5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture # 33 Supplement

Based on a lecture written by Professor Patrick H. Vaccaro.

Outline

(i) "true" Eigenstates: A long, hard climb;

(ii) the "total" molecular Hamiltonian and its Schrödinger Equation;

(iii) the electronic Schrödinger Equation;

(iv) transformation of the molecular Schrödinger Equation;

(v) the Adiabatic Approximation;

(vi) Adiabatic corrections;

(vii) Non-Adiabatic corrections;

(viii) the transition moment of the $\widetilde{\mathrm{A}}^1\mathrm{A}_2 \leftarrow \widetilde{\mathrm{X}}^1\mathrm{A}_1$ absorption in $\mathrm{H_2CO}$: a vibronic coupling model.

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Figure 1: Various routes to approach the exact non-adiabatic wavefunction. From "What Does the Term 'Vibronic Coupling' Mean" by T. Azumi and K. Matsuzaki, *Photochemistry and Photobiology* **25**, 315-326 (1977).

Time-Independent Schrödinger Equation for a Molecular System

$$\mathcal{H}_{\text{total}}(r,Q)\Psi_t(r,Q) = E_t\Psi_t(r,Q)$$

where

$$\mathcal{H}_{\text{total}}(r,Q) = T_e(r) + T_N(Q) + U(r,Q) + V(Q)$$

"r" represents electronic coordinates

"Q" represents mass-weighted nuclear coordinates describing displacements from a reference configuration "Q_0"

$$T_e(r) \approx \frac{-\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial r_i^2}$$ represents the electronic kinetic energy

$$T_N(Q) \approx \frac{-\hbar^2}{2}\sum_n \frac{\partial^2}{\partial Q_n^2}$$ represents the nuclear kinetic energy

$U(r,Q)$ represents the Coulombic potential energy

$V(Q)$ represents the potential energy of the nuclei

PROBLEM: Hamiltonian does not permit separation of variables. Therefore, exact solution is not possible.

Consider only the terms depending on the electronic coordinates (i.e. the so-called Electronic Hamiltonian)

$$\begin{aligned}\mathcal{H}_{\text{elec}}(r,Q) &= T_e(r) + U(r,Q)\\ &= T_e(r) + U(R,Q_0) + \Delta U(r,Q)\\ &= \mathcal{H}_{\text{elec}}(r,Q_0) + \Delta U(r,Q)\end{aligned}$$

where

$$\begin{aligned}U(r,Q) &= U(r,Q_0) + \Delta U(r,Q)\\ \mathcal{H}_{\text{elec}}(r,Q_0) &= T_e(r) + U(r,Q_0).\end{aligned}$$

Note that:

$$\begin{aligned}U(r,Q) = U(r,Q_0) &+ \sum_n \left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0 Q_n\\ &+ \frac{1}{2}\sum_{nm}\left[\frac{\partial^2 U(r,Q)}{\partial Q_n \partial Q_m}\right]_0 Q_n Q_m + \ldots\end{aligned}$$

Consequently:

$$\Delta U(r,Q) \approx \sum_n \left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0 Q_n + \frac{1}{2}\sum_{n,m}\left[\frac{\partial^2 U(r,Q)}{\partial Q_n \partial Q_m}\right]_0 Q_n Q_m + \dots$$

Define two types of Electronic Schrödinger Equations

(i) The Dynamical equation for $\mathcal{H}_{\text{elec}}(r,Q)$

$$\{\text{the “Born” representation}\}$$

$$\mathcal{H}_{\text{elec}}(r,Q)\psi_i(r,Q) = \epsilon_i(Q)\psi_i(r,Q)$$

$$[T_e(r) + U(r,Q)]\psi_i(r,Q) = \epsilon_i(Q)\psi_i(r,Q)$$

$$\text{dynamical electronic wavefunctions: } \psi_i(r,Q) \Rightarrow \text{ Born Space}$$

(ii) The static equation for $\mathcal{H}_{\text{elec}}(r,Q_0)$

$$\{\text{the “Longuet-Higgins” representation}\}$$

$$\mathcal{H}_{\text{elec}}(r,Q_0)\psi_i^0(r,Q_0) = \epsilon_i^0(Q_0)\psi_i^0(r,Q_0)$$

$$[T_e(r) + U(r,Q_0)]\psi_i^0(r,Q_0) = \epsilon_i^0(Q_0)\psi_i^0(r,Q_0)$$

$$\text{static electronic wavefunctions: } \psi_i^0(r,Q_0) \Rightarrow \text{Longuet-Higgins Space}$$

The Eigenstates of the Total Hamiltonian can now be expanded in either of these two electronic basis sets:

(i) The dynamical or Born Representation:

$$\Psi_t(r,Q) = \sum_k \psi_k(r,Q)\chi_{kt}^{\text{D}}(Q)$$

(ii) The static or Longuet-Higgins Representation:

$$\Psi_t(r,Q) = \sum_k \psi_k^0(r,Q_0)\chi_{kt}^{S}(Q).$$

Note that

$$\psi_k(r,Q) = \sum_\ell \psi_\ell^0(r,Q_0)\lambda_{\ell k}(Q)$$

and

$$\begin{aligned}\Psi_t(r,Q) &= \sum_k \psi_k(r,Q)\chi_{kt}^{\text{D}}(Q)\\ &= \sum_k \left[\sum_\ell \psi_\ell^0(r,Q_0)\lambda_{\ell k}(Q)\right]\chi_{kt}^{\text{D}}(Q)\\ &= \sum_\ell \psi_\ell^0(r,Q_0)\chi_{\ell t}^{S}(Q).\end{aligned}$$

where

$$\chi^{S}_{\ell t}(Q) = \sum_k \lambda_{\ell k}(Q)\chi^{\mathrm{D}}_{kt}(Q)$$

Now recall the Schrödinger Equation for the total Hamiltonian

(i) the dynamical or Born Representation:

$$\begin{aligned} \mathcal{H}_{\mathrm{total}}(r,Q)\Psi_t(r,Q) &= E_t\Psi_t(r,Q) \\ [T_e(r) + U(r,Q) + T_N(Q) + V(Q) - E_t]\Psi_t(r,Q) &= 0 \\ [\mathcal{H}_{\mathrm{elec}}(r,Q) + T_N(Q) + V(Q) - E_t]\sum_k \psi_k(r,Q)\chi^{\mathrm{D}}_{kt}(Q) &= 0 \end{aligned}$$

substitute the dynamical electronic Schrödinger Equation and the explicit expression for $T_N(Q)$:

$$\sum_k \Bigg[\{\epsilon_k(Q) + V(Q) - E_t\}\,\psi_k(r,Q)\chi^{\mathrm{D}}_{kt}(Q) \\ -\frac{\hbar^2}{2}\sum_n \left\{ \frac{\partial^2\psi_k(r,Q)}{\partial Q_n^2}\chi^{\mathrm{D}}_{kt}(Q) + \psi_k(r,Q)\frac{\partial^2\chi^{\mathrm{D}}_{kt}(Q)}{\partial Q_n^2} + 2\frac{\partial\psi_k(r,Q)}{\partial Q_n}\frac{\partial\chi^{\mathrm{D}}_{kt}(Q)}{\partial Q_n} \right\} \Bigg] = 0$$

Multiply from the left by $\psi_j^\star(r,Q)$ and integrate over the electronic coordinates realizing that:

$$\langle \psi_j(r,Q)|\psi_k(r,Q)\rangle = \delta_{jk}.$$

One thus obtains a set of coupled differential equations:

$$\{T_N(Q) + V(Q) + \epsilon_j(Q) + \langle\psi_j(r,Q)|T_N(Q)|\psi_j(r,Q)\rangle - E_t\}\,\chi^{\mathrm{D}}_{jt}(Q) \\ +\sum_{k\neq j}\left\{ \langle\psi_j(r,Q)|T_N(Q)|\psi_k(r,Q)\rangle - \hbar^2\sum_n \left\langle \psi_j(r,Q)\left|\frac{\partial}{\partial Q_n}\right|\psi_k(r,Q)\right\rangle \frac{\partial}{\partial Q_n}\right\}\chi^{\mathrm{D}}_{kt}(Q) = 0$$

Problem still not solvable.

(ii) The static or Longuet-Higgins Representation:

$$\begin{aligned} \mathcal{H}_{\mathrm{total}}(r,Q)\Psi_t(r,Q) &= E_t\Psi_t(r,Q) \\ [T_e(r) + U(r,Q) + T_N(Q) + V(Q) - E_t]\Psi_t(r,Q) &= 0 \\ [\mathcal{H}_{\mathrm{elec}}(r,Q_0) + \Delta U(r,Q) + T_N(Q) + V(Q) - E_t]\sum_k \psi^0_k(r,Q_0)\chi^{S}_{kt}(Q) &= 0. \end{aligned}$$

By similar manipulations, realizing that

$$\begin{aligned} \langle\psi^0_j(r,Q_0)|\psi^0_k(r,Q_0)\rangle &= \delta_{gk} \\ \left\langle \psi^0_j(r,Q_0)\left|\frac{\partial}{\partial Q_n}\right|\psi^0_k(r,Q_0)\right\rangle &= \left\langle \psi^0_j(r,Q_0)\left|\frac{\partial^2}{\partial Q_n^2}\right|\psi^0_k(r,Q_0)\right\rangle \\ &= 0 \qquad \text{for all } j,k \end{aligned}$$

one obtains

$$\begin{aligned}&\left\{T_N(Q)+V(Q)+\epsilon_j^0(Q_0)+\left\langle\psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_j^0(r,Q_0)\right\rangle-E_t\right\}\\ &\times\chi_{jt}^S(Q)+\sum_{k\neq j}\left\langle\psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_k^0(r,Q_0)\right\rangle\chi_{kt}(Q)=0\end{aligned}$$

Adiabatic Approximations

Definition: Adiabatic refers to any vibronic approximation scheme in which the wavefunction is factorized in the form:

$$\Psi^{\mathrm{AD}}(r,Q)=\psi(r,X)\chi^{\mathrm{AD}}(Q)$$

One **must** distinguish between several adiabatic schemes:

Any adiabatic scheme is valid only if the "effective potential surface" is well separated from all other potential surfaces.

(i.e. concept of a potential surface for the nuclear motion has meaning only if the adiabatic separation is a sufficiently good approximation for the description of the molecular state under consideration)

Three Commonly Encountered Adiabatic schemes

I. The Born-Huang (BH) Adiabatic Approximation

In the set of dynamical differential equations, eliminate the coupling terms between

$$X_{jt}^{\mathrm{D}}(Q) \text{ and } X_{kt}^{\mathrm{D}}(Q) \text{ where } k\neq j$$

by assuming

$$\begin{aligned}\langle\psi_j(r,Q)|T_N(Q)|\psi_k(r,Q)\rangle&=0 \qquad \text{for } k\neq j\\ \left\langle\psi_j(r,Q)\left|\frac{\partial}{\partial Q_n}\right|\psi_k(r,Q)\right\rangle&=0 \qquad \text{for all } k,j.\end{aligned}$$

Thus, the decoupled equations become

$$[T_N(Q)+\overbrace{V(Q)+\epsilon_j(Q)+\langle\psi_j(r,Q)|T_N(Q)|\psi_j(r,Q)\rangle}^{\text{effective potential}}]\chi_{jt}^{\mathrm{BH}}(Q)=E_{jt}^{\mathrm{BH}}\chi_{jt}^{\mathrm{BH}}(Q)$$

which implies

$$\Psi_{jt}^{\mathrm{BH}}(r,Q)=\psi_j(r,Q)\chi_{jt}^{\mathrm{BH}}(Q).$$

II. The Born-Oppenheimer (BO) Adiabatic Approximation

In the set of dynamical differential equations, eliminate the coupling terms between

$$\chi_{jt}^{\mathrm{D}}(Q) \text{ and } \chi_{kt}^{\mathrm{D}}(Q) \text{ where } k\neq j$$

by assuming

$$\langle \psi_j(r,Q)|T_N(Q)|\psi_k(r,Q)\rangle = 0 \qquad \text{for all } j,k$$
$$\left\langle \psi_j(r,Q) \left| \frac{\partial}{\partial Q_n} \right| \psi_k(r,Q) \right\rangle = 0 \qquad \text{for all } j,k.$$

Thus, the decoupled equations become

$$\{T_N(Q) + \overbrace{V(Q) + \epsilon_j(Q)}^{\text{effective potential}}\}\chi_{jt}^{\text{BO}}(Q) = E_{jt}^{\text{BO}}\chi_{jt}^{\text{BO}}(Q)$$

which implies

$$\Psi_{jt}^{\text{BO}}(r,Q) = \psi_j(r,Q)\chi_{jt}^{\text{BO}}(Q).$$

III. The <u>Crude Adiabatic</u> (CA) Approximation

In the set of static differential equations, eliminate the coupling terms between

$$\chi_{jt}^{S}(Q) \text{ and } \chi_{kt}^{S}(Q) \text{ where } j \neq k$$

by assuming

$$\left\langle \psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_k^0(r,Q_0)\right\rangle = 0 \text{ for } k \neq j.$$

Thus, the decoupled equations become

$$\left[T_N(Q) + V(Q) + \epsilon_j^0(Q) + \left\langle \psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_j^0(r,Q_0)\right\rangle\right]\chi_{jt}^{\text{CA}}(Q) = E_{jt}^{\text{CA}}\chi_{jt}^{\text{CA}}(Q)$$

which implies

$$\Psi_{jt}^{\text{CA}}(r,Q) = \psi_j^0(r,Q_0)\chi_{jt}^{\text{CA}}(Q).$$

	Crude Adiabatic Approximation	Born-Oppenheimer Adiabatic Approximation	Born-Huang Adiabatic Approximation
Adiabatic Wavefunction	$\Psi_{jt}^{\mathrm{CA}}(r,Q) = \psi_j^0(r,Q)\chi_{jt}^{\mathrm{CA}}(Q)$	$\Psi_{jt}^{\mathrm{BO}}(r,Q) = \psi_j(r,Q)\chi_{jt}^{\mathrm{BO}}(Q)$	$\Psi_{jt}^{\mathrm{BH}}(r,Q) = \psi_j(r,Q)\chi_{jt}^{\mathrm{BH}}(Q)$
Electronic Equation	$[T_e(r) + U(r,Q_0)]\psi_j^0(r,Q_0)$ $= \epsilon_j^0(Q)\psi_j^0(r,Q_0)$	$[T_e(r) + U(r,Q)]\psi_j(r,Q)$ $= \epsilon_j(Q)\psi_j(r,Q)$	$[T_e(r) + U(r,Q)]\psi_j(r,Q)$ $= \epsilon_j(Q)\psi_j(r,Q)$
Vibrational Equation	$[T_N(Q) + V(Q) + \epsilon_j^0(Q)$ $+ \left\langle \psi_j^0(r,Q_0) \vert \Delta U(r,Q) \vert \psi_j^0(r,Q_0) \right\rangle]$ $\times\chi_{jt}^{\mathrm{CA}}(Q) = E_{jt}^{\mathrm{CA}}\chi_{jt}^{\mathrm{CA}}(Q)$	$[T_N(Q) + V(Q) + \epsilon_j(Q)]$ $\times\chi_{jt}^{\mathrm{BO}}(Q) = E_{jt}^{\mathrm{BO}}\chi_{jt}^{\mathrm{BO}}(Q)$	$[T_N(Q) + V(Q) + \epsilon_j(Q)$ $+ \langle \psi_j(r,Q_0) \vert T_N(Q) \vert \psi_j(r,Q) \rangle]$ $\times\chi_{jt}^{\mathrm{BH}}(Q) = E_{jt}^{\mathrm{BH}}\chi_{jt}^{\mathrm{BH}}(Q)$
Approximations Utilized	$\left\langle \psi_j^0(r,Q_0) \vert \Delta U(r,Q) \vert \psi_k^0(r,Q_0) \right\rangle = 0$ for $k \neq j$	$\langle \psi_j(r,Q) \vert T_N(Q) \vert \psi_k(r,Q) \rangle = 0$ and $\left\langle \psi_j(r,Q) \middle\vert \frac{\partial}{\partial Q_N} \middle\vert \psi_k(r,Q) \right\rangle = 0$	$\langle \psi_j(r,Q) \vert T_N(Q) \vert \psi_k(r,Q) \rangle = 0$ for $k \neq j$ and $\left\langle \psi_j(r,Q) \middle\vert \frac{\partial}{\partial Q_N} \middle\vert \psi_k(r,Q) \right\rangle = 0$

Example of Corrections within the Adiabatic Approximation

Improvement from the Crude Adiabatic (CA) Approximation to the Born-Oppenheimer (BO) Approximation (Herzberg-Teller vibronic coupling)

$$\psi^0(r,Q_0) \longrightarrow \psi(r,Q)$$

The difference in the electronic Hamiltonians comes from the term $\Delta U(r,Q)$ where:

$$\Delta U(r,Q) \approx \sum_n \left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0 Q_n + \frac{1}{2}\sum_{n,m}\left[\frac{\partial^2 U(r,Q)}{\partial Q_n \partial Q_m}\right]_0 Q_n Q_m + \ldots$$

By perturbation theory

$$\psi_i(r,Q) \approx \psi_i^0(r,Q_0) + \sum_{j\neq i} A_{ji}(Q)\psi_j^0(r,Q_0)$$

where

$$A_{ji}(Q) = \frac{\langle \psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_i^0(r,Q_0)\rangle}{\epsilon_i^0(Q_0) - \epsilon_j^0(Q_0)};$$

thus

$$\begin{aligned}\Psi_{ir}^{\text{BO}}(r,Q) &= \psi_i(r,Q)\chi_{ir}^{\text{BO}}(Q)\\ &\approx \left[\psi_i^0(r,Q_0) + \sum A_{ji}(Q)\psi_j^0(r,Q_0)\right]\chi_{ir}^{\text{BO}}(Q).\end{aligned}$$

Corrections of Adiabatic Schemes to Non-Adiabatic Schemes

Goal: To express the total non-adiabatic wavefunctions in terms of adiabatic wavefunctions via non-degenerate perturbation theory:

$$\Psi_{ir}(r,Q) = \Psi_{ir}^{\text{AD}}(r,Q) + \sum_{kt\neq ir} c_{kt,ir}\Psi_{kt}^{\text{AD}}(r,Q)$$

where

$$c_{kt,ir} = \frac{\left\{\Psi_{kt}^{\text{AD}}(r,Q)|\mathcal{H}'(r,Q)|\Psi_{ir}^{\text{AD}}(r,Q)\right\}}{E_{ir}^{\text{AD}} - E_{kt}^{\text{AD}}}.$$

The perturbation operator represents the breakdown of the adiabatic approximation:

$$\begin{aligned}\mathcal{H}'(r,Q) &= \mathcal{H}_{\text{total}}(r,Q) - \mathcal{H}^{\text{AD}}(r,Q)\\ &= \mathcal{H}_{\text{total}}(r,Q) - \sum_{kt}\left|\Psi_{kt}^{\text{AD}}(r,Q)\right\} E_{kt}^{\text{AD}}\left\{\Psi_{kt}^{\text{AD}}(r,Q)\right|\end{aligned}$$

This leads to **Born-Huang (BH) Coupling** and **Born-Oppenheimer (BO)** Coupling.

The Transition Moment of the $\widetilde{\text{A}}^1\text{A}_2 \leftarrow \widetilde{\text{X}}^1\text{A}_1$ Absorption Transition in Formaldehyde

The transition moment between adiabatic wavefunctions is given by

$$\begin{aligned}M_{jt;ir}^{\text{AD}} &= \left\{\Psi_{jt}^{\text{AD}}(r,Q)|\widehat{\text{O}}(r)|\Psi_{ir}^{\text{AD}}(r,Q)\right\}\\ &= \left(\chi_{jt}^{\text{AD}}(Q)\left|\left\langle\psi_j(r,Q)|\widehat{\text{O}}(r)|\psi_i(r,Q)\right\rangle\right|\chi_{ir}^{\text{AD}}(Q)\right).\end{aligned}$$

To proceed, need to know Q-dependence of electronic integral.

Let us apply this, with the Born-Oppenheimer, Adiabatic representation; to the $\widetilde{\mathrm{A}}^1\mathrm{A}_2 \leftarrow \widetilde{\mathrm{X}}^1\mathrm{A}_1$ transition of formaldehyde.

Lowest Singlet Electronic States in $\mathrm{H_2CO}$

Energy (ev)	State Designation	State Number
0	$^1\mathrm{A}_1$	0
3.50	$^1\mathrm{A}_2(n,\pi^\star)$	1
7.08	$^1\mathrm{B}_2(n,\sigma^\star)$	2
7.97	$^1\mathrm{A}_1(\pi,\pi^\star)$	3
9.45	$^1\mathrm{B}_1(\sigma n,\pi^\star)$	4

Assume that the electronic eigenfunction of the ground state can be expressed in terms of a non-mixed crude adiabatic function:

$$\begin{aligned}\Psi_{0t}^{\mathrm{BO}}(r,Q) &= \psi_0(r,Q)\chi_{0t}^{\mathrm{BO}}(Q)\\ &\approx \psi_0^0(r,Q_0)\chi_{0t}^{\mathrm{CA}}(Q).\end{aligned}$$

Perform a "Herzberg–Teller" expansion of the wavefunction for the first excited singlet state:

$$\begin{aligned}\Psi_{1r}^{\mathrm{BO}}(r,Q) &= \psi_1(r,Q)\chi_{1r}^{\mathrm{BO}}(Q)\\ \psi_1(r,Q) &\approx \psi_1^0(r,Q_0) + \sum_{j>1} A_{j1}(Q)\psi_j^0(r,Q_0)\end{aligned}$$

where

$$A_{j1}(Q) = \frac{\langle \psi_j^0(r,Q_0)|\Delta U(r,Q)|\psi_1^0(r,Q_0)\rangle}{\epsilon_1^0(Q_0) - \epsilon_j^0(Q_0)}$$

and

$$\Delta U(r,Q) \approx \sum_n \left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0 Q_n.$$

Thus

$$\begin{aligned}A_{j1}(Q) &= \sum_n \frac{\left\langle \psi_j^0(r,Q_0)\left|\left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0\right|\psi_1^0(r,Q_0)\right\rangle}{\epsilon_1^0(Q_0) - \epsilon_j^0(Q_0)} Q_n\\ &= \sum_n \gamma_{j1}^n Q_n.\end{aligned}$$

Now

$$\psi_1(r,Q) \approx \psi_1^\circ(r,Q_0) + \sum_{j>1}\sum_n \gamma_{j1}^n Q_n \psi_j^\circ(r,Q_0)$$

and the Born-Oppenheimer Adiabatic wavefunction for the first excited singlet state becomes:

$$\begin{aligned}\Psi_{1r}^{\mathrm{BO}}(r,Q) &= \psi_1(r,Q)\chi_{1r}^{\mathrm{BO}}(Q)\\ &\approx \left[\psi_1^0(r,Q_0) + \sum_{j>1}\sum_n \gamma_{j1}^n Q_n \psi_j^0(r,Q_0)\right]\chi_{1r}^{\mathrm{CA}}(Q).\end{aligned}$$

The transition moment now becomes:

$$\begin{aligned}
\mathrm{M}^{\mathrm{BO}}_{0t;1r} &= \left\{ \Psi^{\mathrm{BO}}_{0t}(r,Q)|\widehat{\mathrm{O}}(r)|\Psi^{\mathrm{BO}}_{1r}(r,Q)\right\} \\
&= \left(\chi^{\mathrm{CA}}_{0t}(Q) \left| \left\langle \psi^0_0(r,Q_0) \left| \widehat{\mathrm{O}}(r) \right| \psi^0_1(r,Q_0) \right| \right\rangle + \sum_{j>1}\sum_{n} \gamma^n_{j1} Q_n \left| \psi^0_j(r,Q_0) \right\rangle \chi^{\mathrm{CA}}_{1r}(Q) \right).
\end{aligned}$$

Simplification yields:

$$\begin{aligned}
\mathrm{M}^{\mathrm{BO}}_{0t;1r} &= \left\langle \psi^0_0(r,Q_0)|\widehat{\mathrm{O}}(r)|\psi^0_1(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \sum_{j>1}\sum_{n} \gamma^n_{j1} \left\langle \psi^0_0(r,Q_0)|\widehat{\mathrm{O}}(r)|\psi^0_j(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_n|\chi^{\mathrm{CA}}_{1r}(Q)\right).
\end{aligned}$$

Now consider the coefficients γ^n_{j1}:

$$\gamma^n_{j1} = \frac{\left\langle \psi^0_j(r,Q_0) \left| \left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0 \right| \psi^0_1(r,Q_0) \right\rangle}{\epsilon^0_1(Q_0) - \epsilon^0_j(Q_0)}.$$

Since the Hamiltonian must be invarient under all symmetry operations,

$$\left[\frac{\partial U(r,Q)}{\partial Q_n}\right]_0 \qquad \text{must transform as } Q_n.$$

Given that $\psi^0_1(r,Q_0)$ transforms as A_2, it is easy to find the appropriate combinations of Q_n and $\psi^0_j(r,Q_0)$ such that γ^n_{j1} does not vanish via symmetry. Three non-zero coefficients are obtained:

$$\gamma^4_{21} \quad , \quad \gamma^5_{41} \quad , \quad \gamma^6_{41}.$$

Thus the transition moment for H_2CO can be written, more explicitly, as

$$\begin{aligned}
\mathrm{M}^{\mathrm{BO}}_{0t;1r} &= \left\langle \psi^0_0(r,Q_0)|\widehat{\mathrm{O}}(r)|\psi^0_1(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \gamma^4_{21} \left\langle \psi^0_0(r,Q_0)|\widehat{\mathrm{O}}(r)|\psi^0_2(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_4|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \gamma^5_{41} \left\langle \psi^0_0(r,Q_0)|\widehat{\mathrm{O}}(r)|\psi^0_4(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_5|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \gamma^6_{41} \left\langle \psi^0_0(r,Q_0)|\widehat{\mathrm{O}}(r)|\psi^0_4(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_6|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&= \left\langle {}^1\mathrm{A}_1(r,Q_0)|\widehat{\mathrm{O}}(r)|{}^1\mathrm{A}_2(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \gamma^4_{21} \left\langle {}^1\mathrm{A}_1(r,Q_0)|\widehat{\mathrm{O}}(r)|{}^1\mathrm{B}_2(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_4|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \gamma^5_{41} \left\langle {}^1\mathrm{A}_1(r,Q_0)|\widehat{\mathrm{O}}(r)|{}^1\mathrm{B}_1(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_5|\chi^{\mathrm{CA}}_{1r}(Q)\right) \\
&\quad + \gamma^6_{41} \left\langle {}^1\mathrm{A}_1(r,Q_0)|\widehat{\mathrm{O}}(r)|{}^1\mathrm{B}_1(r,Q_0)\right\rangle \left(\chi^{\mathrm{CA}}_{0t}(Q)|Q_6|\chi^{\mathrm{CA}}_{1r}(Q)\right).
\end{aligned}$$

Note that:

$$\begin{array}{lll}
\mu_z \Longrightarrow \mathrm{A}_1 & \mu_x \Longrightarrow \mathrm{B}_1 & \mu_y \Longrightarrow \mathrm{B}_2 \\
m_z \Longrightarrow \mathrm{A}_2 & m_x \Longrightarrow \mathrm{B}_2 & m_y \Longrightarrow \mathrm{B}_1
\end{array}$$