Determine the symmetry of those normal modes involving just N–H stretches, sketch these modes and state whether or not their fundamentals will be active in the infra-red or Raman.



NH_3 *Triangular pyramid* *a) C_{3v}* *S&B Ex.36*



b) $N_z \sim A_1$ $(N_x, N_y) \sim E$

C_{3v}	E	$2C_3$	$3\sigma_v$	Basis components		
A_1	1	1	1	z		x^2+y^2, z^2
A_2	1	1	−1		R_z	
E	2	−1	0	(x,y)	(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$

(a_1, a_2, a_3)	3	0	1	$A_1 \oplus E$
(b_1, b_2, b_3)	3	0	-1	$A_2 \oplus E$
(c_1, c_2, c_3)	3	0	1	$A_1 \oplus E$

Total ($3N$=12)	$3A_1 \oplus A_2 \oplus 4E$
–translations (x,y,z)	$A_1 \oplus \quad E$
–rotations (R_x,R_y,R_z)	$A_2 \oplus E$
Vibrations (3N-6)	$2A_1 \oplus \quad 2E$

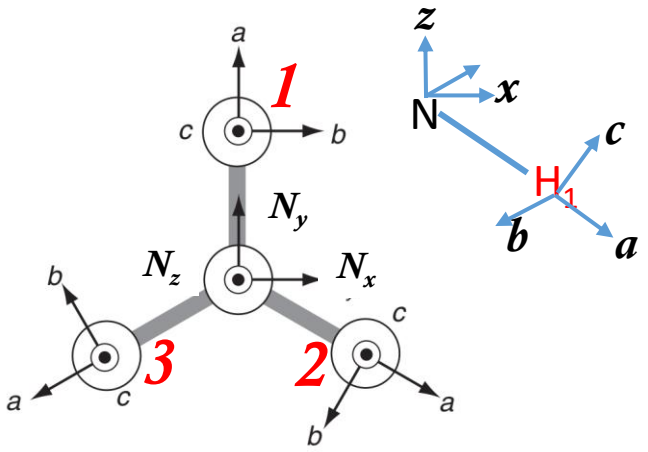
c) The fundamental transition for each NM.

i	Γ^i_{nm}	$\hat{\mu}$	$\hat{\alpha}$	IR	Raman
1,2	A_1	z;	z^2	*active*	*active*
3,4	E	(x, y);	(yz, xz)	*active*	*active*

- ***Four*** *features in both IR and Raman spectra.*
- ***Four*** *coincidences*

NH_3 *Triangular pyramid*

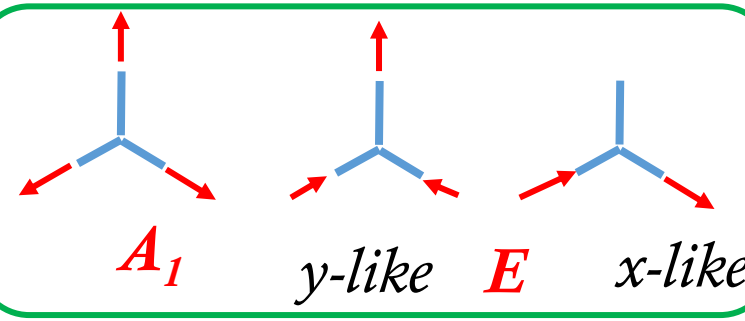
S&B Ex.36



C_{3v}	E	$2C_3$	$3\sigma_v$	Basis components		
A_1	1	1	1	z		x^2+y^2,z^2
A_2	1	1	−1		R_z	
E	2	−1	0	(x,y)	(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$

(a_1, a_2, a_3) 3 0 1 $A_1 \oplus E$

(r_1, r_2, r_3) $A_1 \oplus E$



e) 3 N-H stretches (r_1,r_2,r_3): similar to the basis of (a_1,a_2,a_3)

all IR and Raman active!

The organometallic species $Cr(CO)_6$ has octahedral coordination about the metal atom; for each ligand the Cr–C–O fragment is linear. The C–O stretches have a much higher frequency than any of the other bonds in this molecule and so, to a good approximation, can be considered separately.

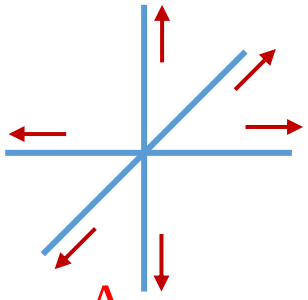
a) State the point group of this molecule.

b) Determine the symmetries of the normal modes involving C–O stretches; sketch these modes.

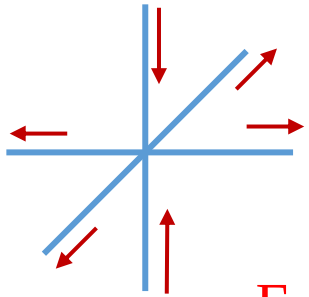
c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
Γ_{6CO}	6	0	2	2	0	0	0	4	0	2

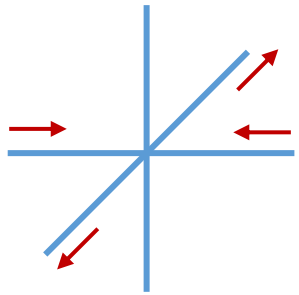
$A_{1g} \oplus E_g \oplus T_{1u}$



A_{1g}

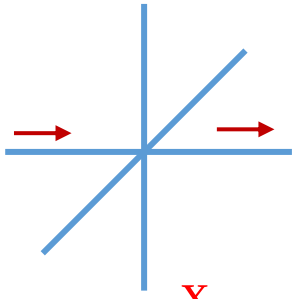


$2z^2\text{-}x^2\text{-}y^2$ E_g



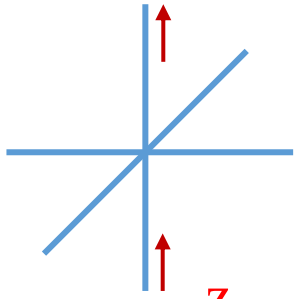
$x^2\text{-}y^2$

Fundamental transition Raman active, IR inactive

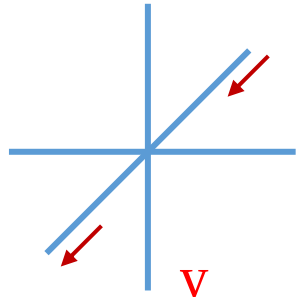


x

T_{1u}



z



y

Fundamental transition IR active, aman inactive

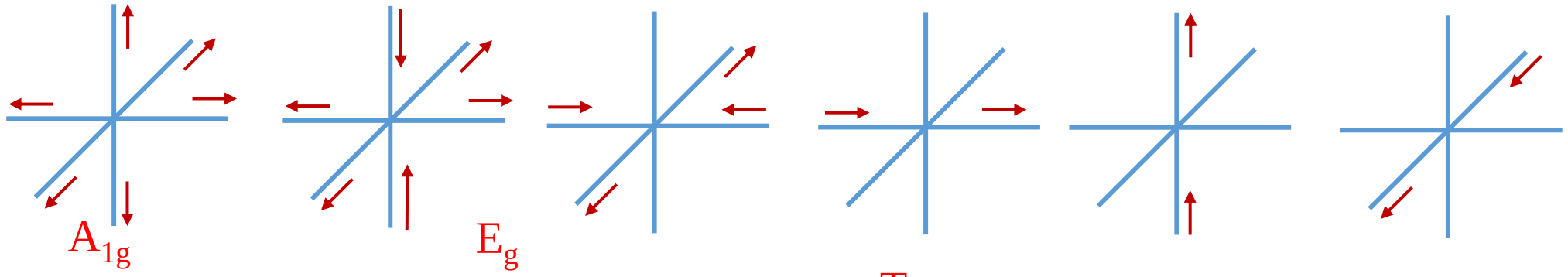
The organometallic species $Cr(CO)_6$ has octahedral coordination about the metal atom; for each ligand the Cr–C–O fragment is linear. The C–O stretches have a much higher frequency than any of the other bonds in this molecule and so, to a good approximation, can be considered separately.

d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?

Raman: 2个特征峰　　IR: 1个特征峰　　无共同特征峰

e) The experimental infra-red spectrum of this molecule shows a single strong absorbtion in the carbonyl region. Is this consistent with the assumed geometry?

Yes, consistent!

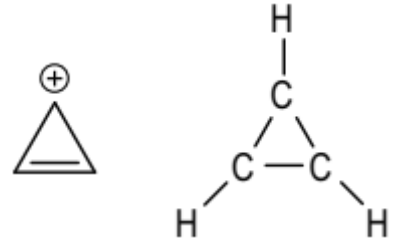


Fundamental transition Raman active, IR inactive

Fundamental transition IR active, raman inactive

Ex.38

The cyclopropenyl cation, $[C_3H_3]^+$ has a structure in which the three carbon atoms, and the three hydrogen atoms, are arranged equilateral triangles.



(a) State the point group of this molecule.

(b) Determine the symmetries of the normal modes. (Think carefully about your choice of displacement vectors.)

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?

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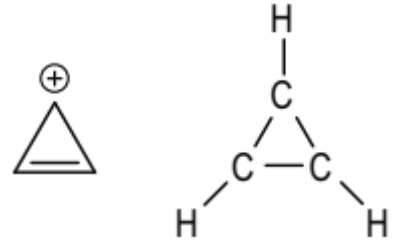
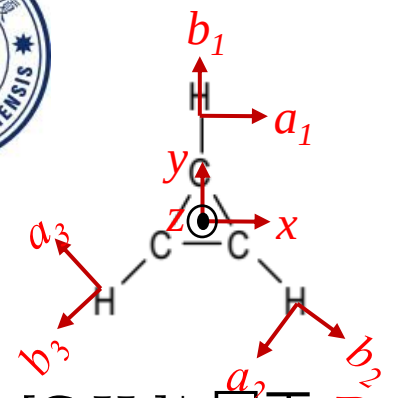


(a) State the point group of this molecule.

(b) Determine the symmetries of the normal modes. (Think carefully about your choice of displacement vectors.)

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?



$\mathcal{D}_{3h}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2;z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x,y)		$(x^2-y^2,2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x,R_y)	(xz,yz)

(a) $[C_3H_3]^+$ 属于 D_{3h} 点群.

(b) 主轴为z轴，三个H原子的局域坐标系如上图所示, 类似地设置三个C原子的局域坐标; 因此各原子核位移矢量可如下分类, 所得表示的约化结果亦列表如下

$\mathcal{D}_{3h}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
3 $z_{,H}$	3	0	-1	–3	0	1	$E''\oplus A_2''$
3 $a_{,H}$	3	0	-1	3	0	-1	$E'\oplus A_2'$
3 $b_{,H}$	3	0	1	3	0	1	$E'\oplus A_1'$

三个C原子的位移矢量为基得到的群表示亦雷同!

则分子总自由度(3N=18) $2A_1'\oplus 2A_2'\oplus 4E'\oplus 2E''\oplus 2A_2''$

平动(x,y,z) $E'\oplus A_2''$

转动(R_x, R_y, R_z) $E''\oplus A_2'$

振动 (3N-6=12) $2A_1'\oplus A_2'\oplus 3E'\oplus A_2''\oplus E''$

(c) 基频跃迁活性

	IR(4)	Raman (6)
$2A_1'$	N.A.	A.
A_2'	N.A.	N.A.
$3E'$	A.	A.
A_2''	A.	N.A.
E''	N.A.	A.

不存在活性互斥!

(d) 3 coin.

$Ni(CN)_4^{2-}$

Basis: 4 C-N bond stretches

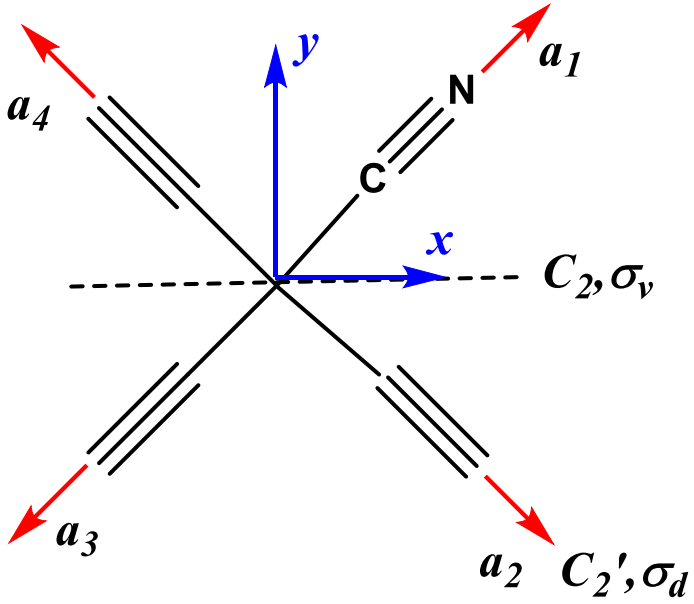
(a) Point group: ?

S&B Ex.39

(b) Determine the symmetries of the normal modes involving C–N stretches; sketch these modes.

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?

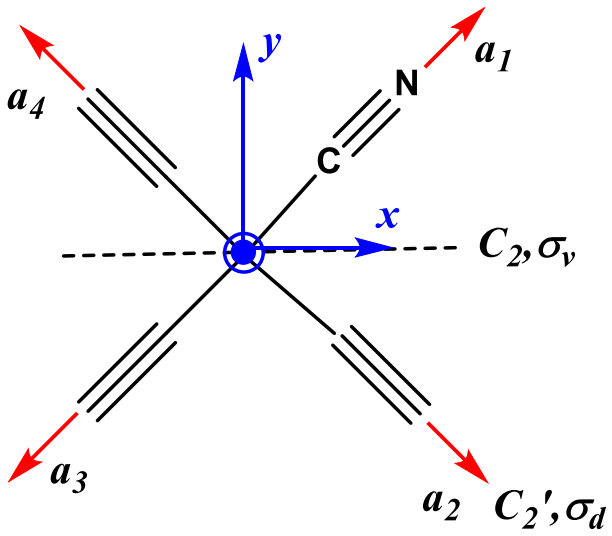


D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

$Ni(CN)_4^{2-}$

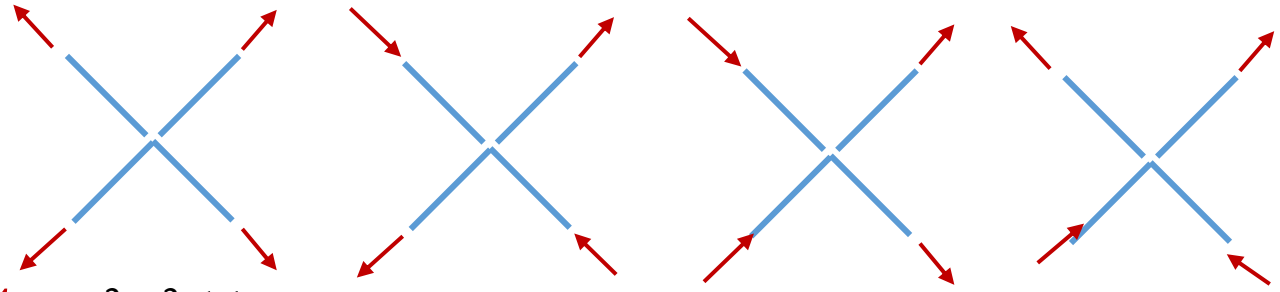
Basis: 4 C-N bond stretches

S&B Ex.39



D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

$\Gamma(4C\text{-}N)$ 4 0 0 0 2 0 0 4 0 2 $= A_{1g} \oplus B_{2g} \oplus E_u$



A_{1g}, x^2-y^2 like | B_{2g} xy-like | x-like | E_u | y-like

IR: × × √ √

Raman: √ √ × ×

Mutual exclusion applies!

Two features in Raman scattering

One feature in IR

No coincidence!

Ex.39. The complex $[Ni(CN)_4]^{2-}$ has square-planar coordination about the metal atom; for each ligand the Ni–C–N fragment is linear. The C–N stretches have a much higher frequency than any of the other bonds in this molecule and so, to a good approximation, can be considered separately.

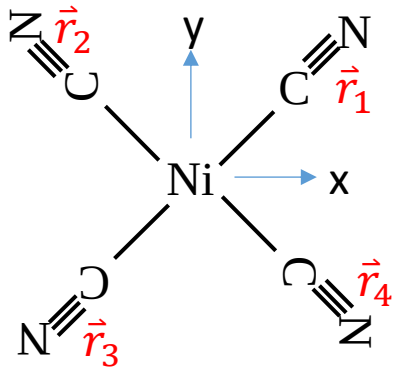
(a) State the point group of this molecule.

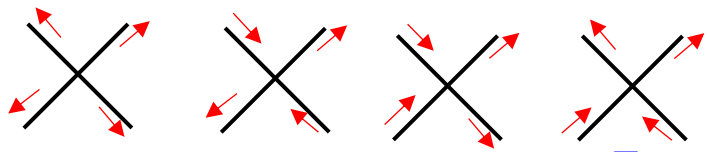
(b) Determine the symmetries of the normal modes involving C–N stretches; sketch these modes.

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?

Ans. : (a) D_{4h}. (b) use the 4 r_{CN} bond stretch as basis!





A_{1g} (x^2+y^2-like) B_{2g} (xy-like) E_u (x-like) E_u (y-like)

(c) Fundamental transitions

Raman active Raman inactive

IR inactive IR active

$\mathcal{D}_{4h}$	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
				(x/y)								
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x,R_y)	(xz,yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x,y)	
$\Gamma(4xr_{CN})$	4	0	0	0	2	0	0	4	0	2	$= A_{1g} \oplus B_{2g} \oplus E_u$	

(d) 1 feature in IR, 2 features in Raman, no coincidence.