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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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Lecture #32: The $\text{H}_2\text{CO } \tilde{\text{A}}^1\text{A}_2 \leftarrow \tilde{\text{X}}^1\text{A}_1$ Transition

H_2CO was 1st (asymmetric top) polyatomic electronic transition to be rotationally analyzed.

G. H. Dieke and G. B. Kistiakowsky *Phys. Rev.* **45**, 4 (1934).

It is more complicated than linear HCCH because many values of the K_a rotational quantum number can have significant thermal population in the $\tilde{\nu}'' = 0$ level. For a linear molecule in a Σ -state, $K_a = 0$, and $\ell = 0$ in $\tilde{\nu}'' = 0$.

The $S_1 \leftarrow S_0$ transition in H_2CO

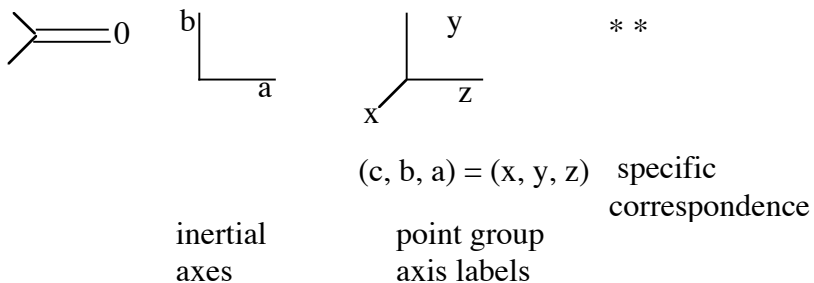
- * is electronically forbidden in C_{2v} (a) $[(x, y, z) = (c, b, a)]$
- * the excited state is expected and appears to be non planar - hence C_{2v} may not be relevant.
- * “quasi-planar” molecule – inversion barrier is low resulting in *staggering* of bending levels
- * 3 distinct transition mechanisms, each with its own selection rules, contribute to $\tilde{\text{A}} - \tilde{\text{X}}$ system.

Outline:

- i. classification of orbitals and normal modes
- ii. what do we expect (geometry and vibrational structure of S_1)
- iii. “vibronically” rather than electronically allowed system – false origin, promoter mod
- iv. surprise in hot band spectrum – peculiar spacings in upper state out-of-plane bend
- v. low barrier to inversion through planarity

Next time: Vibronic Coupling (beyond Franck-Condon)

Body fixed axis system:



Molecular orbitals from atomic orbitals:

IP	CO	14.014eV	
IP	H	13.595	\therefore H atom 1s orbitals lie above CO HOMO
IP	C	11.264	
IP	O	13.614	\therefore $\sigma 2s, \pi 2p$ are polarized toward O

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	$T_z = a$
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	$T_x = c, R_y$
B_2	1	-1	-1	1	$T_y = b, R_x$

*** see p. 2002 ***
 "Report on Notation"
 z is axis of symmetry
 x \perp to plane

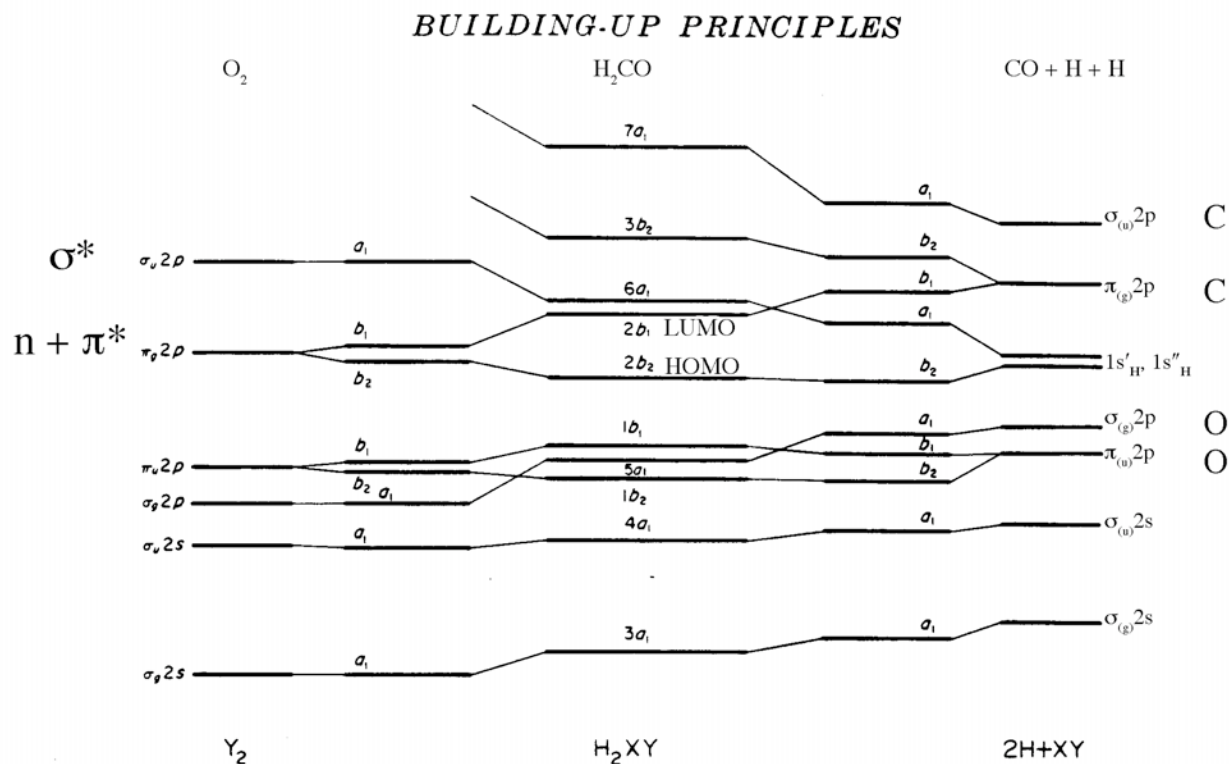
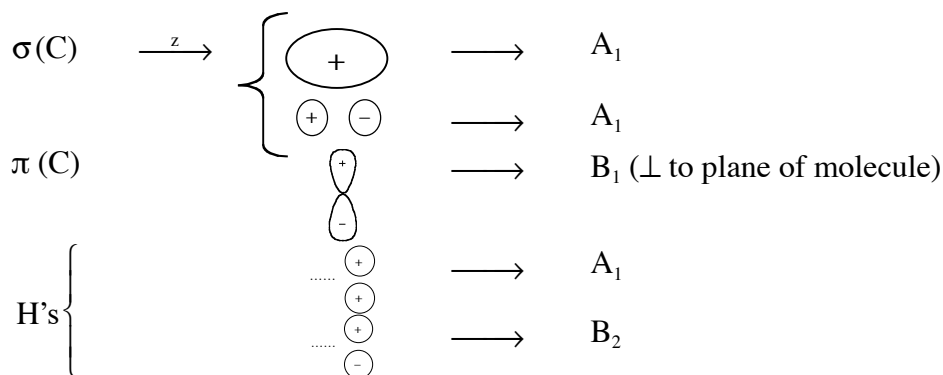


Figure 1: Correlation of the orbitals of planar H_2XY to those of the united molecule Y_2 and to those of $2H + XY$. The variable along the abscissa is the XH distance. Note that at the left, since Y_2 is homonuclear, the orbitals are $\sigma_g, \sigma_u, \pi_g, \pi_u$ while at the right, since XY is heteronuclear, the g, u characteristic does not strictly apply. However, just as at the left, the orbitals σ_{2s} are mixtures (but not 50:50 mixtures) of the $2s$ orbitals of X and Y and similarly for the other XY orbitals. The order of $\pi_{(u)}2p$ and $\sigma_{(g)}2p$ is reversed at the right compared to the left in accordance with the situation in CO as compared to O_2 (see Herzberg, Vol. I, p. 346). At the left, the splitting of π_u and π_g into b_2 (π in-plane) and b_1 ($\pi \perp$ plane) corresponds to breaking the cylindrical symmetry of the $C + H + H = O$ united atom.

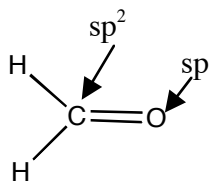


π (C) orbitals \perp to plane of paper
 paper is yz plane
 $\pi(\text{CO}) \perp$ plane
 $\pi(\text{O})$ in plane of molecule $\rightarrow B_2$

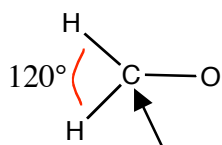


B_1 (no amplitude on the H atoms)

Lewis Structure

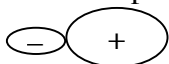


(one σ bond, one π bond, two lone pairs on O, one non-bonding π , one non-bonding σ)



π is necessarily \perp to plane

The two “lone pair” or “non-bonding” (n) orbitals on O are



and $\begin{matrix} \oplus \\ \ominus \end{matrix}$ (in the molecular plane)

A_1 (σ)

B_2 (π)

sp-polarized

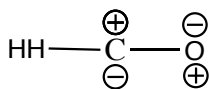
more stable because

avoids e^- in C—O

region

HOMO

The C-O antibonding orbital, viewed edge-on, is the LUMO: B_1 [odd wrt C_2 , even wrt $\sigma_v(xz)$]



paper is xz plane

HOMO \rightarrow LUMO is $B_1 \leftarrow B_2$ $\pi^* \leftarrow n$

S_1 state configuration is ... $b_1^1 b_2^1$

$B_1 \otimes B_2 = A_2$ which is electric dipole forbidden from the $\tilde{X}^1 A_1$ electronic ground state (because A_2 does not transform as T_x , T_y , or T_z).

What do we know about the $\tilde{X}^1 A_1$ ground state?

Figure out symmetries of vibrations from $\Gamma_{\text{RED}} = [12, -2, 2, 4] = 4\Gamma_{A_1} + 1\Gamma_{A_2} + 3\Gamma_{B_1} + 4\Gamma_{B_2}$

Vibrations: $3 \times A_1, 0A_2, 1B_1, 2B_2$ (after removing 3 translations and 3 rotations)

$2e^-$ in each orbital $\tilde{X}^1 A_1$

$$\begin{aligned} A_0 & 9.4053 \text{ cm}^{-1} \\ B_0 & 1.2954 \\ C_0 & 1.1343 \end{aligned}$$

$$\begin{aligned} r_{\text{CO}} &= 1.210 \text{ \AA} \\ R_{\text{CH}} &= 1.102 \text{ \AA} \\ \theta_{\text{HCH}} &= 121.1^\circ \end{aligned}$$

$$\frac{1}{A} + \frac{1}{B} - \frac{1}{C} = -0.0033 \text{ cm} \text{ (small and negative inertial defect implies planarity)}$$

$\omega_1(a_1)$	2766.4 cm^{-1}	sym CH stretch
$\omega_2(a_1)$	1746.1	CO stretch
$\omega_3(a_1)$	1500.6	scissors
$\omega_4(b_1)$	1167.3	out of plane
$\omega_5(b_2)$	2843.4	anti-sym CH
$\omega_6(b_2)$	1251.2	in plane wag

Numbering of vibrational modes, by convention in order of frequency within each symmetry type, symmetries in order A_1, A_2, B_1, B_2 .

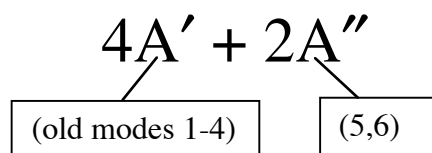
What do we expect for $\pi^* \leftarrow n$ electronic transition, provided that it is observable?

* lengthen C—O bond

* change hybridization on C from sp^2 to sp^3 to minimize antibonding interaction! (Could also think of this in a Walsh diagram sense, out of plane distortion allows H atoms to derive some bonding character from $\pi^*(b_1)$ and thereby polarize it out of the antibonding C—O region.)

This could cause $\left\{ \begin{array}{l} \theta_{\text{HCH}} \rightarrow 109^\circ \text{ (decrease from } 121.1^\circ) \\ \text{nonplanar distortion} \end{array} \right.$

If the molecule becomes non-planar, we can no longer work in the C_{2v} point group. The vibrations no longer divide into 3 symmetry species. In C_s we have



Mode 4 (out of plane bend) could become symmetry active in all quanta, not merely even quanta! If C_s , expect progression in ν'_4 . So whether we see odd and even quanta of ν'_4 seems to be a key question.

Strongly F—C active modes in C_s symmetry:

definitely CO ω_2

possibly scissors ω_3

(possibly active because of $sp^2 \rightarrow sp^3$ change of hybridization on C)

possibly out-of-plane ω_4

Observe long progression in 1182 cm^{-1} : must be C—O stretch. (Note that $\pi^* \leftarrow n$ decreases bond order from 2.0 to 1.5.) Each strong band is observed with short progressions built on it:

in 824 cm^{-1} out-of-plane

and 1322 cm^{-1} scissors

and 2872 cm^{-1} symmetric CH

But is 824 cm^{-1} ω'_4 or $2\omega'_4$? (Why would we even think of $2\omega'_4$? Seems too low a frequency.)

HINT: $\begin{cases} A = 8.69 & B = 1.156 & C = 1.041 & \text{for excited state} \\ \frac{1}{A} + \frac{1}{B} - \frac{1}{C} = 0.0195 \text{ cm} & \text{much larger (and positive!) inertial defect than in } \tilde{X} \text{ state.} \end{cases}$

suggests much less planar than \tilde{X}^1A_1 state, so if equilibrium geometry is nonplanar $\rightarrow C_s$ point group $\rightarrow 824 \text{ cm}^{-1}$ is $1\omega'_4$ not $2\omega'_4$. (In C_s , there are $4A'$ symmetry allowed normal modes and two A'' forbidden normal modes. The fourth A' mode would be an out of plane bend.) In C_{2v} the $^1A_2 \leftarrow ^1A_1$ transition is electronically forbidden, but it might be vibronically allowed.

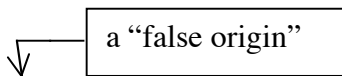
$$\Gamma_{(ev)'} \otimes \Gamma_{(ev)''} = \Gamma_a \text{ or } \Gamma_b \text{ or } \Gamma_c$$

Start with cold bands $\Gamma_{(ev)'} = \Gamma_{A_1}$.

In C_{2v} , expect to only find strong transitions built on odd quanta of non-totally symmetric modes:

$$\left. \begin{array}{l} v'_4(b_1) \Rightarrow \Gamma_{(ev)'} = A_2 \otimes B_1 = \Gamma_{B_2} = \Gamma_b \quad (\text{b-type}) \\ v'_5 \text{ or } v'_6(b_2) \Rightarrow \Gamma_{(ev)'} = A_2 \otimes B_2 = B_1 = \Gamma_{B_1} = \Gamma_c \quad (\text{c-type}) \end{array} \right\} \text{rotational selection rules}$$

Starting from $V'' = 0$:



So expect to see $V' = (0 \text{ or } 1, v_2, 0 \text{ or } 1, 1, 0, 0)$ b-type bands from $\tilde{X}(0, 0, 0, 0, 0, 0)$ level.

Never expect to see $V' = (0, 0, 0, 0, 0, 0)$ i.e. the 0_0^0 band.

Modes 5 and 6 are not expected to be F-C active. (antisymmetric CH stretch, in-plane wag)

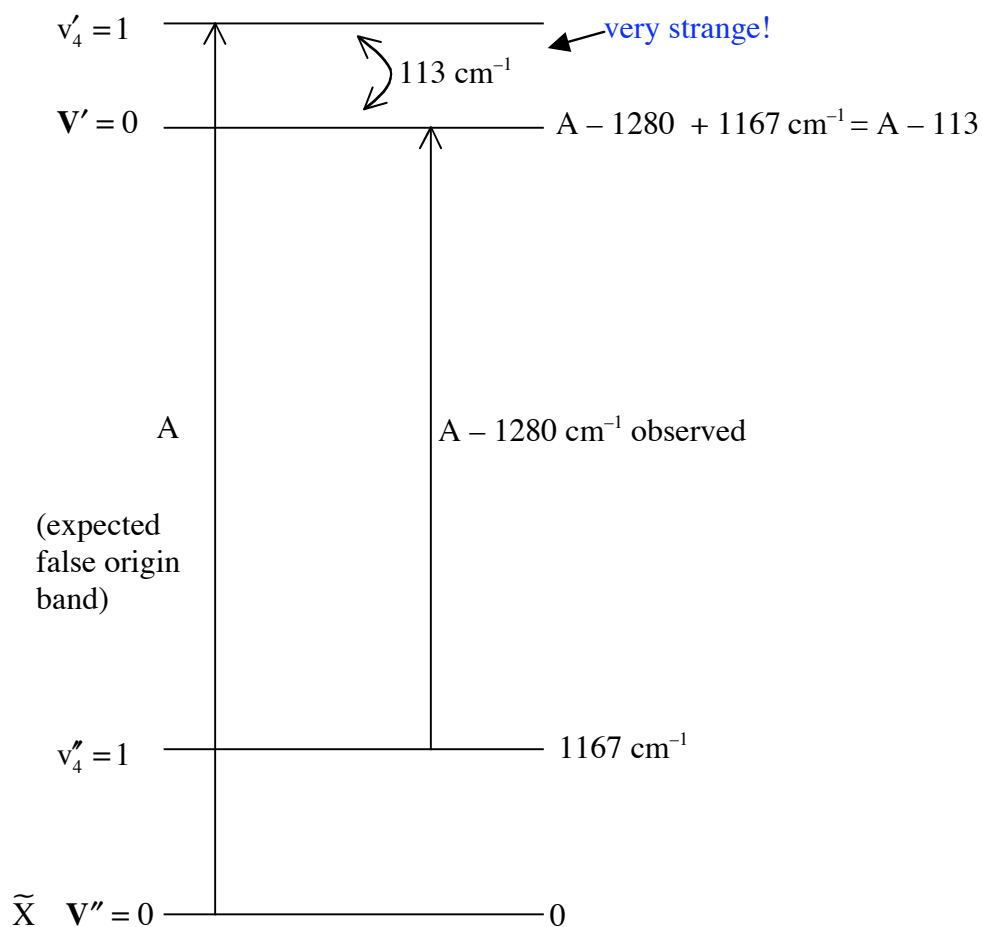
All strong cold bands in $\tilde{A} - \tilde{X}$ spectrum are observed to be b-type ($\Delta K_a = \pm 1, K_c = \text{odd}$).

So all looks clear for a non-planar $^1A' S_1$ electronic state OR a vibronically allowed $^1A_2 \leftarrow ^1A_1$. But is 824 cm^{-1} v'_4 or $2v'_4$? It would have to be $2v'_4$ if the S_1 state is planar (C_{2v}), 1A_2 . It could be v_4 if the S_1 state is nonplanar (C_s) $^1A'$.

Hot bands and emission bands contain some surprises!

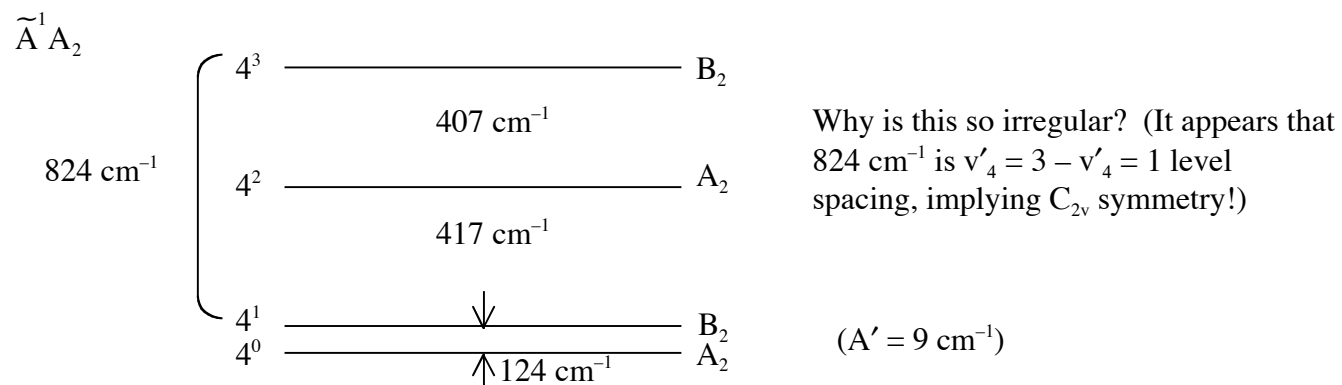
Level diagram - for hot bands

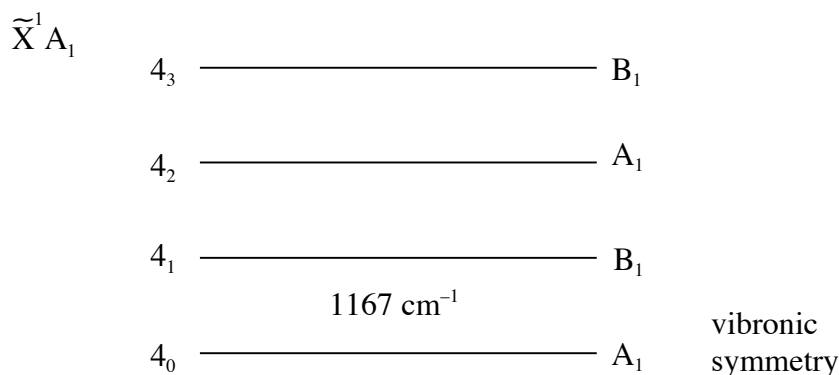
v''_4 is lowest frequency mode in \tilde{X} -state.



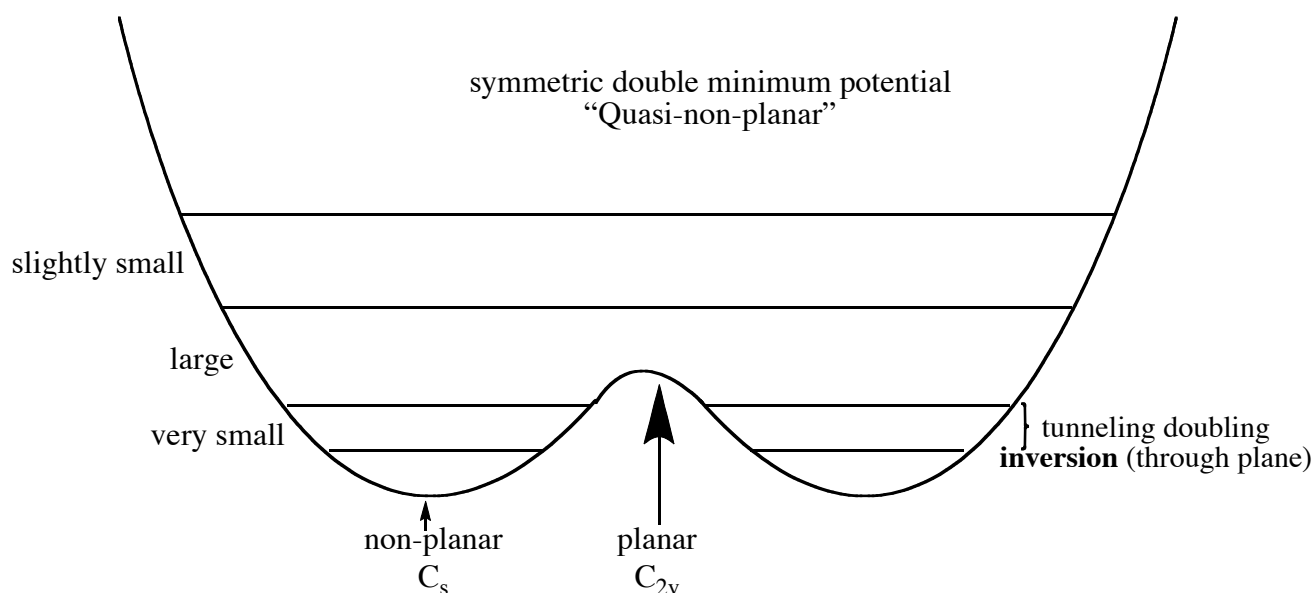
These vibrational bands have some contribution from the rotational constants A' or A'' for $K' = 1$ or $K'' = 1$ included, which we will ignore here.

Observed Bending Level Diagram





Bending potential for \tilde{A}^1A'' State



get a situation where it is appropriate to work in the higher symmetry group.

J. C. D. Brand, *J. Chem. Soc.* p. 858 (1956)

deduced that zero point energy in the inversion potential for the \tilde{A} -state is only 400 cm⁻¹, and that the top of the barrier is 650 cm⁻¹, thus the $v_4 = 1$ level lies just below top of barrier.

What mechanisms could make the $\tilde{A}^1A_2 - \tilde{X}^1A_1$ transition observable?

- Vibronic coupling via the Q₄ out-of-plane vibration: $\left\{ \begin{array}{l} \text{see only alternate quanta of } v'_4 \text{ or } v''_4 \\ \text{b-type rotational selection rules} \end{array} \right.$
- Magnetic dipole ($A_1 \otimes A_2$) = A₂ = R_z
 - ↙ z-component of magnetic dipole
 - ↘ a-type transitions

a-type rotational selection rules [actually observed as very weak a-type transitions into the inversion doublet component opposite to that observed via the main bands]

3. Vibronic coupling via the ν_5 or ν_6 in plane vibrations $\left\{ \begin{array}{l} \text{built on } \nu'_5 = 1 \text{ or } \nu'_6 = 1 \\ \text{c-type bands} \end{array} \right.$.

Weak bands of this type are also observed.

The $\tilde{A} - \tilde{X}$ transition does derive its intensity from 3 mechanisms:

1. *b-type* Vibronic coupling to a 1B_1 excited electronic state via the ν_4 (b_1) promoting mode (this is the only B_1 overall vibrational level)
2. *c-type* Vibronic coupling to a 1B_2 excited electronic state via ν_5 and ν_6 (b_2) promoting modes (only B_2 overall vibrational levels)
3. *a-type* magnetic dipole transitions (only totally symmetric vibrations). All 3 symmetric modes are governed by Franck-Condon like intensity factors.

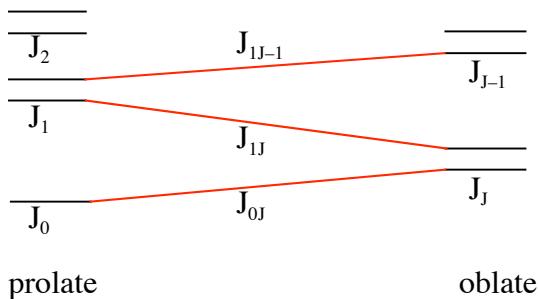
In the vibronic coupling cases, we have to worry about the vibrational structure of the state from which intensity is borrowed, times a factor controlling the strength of the vibronic coupling which increases monotonically with the number of odd quanta in the promoting mode.

Rotational structure:

A_2 has $\chi(\sigma_v) = -1$ (odd parity)

total parity of A_1 vs. A_2 states

A_1	$K = 0$	A_2		A_1	$K = 1$	A_2
-	$\frac{\quad}{3}$	+		\pm	$\frac{\quad}{\quad}$	\mp
+	$\frac{\quad}{2}$	-		\mp	$\frac{2_{11}}{\quad}$	\pm
-	$\frac{\quad}{1}$	+		\pm	$\frac{2_{12}}{\quad}$	\mp
+	$\frac{\quad}{J=0}$	-		\mp	$\frac{1_{10}}{\quad}$	\pm
	J_{0J}				$\frac{1_{11}}{\quad}$	



The J_{1J-1} level always lies at higher energy than the J_{1J} level. The b-type vibronic (via the $\nu'_4(b_1)$ promoting mode, admixing 1B_1 electronic character) rotational transition $J_{1J-1} \leftarrow J_{0J} \text{ } ^1Q_0(J)$ terminates on

the upper asymmetry component, whereas the c-type vibronic (via the ν'_5 or ν'_6 (b_2) promoting mode, admixing 1B_2 electronic character) rotational transition $J_{1J} \leftarrow J_{0J} {}^1Q_0(J)$ terminates on the lower asymmetry component. The sign of the observed asymmetry splitting, determined by A, B, C, thus provides a way of distinguishing between the two vibronic coupling mechanisms. For a magnetic dipole allowed transition, parity does not change. An a-type magnetic dipole ${}^1A_2 - {}^1A_1$ rotational transition

$$(J + 1)_{1(J+1)} \leftarrow J_{1J} \quad {}^aR_1(J)$$

is from the lower energy asymmetry component in the lower state to the lower energy asymmetry component in the upper state. The allowed R and P branch magnetic dipole transitions are lower to lower and upper to upper.