Lecture #32: The H$_2$CO $\tilde{A}^1A_2 \leftrightarrow \tilde{X}^1A_1$ Transition

H$_2$CO was 1st (asymmetric top) polyatomic electronic transition to be rotationally analyzed.


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

The $S_1 \leftrightarrow S_0$ transition in H$_2$CO

* 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 $\tilde{A} - \tilde{X}$ 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:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IP</td>
<td>CO</td>
<td>14.014eV</td>
</tr>
<tr>
<td>IP</td>
<td>H</td>
<td>13.595</td>
</tr>
<tr>
<td>IP</td>
<td>C</td>
<td>11.264</td>
</tr>
<tr>
<td>IP</td>
<td>O</td>
<td>13.614</td>
</tr>
</tbody>
</table>
**Figure 1:** Correlation of the orbitals of planar H₂XY to those of the united molecule Y₂ and to those of 2H + XY. The variable along the abscissa is the XH distance. Note that at the left, since Y₂ is homonuclear, the orbitals are σᵣ, σᵤ, πᵣ, πᵤ while at the right, since XY is heteronuclear, the g, u characteristic does not strictly apply. However, just as at the left, the orbitals σ₂s 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 πᵤ₂p and σᵤ₂s is reversed at the right compared to the left in accordance with the situation in CO as compared to O₂ (see Herzberg, Vol. I, p. 346). At the left, the splitting of πᵣ and πᵤ into b₂ (π in-plane) and b₁ (π ⊥ plane) corresponds to breaking the cylindrical symmetry of the C + H + H = O united atom.

\[
\begin{align*}
\text{σ (C)} & \xrightarrow{z} \begin{cases}
+ & \rightarrow A_1 \\
+ & \rightarrow A_1 \\
- & \rightarrow B_1 (\perp \text{to plane of molecule})
\end{cases} \\
\text{π (C)} & \rightarrow B_1 \\
\text{H's} & \begin{cases}
- & \rightarrow A_1 \\
0 & \rightarrow B_2
\end{cases}
\end{align*}
\]
\( \pi \) (C) orbitals \( \perp \) to plane of paper  
paper is yz plane  
\( \pi \)(CO) \( \perp \) plane  
\( \pi \)(O) in plane of molecule \( \rightarrow \) \( B_1 \) (no amplitude on the H atoms)

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

\[
\begin{align*}
&+ \quad \text{sp}^2 \\
&- \quad \text{sp}
\end{align*}
\]

The \( \pi \) is necessarily \( \perp \) to plane

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

\[
\text{HOMO} \rightarrow \text{LUMO} \text{ is } B_1 \leftarrow B_2 \quad \pi^* \leftarrow n
\]

S\(_1\) state configuration is ... \( b_1^1b_2^1 \)

\( b_1^1b_2^1 \) which is electric dipole forbidden from the \( \tilde{X}^1A_1 \) electronic ground state (because \( A_2 \) does not transform as \( T_x, T_y, \text{or } T_z \)).

What do we know about the \( \tilde{X}^1A_1 \) 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)
\[ \frac{1}{\kappa} + \frac{1}{\bar{r}} - \frac{1}{c} = -0.0033 \text{ cm} \] (small and negative inertial defect implies planarity)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_1)</td>
<td>2766.4 cm(^{-1})</td>
<td>sym CH stretch</td>
</tr>
<tr>
<td>(\omega_2)</td>
<td>1746.1</td>
<td>CO stretch</td>
</tr>
<tr>
<td>(\omega_3)</td>
<td>1500.6</td>
<td>scissors</td>
</tr>
<tr>
<td>(\omega_4)</td>
<td>1167.3</td>
<td>out of plane</td>
</tr>
<tr>
<td>(\omega_5)</td>
<td>2843.4</td>
<td>anti-sym CH</td>
</tr>
<tr>
<td>(\omega_6)</td>
<td>1251.2</td>
<td>in plane wag</td>
</tr>
</tbody>
</table>

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 \(\theta_{\text{HCH}} \rightarrow 109^\circ\) (decrease from 121.1\(^\circ\))

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

\[ 4A' + 2A'' \]

(5,6)

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

Strongly F–C active modes in C\(_s\) symmetry:
- definitely CO \(\omega_2\)
- possibly scissors \(\omega_3\)
- (possibly active because of sp\(^2\) → sp\(^3\) change of hybridization on C)
- possibly out-of-plane \(\omega_4\)

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

HINT:

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

suggests much less planar than \(\tilde{X}' A_1\) state, so if equilibrium geometry is nonplanar \(\rightarrow\) \(C_s\) point group \(\rightarrow\) 824 cm\(^{-1}\) is 1\(\omega'_4\) not 2\(\omega'_4\). (In \(C_s\), there are 4\(A'\) 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 \(1 A_2 \leftarrow 1 A_1\) 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:

\[
\begin{align*}
v'_4 (b_1) &\Rightarrow \Gamma_{(ev)'} = A_2 \otimes B_1 = \Gamma_{B_2} = \Gamma_b \text{ (b-type)} \\
v'_5 \text{ or } v'_6 (b_2) &\Rightarrow \Gamma_{(ev)'} = A_2 \otimes B_2 = B_1 = \Gamma_{B_1} = \Gamma_c \text{ (c-type)}
\end{align*}
\]

rotational selection rules

Starting from \(V'' = 0\):

\[
\text{a “false origin”}
\]

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 \(0^0\) 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 \(1 A'\) \(S_1\) electronic state OR a vibronically allowed \(1 A_2 \leftarrow 1 A_1\). But is 824 cm\(^{-1}\) \(v'_4\) or 2\(v'_4\)? It would have to be 2\(v'_4\) if the \(S_1\) state is planar \((C_{2v})\), \(1 A_2\). It could be \(v_4\) if the \(S_1\) state is nonplanar \((C_s)\) \(1 A'\).

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

Why is this so irregular? (It appears that $824 \text{ cm}^{-1}$ is $v'_4 = 3 - v'_4 = 1$ level spacing, implying $C_{2v}$ symmetry!) 

$(A' = 9 \text{ cm}^{-1})$
Bending potential for $\tilde{\chi}^1{A}_1$ State

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

deduced that zero point energy in the inversion potential for the $\tilde{\chi}$—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 $\tilde{\chi}^1{A}_2 - \tilde{\chi}^1{A}_1$ transition observable?

1. Vibronic coupling via the $Q_4$ out-of-plane vibration: see only alternate quanta of $v'_4$ or $v''_4$

2. Magnetic dipole ($A_1 \otimes A_2 = A_2 = R_z$) $z$-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 $\nu_5$ or $\nu_6$ in plane vibrations \( \begin{cases} \text{built on } \nu'_5 = 1 \text{ or } \nu'_6 = 1 \\ \text{c-type bands} \end{cases} \). Weak bands of this type are also observed.

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

1. **b-type** Vibronic coupling to a $^1B_1$ excited electronic state via the $\nu_4$ ($b_1$) promoting mode (this is the only $B_1$ overall vibrational level)

2. **c-type** Vibronic coupling to a $^1B_2$ excited electronic state via $\nu_5$ and $\nu_6$ ($b_2$) 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)

<table>
<thead>
<tr>
<th>$A_1$</th>
<th>$K = 0$</th>
<th>$A_2$</th>
<th>$K = 1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$</td>
<td>3</td>
<td>$+$</td>
<td>$\pm$</td>
<td>$\mp$</td>
</tr>
<tr>
<td>$+$</td>
<td>2</td>
<td>$-$</td>
<td>$\mp$</td>
<td>$\pm$</td>
</tr>
<tr>
<td>$-$</td>
<td>1</td>
<td>$+$</td>
<td>$\pm$</td>
<td>$\mp$</td>
</tr>
<tr>
<td>$+$</td>
<td>$J = 0$</td>
<td>$J_{0J}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$J_0$  $J_{0J}$  $J_1$  $J_{1J}$  $J_{1J-1}$  $J_{2}$

polar  oblate

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 $J_{1J-1} \leftarrow J_{0J} \ 'Q_{0}(J)$ terminates on
the upper asymmetry component, whereas the c-type vibronic (via the \( \nu'_5 \) or \( \nu'_6 (b_2) \) promoting mode, admixing \( ^1B_2 \) electronic character) rotational transition \( J_{ij} \leftarrow J_{0j} \) \( ^1Q_0(J) \) 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 \( ^1A_2 \rightarrow ^1A_1 \) rotational transition

\[
(J + 1)_{(J+1)} \leftarrow J_J \quad ^qR_1(J)
\]

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.