CHEM3X17
Spectroscopy and Quantum Theory
2013

Assignment 1
(Symmetry)

Due Date: 10AM Wednesday Week 9   (at lecture)
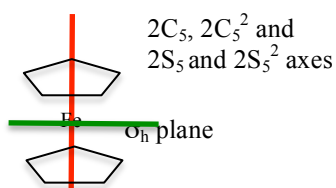
Submitted to:

This assignment is worth 5% of your assessment for this Unit of Study

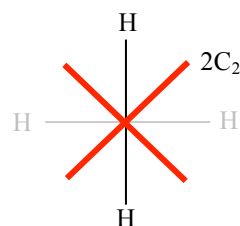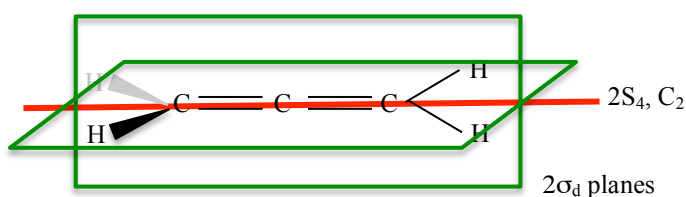1.&selected 2. What are the point groups of:
   (a) HCl   **$C_{\infty v}$**
   (b) eclipsed ferrocene   **D_{5h}**

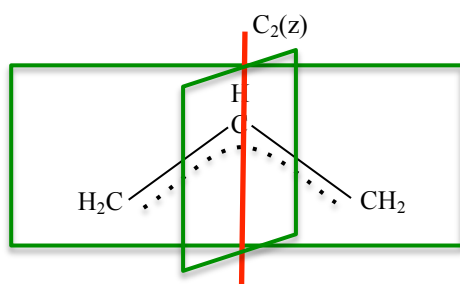*Symmetry elements:* E, $2C_5$, $2C_5^2$, $5C_2'$, σ_h, $2S_5$, $2S_5^2$, $5\sigma_v$

$2C_5$, $2C_5^2$ and $2S_5$ and $2S_5^2$ axes

σ_h plane

$5C_2'$ axes…

$5\sigma_d$ planes

   (c) allene **D_{2d}**

Symmetry elements: E, $2S_4$, C_2, $2C_2'$, $2\sigma_d$

$2S_4$, C_2

$2\sigma_d$ planes

$2C_2'$

   (d) allyl radical   **C_{2v}**

Symmetry elements: E, C_2, $2\sigma_v$

$C_2(z)$

$\sigma_v(yz)$ and $\sigma_v(xz)$ planes

(e) The Great Pyramid of Giza (ideally…)   **C_{4v}**

Symmetry elements: E, $2C_4$, C_4^2, $2\sigma_v$, $2\sigma_d$

$2C_4$, C_4^2 $2\sigma_v$, $2\sigma_d$
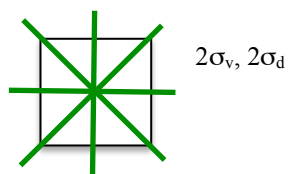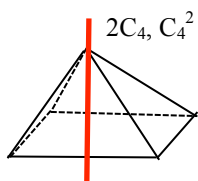
(f) The ion *cis*-$[Co(en)_2Cl_2]^+$

Symmetry elements: E, C_2

en   +
Cl
Co C_2 axis
Cl
en
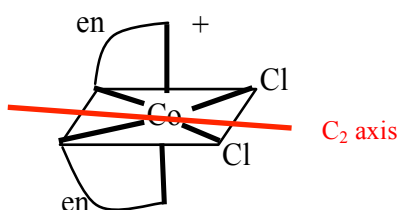
2 marks each for point group, 8 marks for list and draw *all* symmetry elements

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2+4+2+2+12+4+6+4+4

3. Propadienylidene, $:C=C=CH_2$, is a known interstellar molecule. It is a carbene – a carbon molecule with a divalent carbon atom, in this case bearing a lone pair. We may consider the valence orbitals of the carbon atoms to be $2\times sp$ and $1\times sp^2$ hybridized:

(a) What is the point group of $:C=C=CH_2$?   **C_{2v} (2 marks)**

(b) Sketch the symmetry adapted combinations of the 1s orbitals of the H atoms in $:C=C=CH_2$ and label the symmetries of these orbitals (molecule in *yz* plane).

A_1   **B_2**
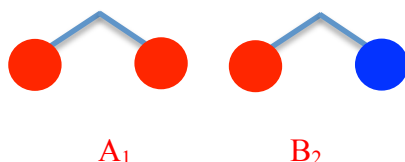
(4 marks, 2 for diagrams, 2 for labels; you should know this it is just like the H_2O example in the lectures and you can just draw them and write down the symmetries by inspection)

(c) Determine the symmetries of the unhybridized $2p_x$ and $2p_y$ orbitals of the C atoms.

$2p_x$ orbitals have symmetry B_1. $2p_y$ orbitals have symmetry B_2.
You can read the symmetries straight from the character table in terms of the symmetries of the *x* and *y* vectors.

ASIDE:
There are 3 $2p_x$ orbitals and 3 $2p_y$ orbitals with symmetry B_2. One of the $2p_y$ orbitals (on the bottom C atom) helps form the σ-bonds with the two hydrogen atoms, interacting with the B_2 symmetry orbital above.

Four of the remaining 2p$_x$ and 2p$_y$ orbitals must make the π and π* bonding and antibonding orbitals. The "left over" 2p$_x$ orbital goes into an approximately non-bonding orbital.
(ie the three 2p$_x$ orbitals form the combinations +++, +.-, and +-+).

(2 marks for 2p$_x$ as B$_1$ and 2p$_y$ as B$_2$, both of which should be read straight from the character table)

(d) How many valence electrons are there? How many of these are tied up in σ bonds?

Each carbon has 4 valence electrons (ie 2s^{2}2p^2) and each hydrogen has 1 valence electron (ie 1s^1) so there are 14 valence electrons total.

The σ bonding framework has 4 bonds, each bond has 2 electrons so 8 electrons are tied up in σ bonds. (TIP: read the question!)

(2 marks total)

(e) The first excited state, S$_1$, has A$_2$ electronic symmetry. Construct a molecular orbital diagram of :C=C=CH$_2$ which includes the lone pair, and the MOs which arise from the unhybridized 2p orbitals (i.e. exclude the σ–bonding and σ*-antibonding orbitals). Label all symmetries, and indicate relative orbital energies. There should be 6 MOs in this diagram, and it should be consistent with a HOMO-LUMO transition giving rise to an A$_2$ electronic state.

The lone pair orbital on the end carbon atom has A$_1$ symmetry (ie comes from part of the 2p$_z$ orbital). As per the diagram of the propadienylidene molecule, there <u>is</u> a lone pair and this orbital must therefore be one of the three occupied orbitals. (This is analogous to the ketene example I did for you in the lectures!). The other two occupied orbitals must be the two π bonds, which <u>must</u> be different symmetry, so must be B$_1$ and B$_2$ symmetry. The unoccupied π* orbitals must therefore also be two B$_1$ and one B$_2$.
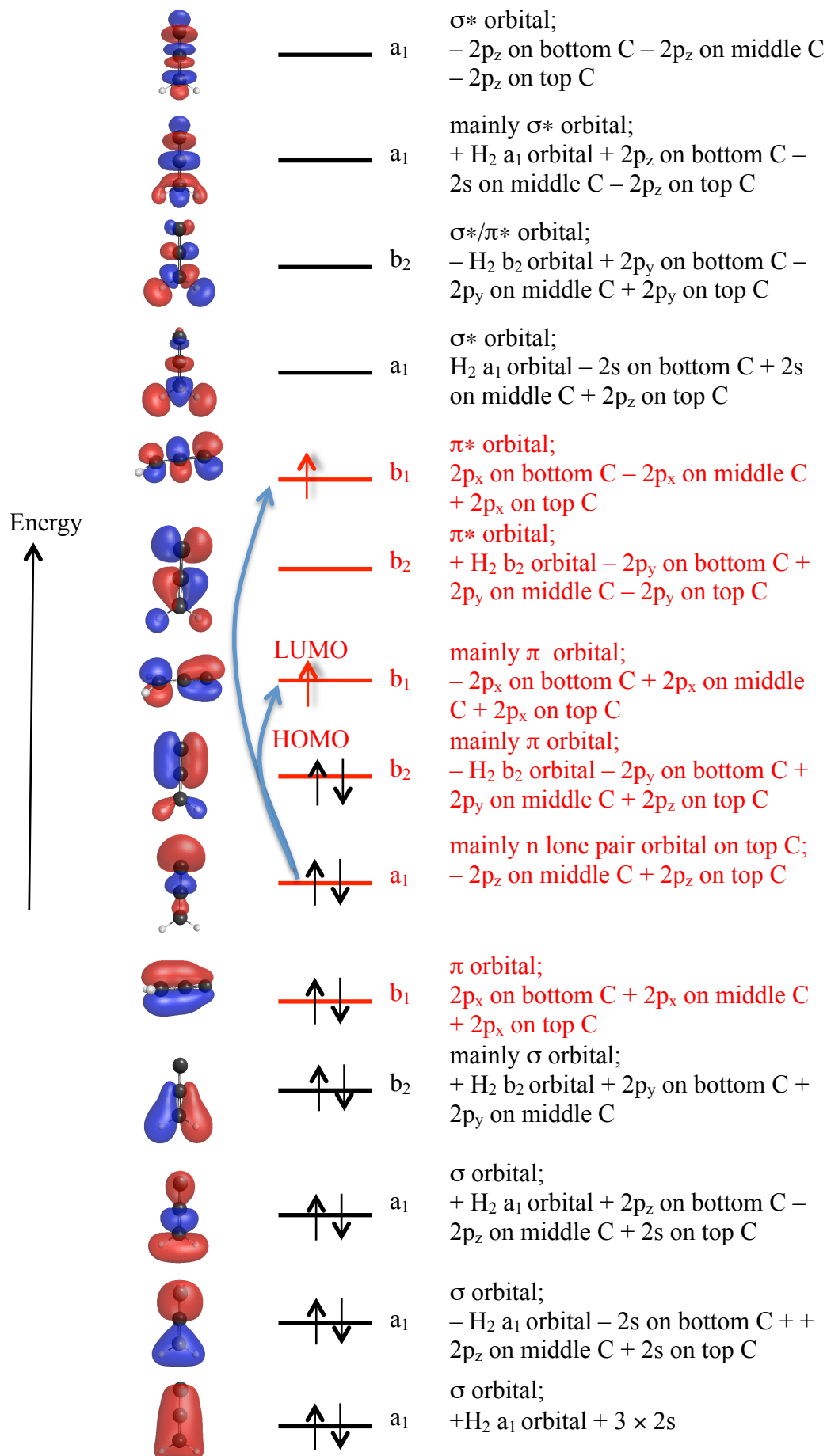
Symmetry does not tell you the energetic order of these orbitals… You need to either use your chemical intuition (eg count the number of nodes), do a calculation or refer to experiment…

However, the <u>only</u> two ways a HOMO-LUMO transition can give rise to an A$_2$ electronic state are HOMO is b$_1$ and LUMO is b$_2$ _OR_ HOMO is b$_2$ and LUMO is b$_1$ (ie b$_1 \otimes$ b$_2$ = b$_2 \otimes$ b$_1$ = a$_2$ and thus the a$_1$ orbital cannot the HOMO).

At this point either option would have received full marks because of the way the question was worded.

Jumping ahead to part (g), however, you are told that the second excited state (which is either the transition SHOMO to LUMO or HOMO to SLUMO, ie transitions involving the second HOMO or the second LUMO) has symmetry B$_1$.

The only way you can get B$_1$ from a$_1$, b$_1$ and b$_2$ orbitals is a$_1 \otimes$ b$_1$, so one of the SHOMO or SLUMO orbitals has to have a$_1$ symmetry. But the a$_1$ orbital is the lone pair and we have already reasoned that this is an occupied orbital. Thus, the SHOMO must have a$_1$ symmetry and the LUMO must therefore have b$_1$ symmetry. Working backwards, the HOMO must thus have b$_2$ symmetry. This gives rise to the MO diagram below. In this diagram I have included all 14 valence orbitals (with pictures) and all 14 valence electrons. The σ/σ* orbitals are black and the 6 you are asked to draw are red. (I've taken red lobe as +ve and blue lobe as –ve).

σ∗ orbital;
a₁ — $-2p_z$ on bottom C $-2p_z$ on middle C $-2p_z$ on top C

mainly σ∗ orbital;
a₁ $+ H_2$ a₁ orbital $+ 2p_z$ on bottom C $- 2s$ on middle C $- 2p_z$ on top C

σ∗/π∗ orbital;
b₂ $- H_2$ b₂ orbital $+ 2p_y$ on bottom C $- 2p_y$ on middle C $+ 2p_y$ on top C

σ∗ orbital;
a₁ H_2 a₁ orbital $- 2s$ on bottom C $+ 2s$ on middle C $+ 2p_z$ on top C

π∗ orbital;
b₁ $2p_x$ on bottom C $- 2p_x$ on middle C $+ 2p_x$ on top C

π∗ orbital;
b₂ $+ H_2$ b₂ orbital $- 2p_y$ on bottom C $+ 2p_y$ on middle C $- 2p_y$ on top C

LUMO — mainly π orbital;
b₁ $- 2p_x$ on bottom C $+ 2p_x$ on middle C $+ 2p_x$ on top C

HOMO — mainly π orbital;
b₂ $- H_2$ b₂ orbital $- 2p_y$ on bottom C $+ 2p_y$ on middle C $+ 2p_z$ on top C

mainly n lone pair orbital on top C;
a₁ $- 2p_z$ on middle C $+ 2p_z$ on top C

π orbital;
b₁ $2p_x$ on bottom C $+ 2p_x$ on middle C $+ 2p_x$ on top C

mainly σ orbital;
b₂ $+ H_2$ b₂ orbital $+ 2p_y$ on bottom C $+ 2p_y$ on middle C

σ orbital;
a₁ $+ H_2$ a₁ orbital $+ 2p_z$ on bottom C $- 2p_z$ on middle C $+ 2s$ on top C

σ orbital;
a₁ $- H_2$ a₁ orbital $- 2s$ on bottom C $+ + 2p_z$ on middle C $+ 2s$ on top C

σ orbital;
a₁ $+H_2$ a₁ orbital $+ 3 \times 2s$

Energy

(f) Is the transition to the lowest excited state, S_1, electronically allowed? Why, or why not?

No
For an allowed transition from Ψ_0 to Ψ_1 we must have $< \Psi_1|\mu| \Psi_0> \neq 0$.
From the MO diagram above the ground state, Ψ_0, has A_1 symmetry, ie 7 of the valence orbitals are filled and:

$(a_1)^2 \otimes (a_1)^2 \otimes (a_1)^2 \otimes (b_2)^2 \otimes (b_1)^2 \otimes (a_1)^2 \otimes (b_2)^2 = A_1$,

(ie the 3 "important" highest occupied orbitals in red).

The excited state, Ψ_1, has A_2 symmetry so we need $\Psi_1 \otimes \mu = A_2$ for the transition moment integral to be non-zero. That is, one of the components of μ: μ_x, μ_y, μ_z, must transform as A_2 for integral to be $\neq 0$. However, there is no vector component with A_2 symmetry so the electronic transition to S_1 is forbidden.

(4 marks 1 for no, 1 for A1 ground state 1 for transforms as vector)

(g) Combining the A_2 electronic state with vibrational states of which symmetries give rise to allowed *vibronic* transitions?

we need $\Psi_1 \otimes \Gamma_{vib}$ to have the same symmetry as μ_x, μ_y or μ_z, ie B_1, B_2 or A_1. Now:

$A_2 \otimes A_1 = A_2$ – forbidden
$A_2 \otimes A_2 = A_1$ – allowed
$A_2 \otimes B_1 = B_2$ – allowed
$A_2 \otimes B_2 = B_1$ – allowed

Thus vibrations with A_2, B_1 or B_2 symmetry may give rise to a vibronic transition.
(6 marks, 2 each for the allowed vibrational symmetries)

(h) The next lowest excited state, S_2, has B_1 symmetry. On your MO diagram, indicate which electronic transition(s) could contribute to this state.

See part (e) for reasoning of orbital order and the transitions are drawn in with an arrow and red electron spin.
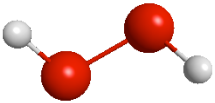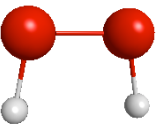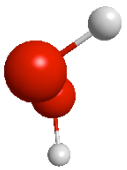
There are 2 possible transition from the a_1 occupied lone pair orbital to either of the b_1 unoccupied orbitals. We do not know the energies of the orbitals (they may be very close in energy…) so we cannot judge whether the lower energy transition dominates and we have to assume that the S_2 state has some character from both of these configurations. (4 marks, 2 each)

(i) The transition to the S_1 state is indeed observed, due to intensity borrowing (stealing) from the S_2 state. Thus, which vibrational symmetry is responsible for the coupling?

4. Vibrational spectroscopy can be used to help determine or confirm molecular structures: For example, and your entertainment, the structure of hydrogen peroxide can be figured out from its gas-phase infrared spectrum.
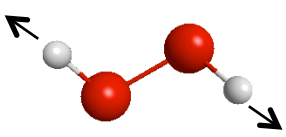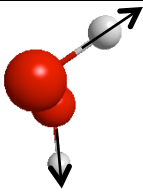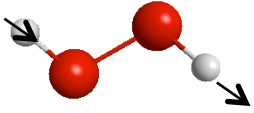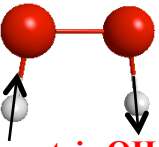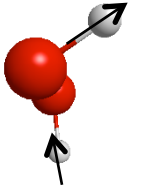
a) Draw *trans*, *cis* and *gauche* structures of H_2O_2, and assign these structures to point groups.

trans	*cis*	*gauche*
C_{2h}	**C_{2v}**	**C_2**

(6 marks, 2 marks each)

b) Two infrared transitions are observed in the O-H stretching region, the symmetric and antisymmetric O-H stretches. Draw these two modes for each of the three structures (draw six modes, using arrows to indicate relative motion).

c) What are the symmetries of these six modes in the respective point groups? Which are IR active?

trans	*cis*	*gauche*
symmetric OH stretch **A_g symmetry** **IR inactive**	**symmetric OH stretch** **A_1 symmetry** **IR active**	**symmetric OH stretch** **A symmetry** **IR active**
antisymmetric OH stretch **B_g symmetry** **IR active**	**antisymmetric OH stretch** **B_2 symmetry** **IR active**	**antisymmetric OH stretch** **B symmetry** **IR active**

((b): 6 marks, one mark for each stretch; (c) 12 for symmetries of stretches, 2 marks each, 6 marks for IR active or inactive, 1 mark each)
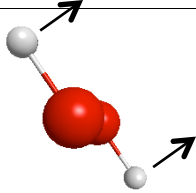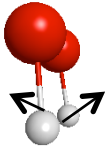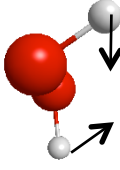
d) Which structure can you now rule out? Why?

We can rule out the trans structure as it only has one IR active vibration in the OH stretching region of the IR spectrum whereas two are observed experimentally.
(2 marks: 1 for trans 1 for why)

e) What symmetry is the HO-OH torsion in each point group? If the torsional mode is observed, what is the structure of hydrogen peroxide, given all the information?
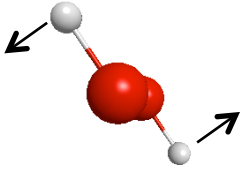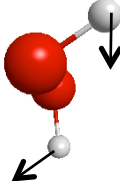
Torsion is the "book opening and closing", with the OH bonds wagging toward or away from each other.

trans	*cis*	*gauche*
A_u symmetry **IR active**	**A_2 symmetry** **IR inactive**	**A symmetry** **IR active**

(6 marks total, 2 marks each for identifying the symmetry of the torsions for each conformer)

Given we have already eliminated the trans conformer, and we are deciding between cis and gauche, the torsion is only IR active for the gauche conformer, therefore H_2O_2 must be gauche. (2 marks)

NB reversing the direction of one of the arrows above actually corresponds to overall rotation of the molecule about the O–O bond (a lot of you did this…), that is:

trans	*cis*	*gauche*
B_g symmetry **(for molecule in xy plane)** **Rotation about OO bond**	**B_1 symmetry** **(for molecule in yz plane)** **Rotation about OO bond**	**B symmetry** **Rotation about OO bond**

f) **Use a basis of vectors and a knowledge about how the H_2O_2 translations and rotations transform, in the point group you have figured out, to determine the symmetries of all the vibrations in H_2O_2.**

C_2	E	C_2
$\chi\{x,y,z\}$	3	–1
# atoms that stay in the same place	4	0
Γ_{red}	12	0

You can reduce Γ_{red} by inspection to 6A + 6B; ie there are only 2 irreducible representations, A and B and both have character 1 for the identity, E, but A has character 1 for C_2 and B has character -1. The only way we can get 0 for C_2 is equal numbers of A and B but we need a total of 12 irreducible representation (ie 12 in the E column above) so we must have 6 each of A and B.

You could also project out the number of A and B irreducible representations.

C_2	E	C_2	
A	1	1	
B	1	–1	
Γ_{red}	12	0	
#A	(+12	+0)/2	=6
#B	(+12	+0)/2	=6

ie Γ_{red} = 6A + 6B

In the C_2 point group, reading straight from the character table, the translations transform as A + 2B and the rotations transform as A + 2B. Subtracting these, the vibrations transform as 4A + 2B (ie 6 vibrations total; 3N – 6 = 3 × 4 – 6 = 6).
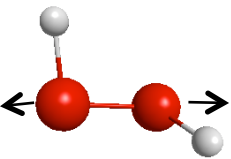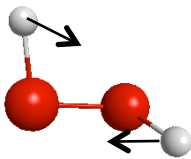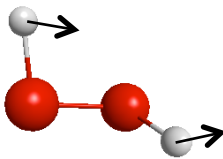
(9 marks total, 2 for # atoms that stay in the same place, 2 for Γ_{red}, 3 for reducing to 6A + 6B and 2 for subtracting off the translations and rotations giving vibrations as Γ_{vib} = 4A + 2B)

g) **What are the symmetries of the missing vibrational modes? (i.e., after accounting for the 2×O-H stretches and torsion) Draw them.**

We have counted A + B for the OH stretches and A for the torsion so there are three vibrations, 2A + B, to account for.

One is the O–O stretch which is totally symmetric and has A symmetry.

The other two are the O–O–H bending vibrations, one of which is symmetric with A symmetry, the other is antisymmetric with B symmetry.

O-O stretch	O–O–H symmetric bend	O–O–H antisymmetric bend
A symmetry	**A symmetry**	**B symmetry**

(6 marks total, 1 for each drawing, 1 for assigning each symmetry)

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