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5.80 Small-Molecule Spectroscopy and Dynamics
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Lecture #33: Vibronic Coupling

Last time: $\text{H}_2\text{CO } \tilde{\text{A}}^1\text{A}_2 - \tilde{\text{X}}^1\text{A}_1$
 Electronically forbidden if $\tilde{\text{A}}$ -state is planar
 vibronically allowed to alternate v'_4 vibrational levels if $\tilde{\text{A}}$ -state is planar
 inertial defect says $\tilde{\text{A}}$ -state is not planar
 expect to see all v'_4 if not planar
 staggering of v'_4 level spacings \Rightarrow inversion through low barrier to planarity
dynamic vs. rigid molecule symmetry classification: molecular symmetry group

How does vibronic coupling really work?

What are the vibrational intensity factors analogous to Franck-Condon factors in the case of vibronically allowed rather than electronically allowed transition?

See T. Azumi and K. Matsuzaki, *Photochemistry and Photobiology* **25**, 315 (1977) for an extremely readable review article.

Outline: Crude Adiabatic Approximation
 Correction of ψ for effect of neglected off-diagonal matrix elements
 $\text{H}_2\text{CO } \tilde{\text{A}}^1\text{A}_2$ example
 What happens to Franck-Condon factors for a “vibronically allowed” transition?
 Two electronic basis sets — prediagonalize “symmetry-breaking” vibronic interaction
 Changes in shapes of potential curves (deperturb to a simpler, “more natural” shape)
 K. K. Innes’ model for vibrational band intensities and level staggering

Recall Born-Oppenheimer or “clamped nuclei” approximation.

We use this procedure to define complete sets of electronic and nuclear motion wavefunctions with which we can FORMALLY expand exact ψ 's and compute (or parametrize) all properties of exact eigenstates.

The simplest basis set is called “CRUDE ADIABATIC” (CA)

$$\psi_{jt}^{\text{CA}}(\mathbf{r}, \mathbf{Q}) = \underbrace{\psi_j^{\text{o}}(\mathbf{r}, \mathbf{Q}_0)}_{\text{electronic state}} \underbrace{\chi_{jt}^{\text{CA}}(\mathbf{Q})}_{\text{vibrational state}}$$

fixed nuclear locations!

\mathbf{Q}_0 is a convenient reference structure (usually the equilibrium geometry or a high-symmetry potential energy maximum or saddle point).

ψ_j^{o} is the electronic wavefunction in the j -th electronic state computed at the chosen and explicitly specified set of fixed nuclear coordinates \mathbf{Q}_0 .

$\chi_{jt}^{CA}(\mathbf{Q})$ is the vibration-rotation wavefunction computed from an approximate nuclear Schrödinger Equation.

$$\left[\underbrace{T_N(\mathbf{Q}) + V(\mathbf{Q}) + \epsilon_j^o(\mathbf{Q}_0) + \langle \psi_j^o(\mathbf{r}, \mathbf{Q}_0) | \Delta U(\mathbf{r}, \mathbf{Q}) | \psi_j^o(\mathbf{r}, \mathbf{Q}_0) \rangle}_{\text{effective potential-energy surface}} \right] \chi_{jt}^{CA}(\mathbf{Q}) = E_{jt}^{CA} \chi_{jt}^{CA}(\mathbf{Q})$$

$\Delta U(\mathbf{r}, \mathbf{Q}) = U(\mathbf{r}, \mathbf{Q}) - U(\mathbf{r}, \mathbf{Q}_0)$
 change in $e^- \leftrightarrow$ nuclear and $e^- \leftrightarrow e^-$
 Coulomb energy

eigenvalue of clamped nuclei electronic Schrödinger Equation at \mathbf{Q}_0

nuclear kinetic energy
 potential energy of bare nuclei

Note that the ΔU integral is evaluated using $\psi_j^o(\mathbf{r}, \mathbf{Q}_0)$ thus cannot contain the exact effect of distortion of molecule from \mathbf{Q}_0 . To get a better representation of the distortion from \mathbf{Q}_0 , we must use perturbation theory.

We have explicitly excluded the effects of off-diagonal matrix elements. In order to get a better approximation to the exact ψ , we must use perturbation theory to correct ψ_{jt} .

$$\begin{aligned}
 \psi_{jt}(\mathbf{r}, \mathbf{Q}) &= \psi_{jt}^{CA}(\mathbf{r}, \mathbf{Q}) + \sum_{kr \neq jt} \frac{\{ \psi_{jt}^{CA} | \Delta U | \psi_{kr}^{CA} \}}{E_{jt}^{CA} - E_{kr}^{CA}} \psi_{kr}^{CA}(\mathbf{r}, \mathbf{Q}) \\
 &= \psi_j^o(\mathbf{r}, \mathbf{Q}_0) \chi_{jt}^{CA}(\mathbf{Q}) + \sum_{k \neq j} \sum_r \frac{\left(\chi_{kr}^{CA} \left| \langle \psi_k^o | \Delta U | \psi_j^o \rangle \right| \chi_{jt}^{CA} \right)}{E_{jt}^{CA} - E_{kr}^{CA}} \\
 &\quad \times \psi_k^o(\mathbf{r}, \mathbf{Q}_0) \chi_{kr}^{CA}(\mathbf{Q})
 \end{aligned}$$

call this a vibronic mixing coefficient

- { } means integrate over \mathbf{r} and \mathbf{Q} (both electronic and nuclear)
- () means integrate over \mathbf{Q} (nuclear)
- \langle \rangle means integrate over \mathbf{r} (electronic)

This form of $\psi_{jt}(\mathbf{r}, \mathbf{Q})$ is called the **Herzberg-Teller expansion**.

Now expand $\Delta U(\mathbf{r}, \mathbf{Q})$ in power series about \mathbf{Q}_0 in each of the normal coordinates.

$$\Delta U = \underbrace{\Delta U(\mathbf{r}, \mathbf{Q}_0)}_{= 0 \text{ by definition of } \Delta U} + \sum_n \underbrace{\left[\frac{\partial U(\mathbf{r}, \mathbf{Q})}{\partial \mathbf{Q}_n} \right]_0}_{\text{electronic factor}} \underbrace{\mathbf{Q}_n}_{\substack{\text{goes into} \\ \text{nuclear} \\ \text{matrix} \\ \text{element}}} + \underbrace{\frac{1}{2} \sum_{n,m} \left[\frac{\partial^2 U}{\partial \mathbf{Q}_n \partial \mathbf{Q}_m} \right]_0}_{\text{to be initially neglected}} \mathbf{Q}_n \mathbf{Q}_m \text{ etc.}$$

Now define the mixing coefficient.

$$\gamma_{kr,jt}^n \equiv \frac{\left\langle \psi_k^o(\mathbf{r}, \mathbf{Q}_0) \left[\frac{\partial U}{\partial \mathbf{Q}_n} \right]_0 \psi_j^o(\mathbf{r}, \mathbf{Q}_0) \right\rangle \langle \chi_{kt}^{CA} | \mathbf{Q}_n | \chi_{jt}^{CA} \rangle}{E_{jt}^{CA} - E_{kt}^{CA}}$$

everything collected into single parameter

$$\psi_{jt}(\mathbf{r}, \mathbf{Q}) = \psi_j^o(\mathbf{r}, \mathbf{Q}_0) \chi_{jt}^{CA}(\mathbf{Q}) + \sum_{k \neq j} \sum_r \sum_n \gamma_{kr,jt}^n \psi_k^o(\mathbf{r}, \mathbf{Q}_0) \chi_{kr}^{CA}(\mathbf{Q})$$

Electronic states vibrational states Promoting mode

note vibrational wavefunction for k-th, NOT j-th electronic state!

But we can see that $\gamma_{kr,jt}^n$ must vanish if

$$\Gamma_k \otimes \Gamma_j \not\subset \Gamma_{Q_n} \quad \text{OR} \quad \Gamma_r \otimes \Gamma_t \not\subset \Gamma_{Q_n} \quad (\text{required by definition of } \Delta U \text{ above})$$

electronic selection rule vibrational selection rule

which is equivalent to requiring that

$$\Gamma_{kr} \otimes \Gamma_{jt} \subset \Gamma_{\text{totally symmetric}} \quad (\text{and } Q_n \text{ is not totally symmetric}).$$

So now we are ready to consider the specific case of the $\text{H}_2\text{CO } \tilde{A}^1A_2$ state.

Out-of-plane Bending mode as promoter b_1 vibration
 $b_1 \otimes A_2 = B_2$ vibronic symmetry

So we are considering vibronic coupling to the 1B_2 state.

Non-Lecture This is a simplified version of Innes' model, to be discussed later.

Let's make a really crude model for the out-of-plane bending levels of both 1A_2 and 1B_2 states. This is an example when nature is too careless. Deperturb back to a simpler picture.

* both are harmonic (NB assume that the \tilde{A} state is NOT a double minimum non-planar state!!)

* both have same frequency ω

* coupling is exclusively via $\frac{\partial U}{\partial Q_n} Q_n$ term.

		O atom π in-plane							
		$n\sigma$	π	n_0	π^*	σ^*			
		↓	↓	↓	↓	↓			
$3a_1^2$	$4a_1^2$	$1b_2^2$	$5a_1^2$	$1b_1^2$	$2b_2^2$	$2b_1^0$	$6a_1^0$	\tilde{X}^1A_1	0 eV
elect. forbidden					$2b_1 \leftarrow 2b_2$			\tilde{A}^1A_2	$\pi^* \leftarrow n_0$ 3.5 eV
elect. allowed (b-type)					$6a_1 \leftarrow 2b_2$			\tilde{B}^1B_2	$\sigma^* \leftarrow n_0$ 7.1 eV
elect. allowed (a-type)					$2b_1 \leftarrow 1b_1$			1A_1	$\pi^* \leftarrow \pi$ 8.0 eV
elect. allowed (c-type)					$2b_1 \leftarrow 5a_1$			1B_1	$\pi^* \leftarrow n\sigma$ 9.45 eV

$\tilde{A} - \tilde{X}$ transition can borrow oscillator strength by “vibronic coupling” with

1B_2 via b_1 vibration because $A_2 \otimes b_1 = B_2$

1A_1 via a_2 vibration because $A_2 \otimes a_2 = A_1$

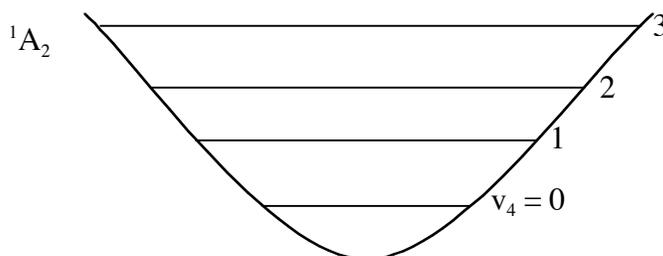
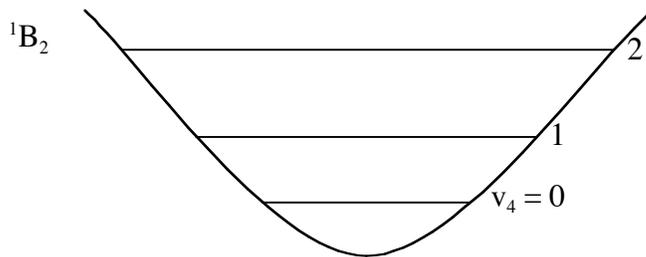
(a_2 vibration doesn't exist)

1B_1 via b_2 vibration because $A_2 \otimes b_2 = B_1$

I will now show, via a simple model, that vibronic coupling accounts for both the oscillator strength of the vibrational bands in the $\tilde{A} - \tilde{X}$ transition and the staggering of v_4 vibrational levels in \tilde{A} -state.

Assume v_4 in \tilde{A} and \tilde{B} states is

convenient for calculating vibrational matrix elements	{	<p>harmonic - not a double minimum non-planar state</p> <p>same ω and not displaced (necessarily not displaced if minimum or maximum is planar — the high-symmetry point)</p> <p>coupling is exclusively via $\frac{\partial U}{\partial Q_n} Q_n$ term</p>
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$$\Psi_{\tilde{A}v} = \Psi_{\tilde{A}}^o \chi_{\tilde{A}v}^{CA} + \sum_{v'} \gamma_{\tilde{B}v', \tilde{A}v}^4 \Psi_{\tilde{B}}^o \chi_{\tilde{B}v'}^{CA} \quad (\text{perturbation theory})$$

mode #4, not 4th power

retaining only levels of \tilde{B} state in the Herzberg-Teller expansion

Similarly for $\Psi_{\tilde{B}v'}$

$$\gamma_{\tilde{B}v', \tilde{A}v}^4 \equiv \left\langle \Psi_{\tilde{B}}^o \left[\frac{\partial U}{\partial Q_4} \right]_0 \middle| \Psi_{\tilde{A}}^o \right\rangle \frac{\langle v'_4 | Q_4 | v_4 \rangle}{E_{\tilde{A}v_4}^{CA} - E_{\tilde{B}v'_4}^{CA}}$$

a mass-independent electronic factor

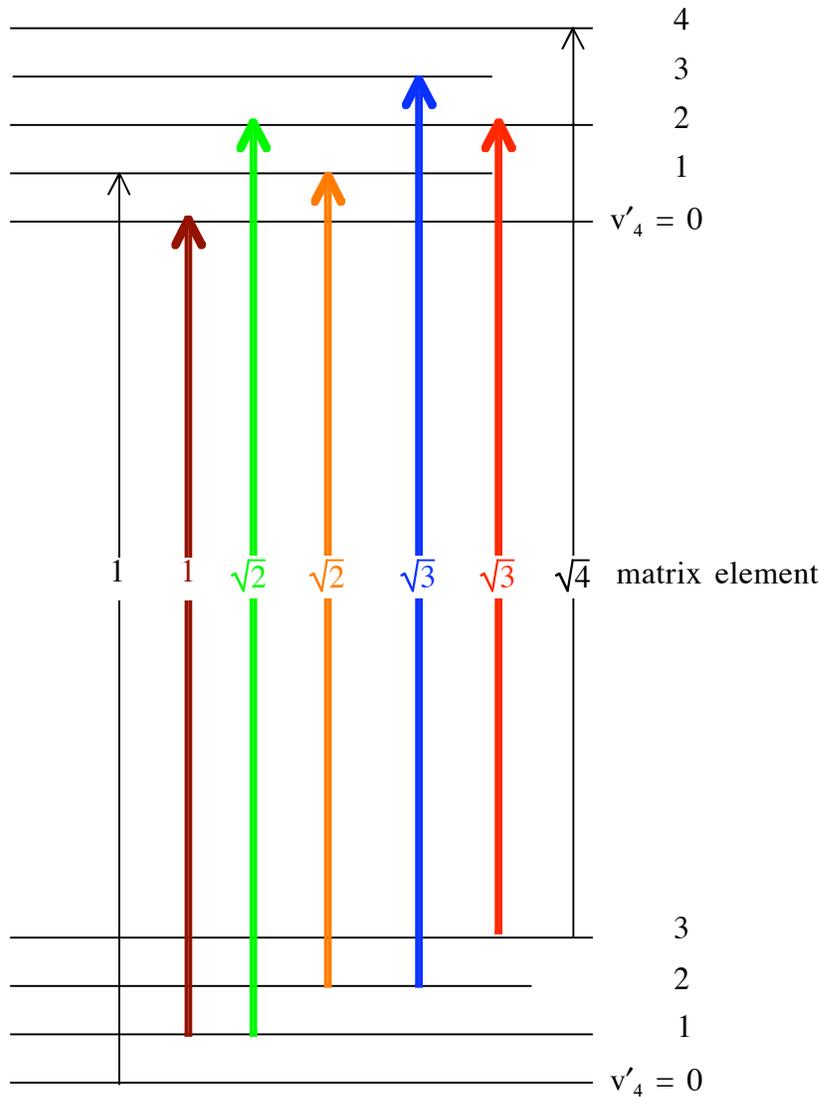
actually Q is mass weighted

$$\equiv \beta_{\tilde{B}\tilde{A}}^4$$

$$\propto \frac{1}{(\mu\omega)^{1/2}} \frac{[\sqrt{v_4+1}\delta_{v'_4, v_4+1} + \sqrt{v_4}\delta_{v'_4, v_4-1}]}{-\Delta T_0^{B-A} - \omega_4(v'_4 - v_4)} \frac{1}{(E_{0A+v_4\omega_4}) - (E_{0B+v'_4\omega_4})}$$

comes from modeling v_4 as the same in both \tilde{B} and \tilde{A} states.

Summary of non-zero matrix elements



So we have

$$\Psi_{\tilde{A}v_4} = \Psi_{\tilde{A}}^o \chi_{\tilde{A}v_4}^{CA} + \beta \Psi_{\tilde{B}}^o \left[\sqrt{v_4} \chi_{\tilde{B}v_4-1}^{CA} + \sqrt{v_4+1} \chi_{\tilde{B}v_4+1}^{CA} \right]$$

lump everything into this adjustable constant

$$\Psi_{\tilde{B}v'_4} = \Psi_{\tilde{B}}^o \chi_{\tilde{B}v'_4}^{CA} - \beta \Psi_{\tilde{A}}^o \left[\sqrt{v'_4} \chi_{\tilde{A}v'_4-1}^{CA} + \sqrt{v'_4+1} \chi_{\tilde{A}v'_4+1}^{CA} \right]$$

same constant but opposite sign because of the energy denominator.

Transition probability for $\tilde{A}v'_4 \leftarrow \tilde{X}v''_4$ (\tilde{B} and \tilde{A} states have same potential surface but \tilde{X} is different).

$$I_{\tilde{A}v'_4, \tilde{X}v''_4} = \left| \langle \Psi_{\tilde{A}v'_4} | \mu | \Psi_{\tilde{X}v''_4} \rangle \right|^2$$

Only the \tilde{B} state is assumed to contribute

$$I_{\tilde{A}v'_4, \tilde{X}v''_4} = \beta^2 \left| \langle \Psi_{\tilde{B}}^o | \mu_b | \Psi_{\tilde{X}}^o \rangle \left[v_4^{1/2} \langle \chi_{Bv_4-1}^{CA} | \chi_{Xv_4}^{CA} \rangle + (v_4 + 1)^{1/2} \langle \chi_{Bv_4+1}^{CA} | \chi_{Xv_4}^{CA} \rangle \right] \right|^2$$

$$= \beta^2 |M_{b, B-X}|^2 \left[v_4 q_{v_4-1}^{B-X} + (v_4 + 1) q_{v_4+1, v_4}^{B-X} + 2 [v_4 (v_4 + 1)]^{1/2} \right] \times \left[\langle \tilde{B}v_4 - 1 | \tilde{X}v_4 \rangle \langle \tilde{B}v_4 + 1 | \tilde{X}v_4 \rangle \right]$$

F-C factor positive squared terms either sign cross terms

Note that this is more complicated than usual FRANCK-CONDON expression for allowed transitions. It is expressed in terms of Franck-Condon factors for B-X NOT A-X!!!! We still have a symmetry selection rule for the v_4 vibrational mode because it is non-totally symmetric.

From $v''_4 = 0$ we can only reach $\tilde{B}v_4 = \text{even}$ (because v_4 is not totally symmetric) which requires $\tilde{A}v'_4 = \text{odd}$. Note that the intensity expression above vanishes for $v'_4 = 0$ and $v''_4 = 0$ because

$$q_{1,0}^{B-X} \equiv 0 \quad (\text{by symmetry}).$$

This can be expressed more generally, for any vibrational band in the $\tilde{A} - \tilde{X}$ system that is made allowed by vibronic coupling to the \tilde{B}^1B_2 state promoted by v'_4 .

individual mode F-C factors (product over all modes except the promoting mode)

$$I_{\tilde{A}v', \tilde{X}v''} = \beta^2 |M_{b, \tilde{B}-\tilde{X}}|^2 \prod_{v_i \neq v_4} q_{v_i^B v_i^X} \left| \sum_{v_4^B} \langle v_4^A | Q_4 | v_4^B \rangle \langle v_4^B | v_4^X \rangle \right|^2$$

b-type symmetry selection rule $v_4^B - v_4^X = \text{even}$
 $v_4^A - v_4^B = \text{odd}$ $\therefore v_4^A - v_4^X = \text{odd}$

K. K. Innes *J. Mol. Spectrosc.* **99**, 294 (1983) performed a vibronic coupling calculation which not only reproduced the mode-4 intensity promotion factors, but also “explained” the level staggering in the \tilde{A} -state.

In order to define complete basis sets, we solve an approximate Schrödinger equation by neglecting specified terms in the exact \mathbf{H} , or by ignoring off-diagonal elements of these terms.

In the crude adiabatic approximation, we define potential curves by ignoring terms of the form

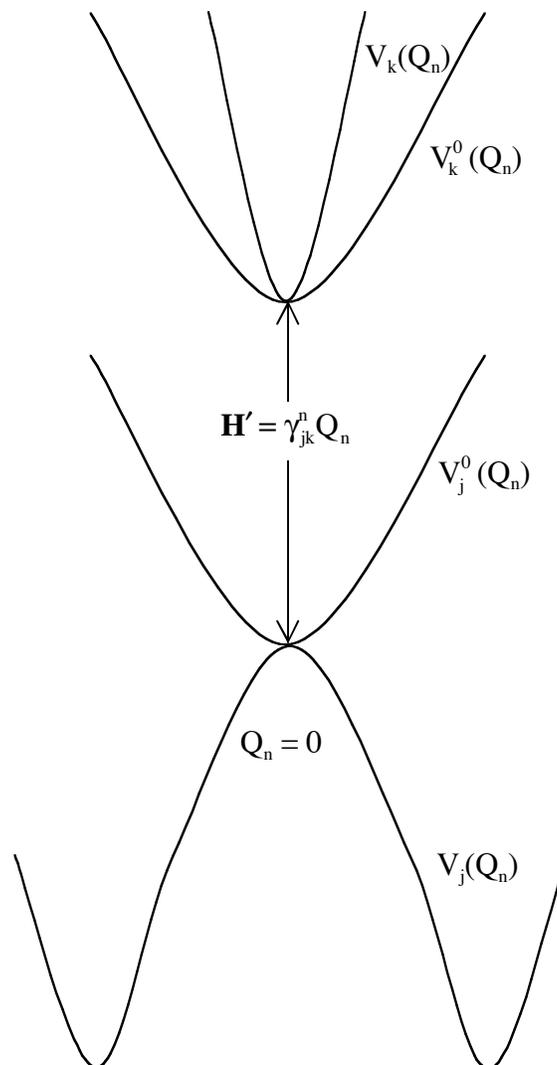
$$\langle \psi_{jt}^{CA} | \Delta \mathbf{H}(r, Q) | \psi_{kr}^{CA} \rangle.$$

We showed that, by expanding ΔU as power series in Q (the normal mode displacements), we get

$$(\mathbf{H}'_{\text{electronic}})_{jk} = \sum_n \left\langle \psi_j^o(r, Q_0) \left[\frac{\partial U}{\partial Q_n} \right] \Big|_{Q_n=0} \Big| \psi_k^o(r, Q_0) \right\rangle Q_n = \sum_n \gamma_{jk}^n Q_n.$$

We can go to a new electronic basis set by diagonalizing $\mathbf{H}^0 + \sum_n \gamma_{jk}^n Q_n$.

Suppose we have two *harmonic* zero-order potential curves, $V^0(Q_n)$, for mode n of electronic states j and k . Then we have the following zero-order and diagonalized potential curves.



Upper curve gets narrower.

Lower curve turns into a double minimum curve.

$Q_n = 0$ points of both curves do not shift because $\mathbf{H}' \rightarrow 0$ at $Q = Q_0$ by definition.

Vibrational eigenstates of lower curve will exhibit the pattern of a *symmetric double minimum* potential.

$$\left. \begin{aligned} V_k^0(Q_n) &= \omega_k^2 Q_n^2 \\ V_j^0(Q_n) &= \omega_j^2 Q_n^2 \end{aligned} \right\} \text{ here we are allowing harmonic frequencies to be different}$$

$$\mathbf{H}'_{ij}(Q_n) = \gamma_{jk}^n Q_n^1$$

Second-order perturbation theory:

$$V_k = \omega_k^2 Q_n^2 + \frac{(\gamma_{jk}^n)^2 Q_n^2}{(\omega_k^2 - \omega_j^2) Q_n^2 + T_{ek} - T_{ej}} = \omega_k'^2 Q_n^2 + \alpha Q_n^4$$

(We do power series expansion of the second term about $Q_n = 0$. There can be no constant term because V_k vanishes at $Q_n = 0$. Note that the coefficient of Q_n^2 changes because it is ω_k^2 plus a Q_n^2 term from the power series.)

$$V_j = \omega_j^2 Q_n^2 - \alpha Q_n^4$$

(same α because it is the same expansion but with opposite sign energy denominator)

$$\omega_k'^2 = \omega_k^2 + \frac{(\gamma_{jk}^n)^2}{T_{ek} - T_{ej}} \quad \text{from power series expansion}$$

$$(\omega_k^2 - \omega_k'^2) = -(\omega_j^2 - \omega_j'^2) = -\frac{(\gamma_{jk}^n)^2}{T_{ek} - T_{ej}} \quad \text{get opposite sign shifts in the effective harmonic frequency}$$

$$\alpha \equiv \frac{(\gamma_{jk}^n)^2}{(T_{ek} - T_{ej})^2} (\omega_k^2 - \omega_j^2) \quad \text{get a quartic term that depends on difference in } \omega\text{'s for } j \text{ and } k.$$

The quartic term vanishes if $\omega_j = \omega_k$.

This shows that upper state ω increases and lower state ω decreases.

“Exact” 2×2 deperturbation treatment for the potential curves

$$\begin{pmatrix} \frac{\Delta V}{2} - E & \mathbf{H}_{12} \\ \mathbf{H}_{12} & -\frac{\Delta V}{2} - E \end{pmatrix} \Rightarrow V_{\pm} = \frac{V_k + V_j}{2} \pm \left[\frac{\Delta V^2}{4} + \mathbf{H}_{12}^2 \right]^{1/2}$$

$\Delta V = (\omega_k^2 - \omega_j^2) Q_n^2 + T_{ek} - T_{ej}$ (includes difference between minima of V_k and V_j)

$$V_{\pm} = \frac{V_k + V_j}{2} + \frac{\omega_k^2 + \omega_j^2}{2} Q_n^2 \pm \left[\frac{(\omega_k^2 - \omega_j^2)^2}{4} Q_n^4 + (\gamma_{jk}^n)^2 Q_n^2 \right]^{1/2}$$

(the $\Delta T_0/2$ term seems to have been omitted from the $[]^{1/2}$ term)

For large γ^n , second term in $[]^{1/2}$ will dominate at small $|Q_n|$ but first term will eventually dominate at large $|Q_n|$. We obtain two perturbed potential energy curves.

Now go back to the original vibronic Hamiltonian and get a degenerate perturbation expression for the energy levels.

A second-order perturbation treatment of this kind of 2-state interaction in the CA picture cannot give this type of level stagger. It is necessary to set up and diagonalize two large dimension matrices

$$H_I \begin{cases} \text{odd quanta of upper state} \\ \text{even quanta of lower state} \end{cases}$$

$$H_{II} \begin{cases} \text{even quanta of upper state} \\ \text{odd quanta of lower state} \end{cases}$$

because of odd-even symmetry of a symmetric (not necessarily harmonic) potential, there can be no coupling matrix elements between these two matrices.

The level shifts are larger for the lower states in H_{II} than those in H_I . For example, the lower state $v = 1$ level is pushed down by $v = 0$ and 2 of the upper state, but the lower state $v = 0$ level is only pushed down by $v = 1$.

This produces level staggering.

K. K. Innes [*J. Mol. Spectrosc.* **99**, 294-301 (1983)] reproduced $\tilde{A} - \tilde{X}$ intensity and \tilde{A} -state level pattern with

$$\Delta T_0^{\tilde{B}-\tilde{A}} = 28035 \text{ cm}^{-1}$$

$$\omega_4^{\tilde{B}} = \omega_4^{\tilde{A}} = 1125 \text{ cm}^{-1}$$

$$H_{\tilde{A}v_{\tilde{A}}, \tilde{B}v_{\tilde{B}}=v_{\tilde{A}}+1}^{\tilde{A}} = \beta (v_{\tilde{A}} + 1)^{1/2} \quad \beta = 3138 \text{ cm}^{-1}$$

$$H_{\tilde{A}v_{\tilde{A}}, \tilde{B}v_{\tilde{B}}=v_{\tilde{A}}-1}^{\tilde{A}} = \beta v_{\tilde{A}}^{1/2}$$