5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

<u>Lecture #31</u>: Electronic Spectra of Polyatomic Molecules

Electronic spectra are more complex than vibration-rotation spectra.
Polyatomic molecule spectra are more complex than diatomic molecule spectra

- * Many vibrational properties (such as Franck-Condon factors) can't be calculated because we know too little about $V'\left(\underset{\approx}{Q}'\right)$ and $V''\left(\underset{\approx}{Q}''\right)$.

  QUALITATIVE IDEAS LIKE NODE COUNT STILL WORK!

- * Inter-surface interactions are more subtle in 3N–6 dimensions than in 1 dimension (avoided crossings along high symmetry directions).

- * Non-radiative processes (other than predissociation and autoionization) cause spectral lines to broaden and fluorescence quantum yields to approach zero. E.g. Bixon and Jortner *J. Chem. Phys*. **48**, 715 (1968).

This subject is so complex that only a case-by-case approach seems feasible.

Some crucial background information:

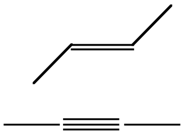
1. <u>Electronic States</u> ← electronic configurations ← MO's.
   symmetry labels
   qualitative effect of each occupied orbital on favored molecular shape (i.e. R_{AB}'s and k_{AB}'s and θ_{ABC}'s)
   Qualitative MO Theory: Walsh diagrams
   localization of orbitals onto "chromophores"

   concept of chromophores is an enormous simplification because:
   * its orbitals and electronic properties are known from other molecules
   **** large changes in molecular shape are confined to the region of the chromophore.

2. <u>Electronic Transitions</u>
   A single orbital promotion, e.g. π*←n, gives direction of transition moment relative to body fixed $\hat{a}$, $\hat{b}$, $\hat{c}$ axes ↔ $\boxed{\text{rotational selection rules}}$
   direct product $\Gamma_{\phi_i} \otimes \Gamma_{\phi_f}$

   Often **mixed transition type** when chromophore does not lie || or ⊥ to a principal axis.
   E.g. HCO $\tilde{B}\,^2A' - \tilde{X}\,^2A'$ ($\vec{\mu}_{AB}$ in plane of molecule)
   Often **axis-switching effects** when $\hat{a}$, $\hat{b}$, $\hat{c}$ axes are not oriented identically in both electronic states because of a large change in geometry

e.g.



$\tilde{A}\,^1A_u$

$\tilde{X}\,^1\Sigma_g^+$ π*←π in HCCH

3. Vibrational Structure

Symmetry selection rules for vibrational bands in an allowed electronic transition

$$\Gamma_{\underset{\sim}{v}'} \otimes \Gamma_{\underset{\sim}{v}''} \subset \Gamma_{\text{totally symmetric}}$$

allowed to see: all v of totally symmetric mode
alternate (even) v's of non totally symmetric modes except in combination with other non-totally symmetric modes

FRANCK-CONDON propensity rules

$\Delta v = 0$ for all normal modes that are unchanged by $\phi' \leftarrow \phi''$ electronic transition.

Long progressions in modes exhibiting large change in ω and Q_e - just as for diatomic molecules.

Only modes localized on the chromophore are expected to exhibit Franck-Condon activity.

Massive Simplification! Crucial diagnostic!

Symmetry Forbidden Electronic Transitions

$$\underbrace{\left(\Gamma_{e'} \otimes \Gamma_{\underset{\sim}{v}'}\right)}_{\text{“vibronic” symmetry}} \otimes \left(\Gamma_{e''} \otimes \Gamma_{\underset{\sim}{v}''}\right) \subset \Gamma_{\text{totally symmetric}}$$

a non-totally symmetric normal mode distorts the molecular framework and causes to be mixed in some character of another electronic state that would give rise to a symmetry allowed electronic transition in the lower symmetry point group. In this case the vibrational intensity depends strongly on the number of quanta in the non-totally symmetric “promoting mode”.

See Vibronic coupling handout and the H_2CO $\tilde{A}\,^1A_2 - \tilde{X}\,^1A_1$ transition.

4. Rotational Structure

a, b, or c-type selection rules determined by

$\Gamma_{e'} \otimes \Gamma_{e''}$	or	$\Gamma_{ev'} \otimes \Gamma_{ev''}$
electronically allowed		vibronically allowed

Rotational structure provides crucial clue to electronic symmetry assignment.

Large changes in A, B, C rotational constants:

* spectra look much more complex than a vibration-rotation band because Q branches are not line-like and do not fall into regular patterns of sub-bands;

* crucial key to configurational assignment because the A, B, and C rotational constants tell us about gross changes in equilibrium geometry.

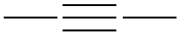
Two classic examples:

1. The *trans-bent* $\pi^* \leftarrow \pi$ excited state of HCCH
   [see K. K. Innes, *J. Chem. Phys.* **22**, 863 (1954) and G. W. King and C. K. Ingold, *Nature* **169**, 1101 (1952)]

2. The non-planar $\pi^* \leftarrow n$ excited state of H_2CO

Acetylene has a linear ground state

14 total e^-



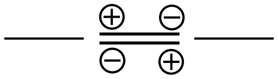
$$\tilde{X}\,{}^1\Sigma_g^+ \quad \underbrace{1\sigma_g^2 1\sigma_u^2}_{\text{C 1s}} \quad \underbrace{2\sigma_g^2 2\sigma_u^2}_{\substack{\text{net of 2}\\ \text{C–H bonds}\\ \text{H1s, C2s}}} \quad \underbrace{3\sigma_g^2}_{\substack{\text{C–C}\\ \sigma\text{-bond}\\ \text{C 2p}}} \quad \overset{\substack{\text{HOMO}\\ \downarrow}}{\underbrace{1\pi_u^4}_{\substack{\text{2 CC}\\ \pi\text{-bonds}}}} \quad \overset{\substack{\text{LUMO}\\ \downarrow}}{\underset{\substack{\uparrow\\ \pi^*}}{1\pi_g^0}} \quad 3\sigma_u^0$$

↘ some sp polarization

Numbering within symmetry type is in order of energy and number of nodal surfaces. Listed in increasing energy order.

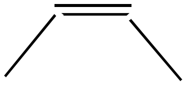
What are the plausibilities for the upper state of a $\pi^* \leftarrow \pi$ transition?

linear upper state



$D_{\infty h}$

cis-bent



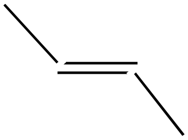
C_{2v}

four possibilities

hole in π (π^{-1}) < in plane / ⊥ to plane

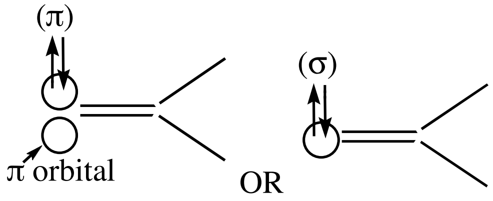
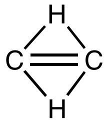
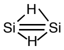
single e^- in π^* < in plane / ⊥ to plane

trans-bent



C_{2h}

Again, 4 possibilities for π^{-1} and π^* orientations.

vinylidene	 (π) necessarily in plane of $C{<}^{H}_{H}$ or $\pi^1\sigma^1$	C_{2v}
diborane planar bridged structure	 see Bogey *Phys. Rev. Lett.* **66** 413 (1991) for non-planar 	D_{2h}
Non-planar (like HOOH)	near *trans* near *cis*	C_2
Unequal CH bond lengths	planar	C_s
	non-planar	C_1

Linear possibility unlikely because $\pi^* \leftarrow \pi$ gives

$$^1\Delta_u,\ ^3\Delta_u,\ ^1\Sigma_u^+,\ ^3\Sigma_u^+,\ ^1\Sigma_u^-,\ ^3\Sigma_u^- \text{ states}$$

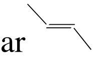
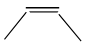
all of which except $^1\Sigma_u^+$ are forbidden from $^1\Sigma_g^+$.

In CO and N_2 the analogous $^1\Sigma_u^+$ state is very high lying and above the first dissociation limit.

$^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ is expected to have || type rotational selection rules (strong R, P, weak Q) and the observed bands obviously contain strong Q lines.

In addition, we do not expect the $\pi^* \leftarrow \pi$ states to be linear because

> a *trans*-bend distortion mixes the C–H bonding $2\sigma_u$ MO into the π^* MO, thereby strengthening the two CH bonds AND DIMINISHING the anti-bonding interaction between the C's
>
> OR
>
> a *cis*-bend distortion mixes the CH bonding $2\sigma_g$ MO into the π^* MO, thereby strengthening the two CH bonds.

So we expect the two planar  and  possibilities to be most likely.

Electronic Spectra of Polyatomic Molecules: Part II

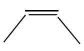
Survey of relevant factors

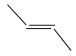
* symmetry selection rules $\left\{\begin{array}{l}\text{electronic}\\ \text{vibrational}\\ \text{rotational}\end{array}\right.$

* propensity rules
    localization onto chromophores
    Franck-Condon factors
* expected shapes of molecules
predictions based on qualitative MO theory
proof of one vs. other structure based mostly on group theory

The $S_1 \leftarrow S_0$ transition in HCCH (first to be rotationally analyzed) rules out linear excited state.

Today: 1. Why would the HCCH $\pi^* \leftarrow \pi$ excited states want to be bent? QMOT (Qualitative Molecular Orbital Theory)

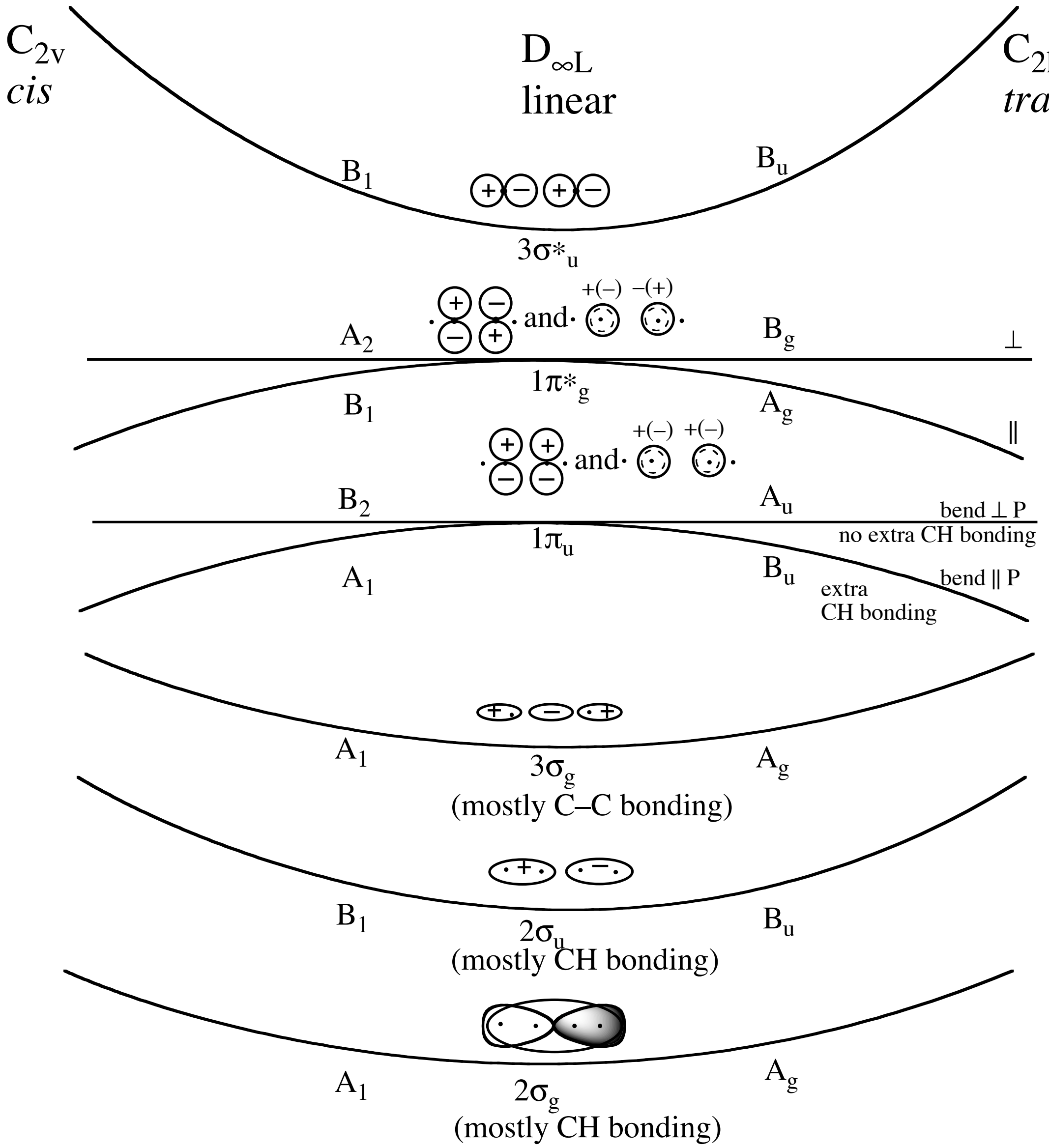
2. rule out  assignment

3. support for  assignment

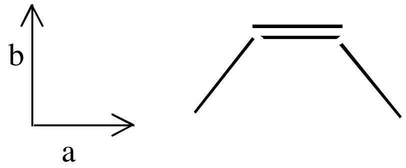
How do various MOs respond to distortion of the molecular shape (e.g. HCCH)?

For QMOT, look at books by John Lowe, Gimarc, and papers by Walsh.

The following diagram shows how MOs in acetylene change energy as the molecule is distorted from linear to *cis*-bent (left side of diagram) or linear to *trans*-bent (right side of diagram).



Anti-bonding interactions are always slightly more unfavorable energetically than corresponding bonding interactions.



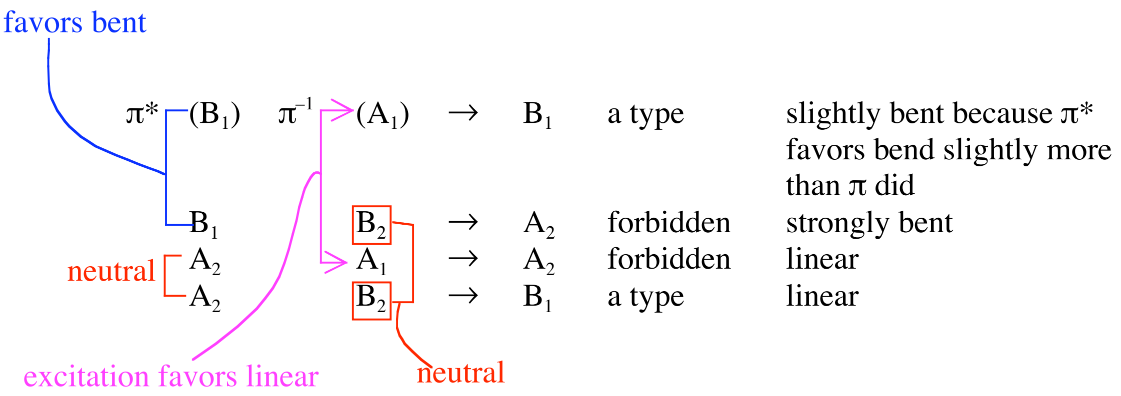
C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	R_z
B_1	1	–1	1	–1	T_x, R_y
B_2	1	–1	–1	1	T_y, R_x

(a, b, c) = (x, z, y)

π^* in plane B_1 $\oplus\ominus$ / $\ominus\oplus$ symmetric with respect to $\sigma_v(xz)$, anti-symmetric with respect to $\sigma(yz)$.

$\perp$ plane A_2

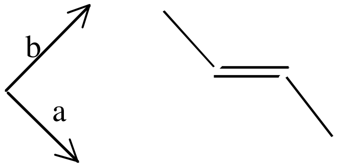
π^{-1} in plane A_1
$\perp$ plane B_2



π^*	π^{-1}				
(B_1)	(A_1)	→	B_1	a type	slightly bent because π^* favors bend slightly more than π did
B_1	$\boxed{B_2}$	→	A_2	forbidden	strongly bent
A_2	A_1	→	A_2	forbidden	linear
A_2	$\boxed{B_2}$	→	B_1	a type	linear

The only allowed transition is $B_1 \leftarrow A_1 \left(=\Sigma_g^+\right)$ which is a-type $\Delta K_a = 0$, weak Q, which does not agree with spectrum. Moreover, the B_1 excited states are expected to be either linear or only slightly bent.

Note the tilt of the a,b axes relative to the C-C bond axis (exaggerated as drawn)!!!!



C_{2h}	E	$C_2(z)$	$\sigma_h(xy)$	i	
A_g	1	1	1	1	R_z
A_u	1	1	–1	–1	T_z
B_g	1	–1	–1	1	R_x, R_y
B_u	1	–1	1	–1	T_x, T_y

(a, b, c) = (x, z, y)

π^* in plane $\oplus\ominus$ / $\ominus\oplus$ $A_g \leftarrow$ favors bent

$\perp$ plane $B_g \leftarrow$ neutral

π^{-1} in plane $B_u \leftarrow$ favors bent
$\perp$ plane $A_u \leftarrow$ neutral

favors bent

neutral

excitation favors	$\boxed{B_u}$	×	A_g	→	B_u	x,y = a,b	next to lowest E weakly bent
linear	$\boxed{B_u}$	×	B_g	→	A_u	z = c	highest E linear
neutral	$\boxed{A_u}$	×	A_g	→	A_u	c	lowest E strongly bent
	$\boxed{A_u}$	×	B_g	→	B_u	a,b	next to highest E linear

expect to find either c-type $^1A_u \leftarrow {}^1\Sigma_g^+$ strongly bent

or a,b-type $^1B_u \leftarrow {}^1\Sigma_g^+$ weakly bent

c-type $\Delta K_a = \pm 1, \Delta K_c =$ even, strong Q
a-type $\Delta K_a = 0, \Delta K_c =$ odd, weak Q
b-type $\Delta K_a = \pm 1, \Delta K_c =$ odd, strong Q

$X^1\Sigma_g^+$ linear ground state is special because it has only $\ell = 0$ (which acts like K_a) in zero-point level.

This means that cold bands will sample only limited number of K_a' values (0 and/or 1).

THIS IS WHY HCCH WAS 1$^{\text{ST}}$ POLYATOMIC MOLECULE FOR ROTATIONAL ANALYSIS OF AN ELECTRONIC TRANSITION.

Observed bands are probably c-type because they consist of strong $K' - \ell'' = \pm 1$ sub-bands and contain a strong Q branch. *This can be checked because, for a near prolate asymmetric top, the prolate-oblate correlation diagram requires that the higher energy member of each asymmetry doublet have the lower* K_c *value.*

$$J_{K_a} \quad \begin{array}{l} \text{———} K_c = J - K_a \\[1em] \text{———} K_c = J - K_a + 1 \end{array}$$

and the magnitude of the asymmetry splitting is controlled mostly by B-C.

So we can figure out which rotational branches are naively[*] allowed for c vs. a,b-hybrid transitions.

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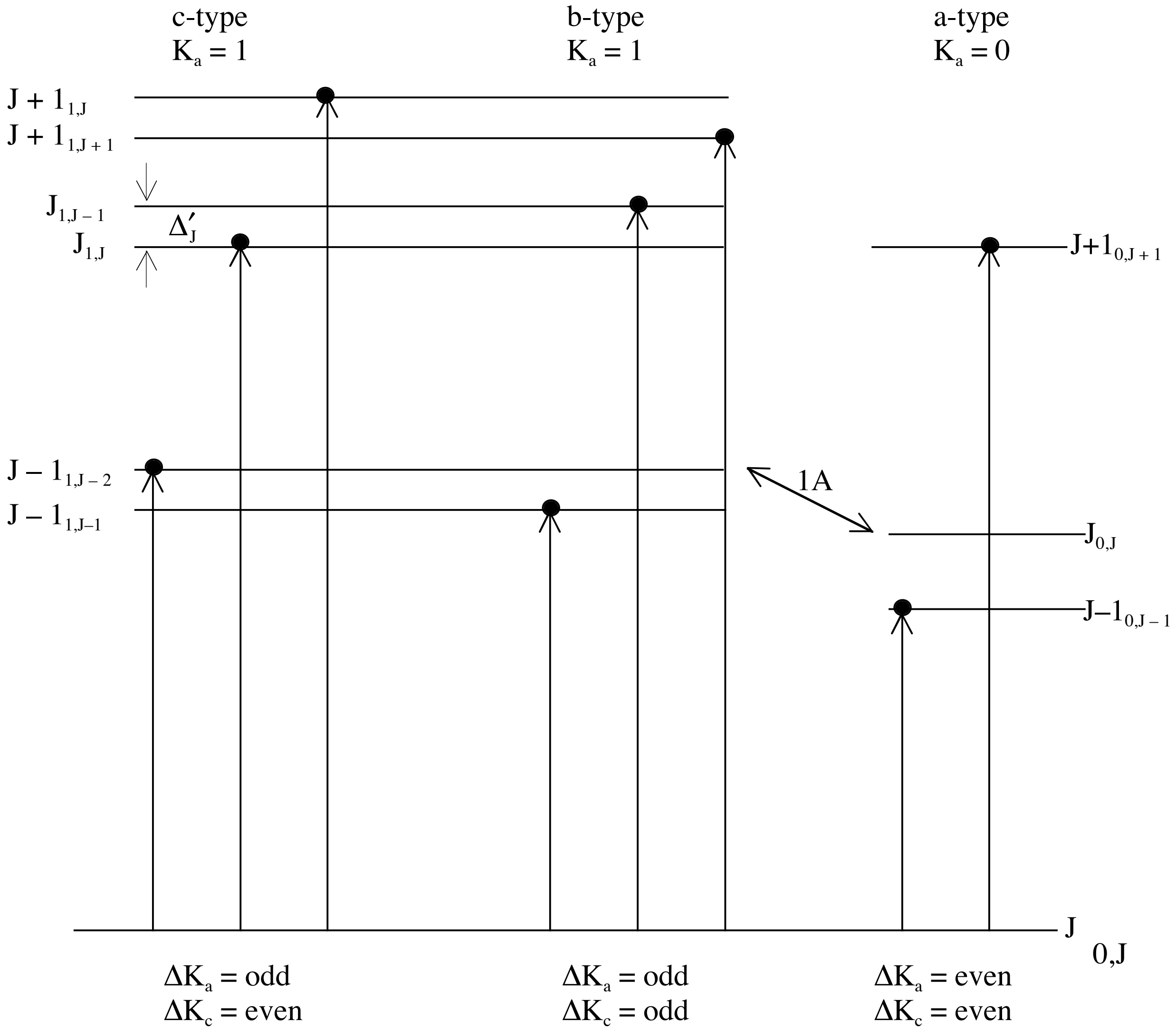
[*] Neglecting nuclear spin and rovibronic symmetry requirements.

Supplement



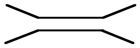
“Combination defects” ← a-type   b-type   no Q

$R(J)-Q(J)=2(J+1)\bar{B}'+\Delta'_J$ $R(J)-Q(J)=2(J+1)\bar{B}'-\Delta'_J$

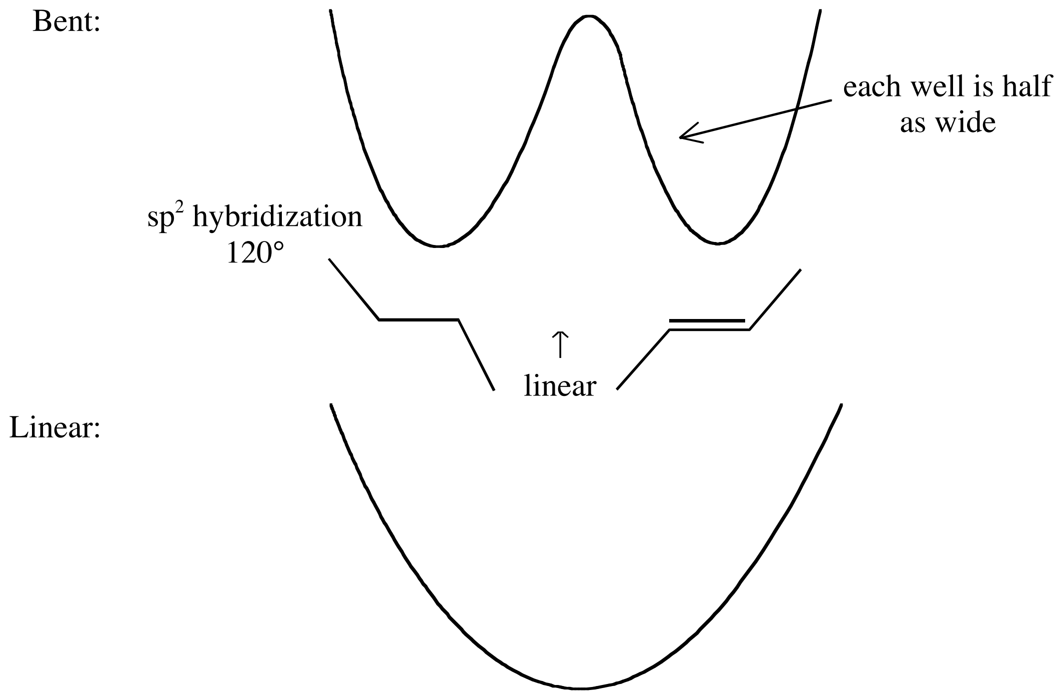
$Q(J)-P(J)=2J\bar{B}'-\Delta'_J$ $Q(J)-P(J)=2J\bar{B}'+\Delta'_J$

What else do we expect?

Activity in the C-C stretch (expect frequency near that of ethylene ground state) because $\pi^*\leftarrow\pi$ should weaken k_{CC} and lengthen r_{CC}

expect $\omega_{CC} \approx 1623\ \text{cm}^{-1}$
ν_2 in  $\tilde{X}$-State

Activity in the *trans*-bend because the bend angle decreases from 180° (sp hybridization) and the bend frequency nearly doubles.

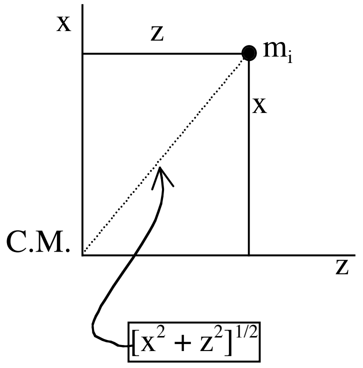


Small activity in symmetric CH stretch because CH might get slightly shorter and stronger (expect ~3100 cm^{-1}).

No activity in torsion (< 1000 cm^{-1}), antisymmetric (~ 3100) CH stretch, and antisymmetric in-plane bend (< 1000 cm^{-1}).

All Confirmed!

Inertial defect $I_A + I_B - I_C = 0$ is useful criterion for planar molecule. All atoms in xz plane.



$$I_x = \sum_i m_i z_i^2$$

$$I_z = \sum_i m_i x_i^2$$

$$I_y = \sum_i m_i \left(x_i^2 + z_i^2\right)$$

HCCH

		$\tilde{A}\,^1A_u$		$\tilde{X}\,^1\Sigma_g^+$
trans-bend	ν_3	1047.70 cm^{-1}	ν_4	608.26
C—C	ν_2	1389	ν_2	1973.5
	A_0	12.94		
	B_0	1.1243	B	1.1766
	C_0	1.0297		
	r_{CH}	1.08Å		1.058
	r_{CC}	1.388Å		1.208
	θ_{CCH}	120°		180°

$$\frac{1}{A}+\frac{1}{B}-\frac{1}{C}=-0.0044\ \text{cm}$$