Symmetry & Bonding

Answers to the Questions 32,33

32. 对甲醛分子进行简正振动分析. a) 该分子属何种点群?

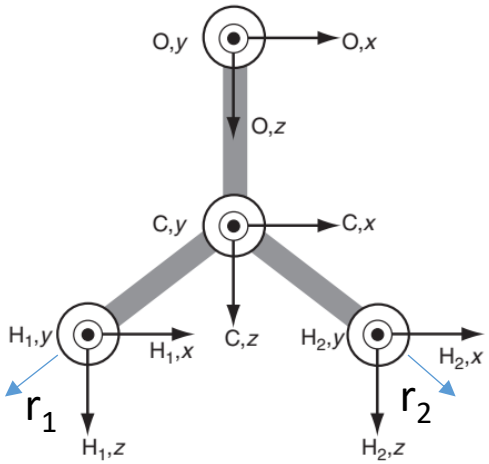
b) 说明为何简正振动的对称性分析时, 需将原子位移矢量($H_{1,x}$, $H_{2,x}$)、($H_{1,y}$, $H_{2,y}$)、 ($H_{1,z}$, $H_{2,z}$)成对考虑，而C和氧原子的各位移矢量均可通过对照特征标表直接分类确定对称性;

c) 确定以($H_{1,x}$, $H_{2,x}$)为基所得表示的特征标，并约化；进而对($H_{1,y}$, $H_{2,y}$)、($H_{1,z}$, $H_{2,z}$)执行同样的分析;

d) 确定C、O原子各位移矢量所属不可约表示；证明所有位移按 $4A_1 \oplus A_2 \oplus 4B_1 \oplus 3B_2$ 进行变换;

e) 确定简正振动所属不可约表示;

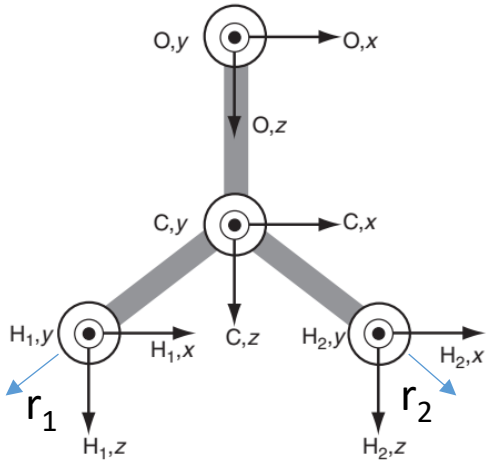
f) 若仅考虑C-H键伸缩振动, 证明其给出A_1和B_1两种简正振动模式, 画出其形式;



Ex.32. formaldehyde

a) C_{2v}

b) 对称操作过程中, 互换空间位置的基需要一起考虑; 空间位置不变的基可以直接查表判断其所属不可约表示。



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

c) Basis

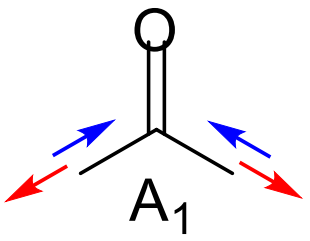
$2H_x$	2	0	2	0	$A_1 \oplus B_1$	$C(O)_x$	B_1
$2H_y$	2	0	-2	0	$A_2 \oplus B_2$	$C(O)_y$	B_2
$2H_z$	2	0	2	0	$A_1 \oplus B_1$	$C(O)_z$	A_1

d) 总自由度(12) $4A_1 \oplus 4B_1 \oplus A_2 \oplus 3B_2$

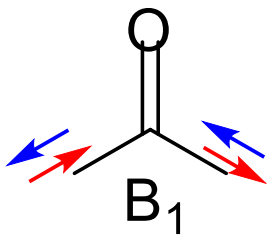
平动(3) $A_1 \oplus B_1 \oplus B_2$

转动(3) $B_1 \oplus A_2 \oplus B_2$

振动(6) $3A_1 \oplus 2B_1 \oplus B_2$



symmetric C-H stretch

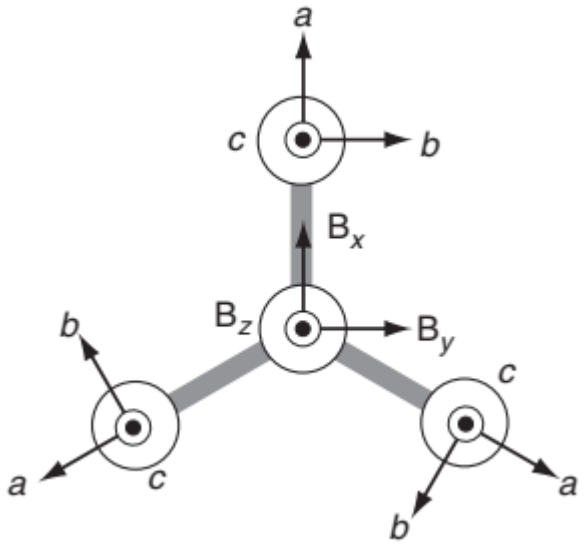


anti-symmetric C-H stretch

e) Basis

$2r_{CH}$	2	0	2	0	$A_1 \oplus B_1$

33.35 BH_3



(a) State the point group of this molecule.

(b) Explain why the analysis of the normal modes of this molecule is made more convenient by the choice of the three sets of displacement vectors *a*, *b* and *c* shown above for the hydrogen atoms.

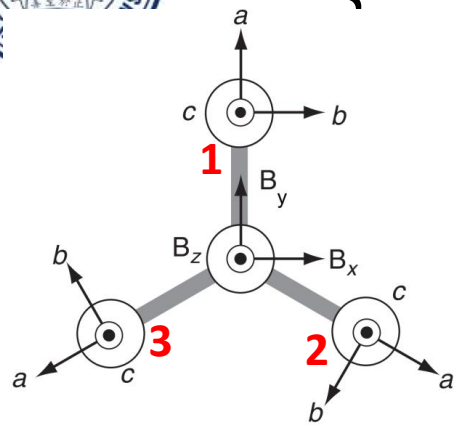
(c) Determine the irreducible representations of the normal modes of this molecule and verify that the total number of normal modes is as expected.

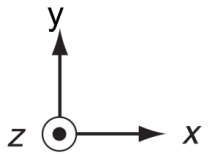
(d) Determine the symmetry of those normal modes involving just B–H stretches; sketch these modes.

Consider again the normal modes of BH_3 found in Ex. 33. 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. 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?

BH_3: Normal mode analysis

S&B Ex.33&35





Why do we not use a *general axis system*?

- Almost the same as what we did for the H_3^+ molecule in class.

- Classify the vectors:

B: $B_z \sim A_2''$, $(B_x, B_y) \sim E'$

3H: $(a_1\, a_2\, a_3) \sim A_1' \oplus E'$

$(b_1\, b_2\, b_3) \sim A_2' \oplus E'$

$(c_1\, c_2\, c_3) \sim A_2'' \oplus E''$

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)

$\Gamma(3H_a)$	3	0	1	3	0	1	$= A_1' \oplus E'$
$\Gamma(3H_b)$	3	0	-1	3	0	-1	$= A_2' \oplus E'$
$\Gamma(3H_c)$	3	0	-1	-3	0	1	$= A_2'' \oplus E''$

B-H stretches?

Total (4x3)	$A_1' \oplus A_2' \oplus 3E' \oplus 2A_2'' \oplus E''$
–translations (x,y,z)	$E' \oplus A_2''$
–rotations (R_x, R_y, R_z)	$E'' \oplus A_2'$
Vibrations (3x4-6)	$A_1' \oplus A_2'' \oplus 2E'$

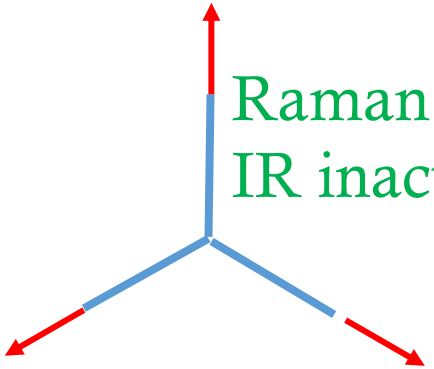
IR	X	√	√	3 features
Raman	√	X	√	3 features

2 coins.

B-H stretching modes in BH_3

- The basis $(a_1\ a_2\ a_3)$ describing the B-H stretches transforms as $A_1' \oplus E'$

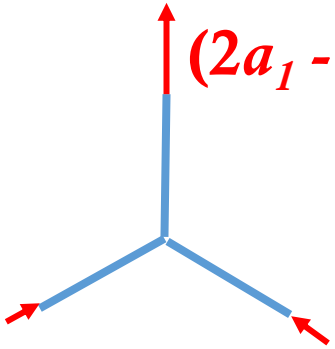
A_1' $(a_1 + a_2 + a_3)$



Raman active
IR inactive

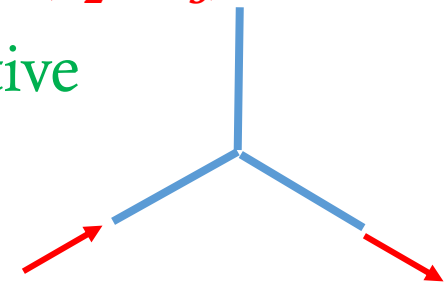
Symmetric stretch

E' *y-like* $(2a_1 - a_2 - a_3)$



Raman active
IR active

x-like $(a_2 - a_3)$



Anti-symmetric

Please figure out their activity in Raman and IR spectrum.

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)