Light on electronically excited states: riding the roller coaster

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Intramolecular Dynamics

The quantumchemical role of nuclear motion in experimental spectroscopy on excited states

or

How does a spectroscopist get the maximum out of his measurements ?

- Decouple electronic and nuclear movement
  Change of harmonic force fields and molecular geometry upon excitation

- Couple electronic and nuclear movement
  Vibronic coupling

- Breakdown Born-Oppenheimer approximation
  Non-Herzberg-Teller intensity
  Radiationless decay in isolated molecules

⋮

What does the experiment learn from theory
and what does theory learn from experiment ?

Transition intensity of one-photon transition between two rovibronic states is given by

$$P_{ge} \sim \left| \int \Psi_g(\vec{r},\vec{R})\, \vec{\mu}(\vec{r},\vec{R})\, \Psi_e(\vec{r},\vec{R})\, d\vec{r}\, d\vec{R} \right|^2$$

Born-Oppenheimer approximation $\Psi(\vec{r},\vec{R}) \hat{=} \psi(\vec{r};\vec{R})\, \chi(\vec{R})$

and $\vec{\mu}(\vec{r},\vec{R}) = -e \sum_i \vec{r}_i + e \sum_s Z_s \vec{R}_s = \vec{\mu}^{el} + \vec{\mu}^{N}$ leads to

$$\int \psi_g(\vec{r};\vec{R})\, \chi_g(\vec{R}) \left[\vec{\mu}^{el} + \vec{\mu}^{N}\right] \psi_e(\vec{r};\vec{R})\, \chi_e(\vec{R})\, d\vec{r}\, d\vec{R} =$$

$$\int \chi_g(\vec{R}) \left[\int \psi_g(\vec{r};\vec{R})\, \vec{\mu}^{el}\, \psi_e(\vec{r};\vec{R})\, d\vec{r} \right] \chi_e(\vec{R})\, d\vec{R}$$

$$+ \int \chi_g(\vec{R})\, \vec{\mu}^{N} \left[\int \psi_g(\vec{r};\vec{R})\, \psi_e(\vec{r};\vec{R})\, d\vec{r} \right] \chi_e(\vec{R})\, d\vec{R}$$

$\psi_g(\vec{r};\vec{R})$ and $\psi_e(\vec{r};\vec{R})$ are orthonormal solutions of the electronic Schrodinger equation so second term falls away, while the first term can be written as

$$\int \chi_g(\vec{R})\, \vec{\mu}^{el}_{ge}(\vec{R})\, \chi_e(\vec{R})\, d\vec{R}$$

$$\vec{\mu}^{el}_{ge}(\vec{R}) \simeq \vec{\mu}^{el}_{ge}(\vec{R}_0)$$

$$\simeq \vec{\mu}^{el}_{ge}(\vec{R}_0) \int \chi_g(\vec{R})\, \chi_e(\vec{R})\, d\vec{R}$$

Separation of rotations from nuclear wavefunctions

$$\vec{\mu}^{el}_{ge}(\vec{R}_0) \int \chi^{v}_g(\vec{Q})\, \chi^{v}_e(\vec{Q})\, d\vec{Q}$$

$$\int \chi^{r}_g(\theta,\phi,\chi)\, \chi^{r}_e(\theta,\phi,\chi)\, \sin\theta\, d\theta\, d\phi\, d\chi$$

neglect of rotation-vibration interactions, and assumption of equal rotational wavefunctions leads to the conclusion

Transition intensity determined by vibrational overlap integral

$$\int \chi_g^v(\vec{Q})\, \chi_e^v(\vec{Q})\, d\vec{Q}$$

Vibrational wavefunctions are obtained by solving approximated Schrödinger equation for nuclei

Summary to define symbols

1. Calculation second-derivative matrix f with elements

$$f_{ij} = \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_{\vec{R}=\vec{R}_0}$$

2. Diagonalization mass-weighted force constant matrix

$$F = M^{-1/2} f M^{-1/2}$$

with M diagonal matrix of atomic masses

3. Diagonalization F gives set eigenvectors L_i and vibrational frequencies ν_i

$$L^{-1} F L = (2\pi\nu)^2 \Leftrightarrow F L = L (2\pi\nu)^2$$

4. Relation normal coordinates Q and Cartesian displacements δR

$$M^{1/2} \delta R = L Q$$

The vibrational wavefunctions $\chi^{v}(\vec{Q})$ are given within the harmonic approximation by the product of harmonic oscillator functions

$$\left(\frac{\Omega_i}{\pi}\right)^{1/4} \cdot \left(2^{m_i} m_i!\right)^{-1/2} \cdot H_{m_i}\left(\Omega_i^{1/2} Q_i\right) \cdot \exp\left\{-\frac{1}{2}\left(\Omega_i^{1/2} Q_i\right)^2\right\}$$

with $\Omega_i = \omega_i/\hbar$ and H_{m_i} a Hermite polynomial of order m_i

$$H_{m_i}(Q_i) = (-1)^{m_i} \exp\{Q_i^2\} \frac{d^{m_i}}{dQ_i^{m_i}}\left[\exp\{-Q_i^2\}\right]$$

in which m_i is the number of vibrational quanta in mode i

Define now

$$m! = \prod_{i=1}^{\mu} m_i! \qquad H_m(X) = \prod_{i=1}^{\mu} H_{m_i}(X_i)$$

$$a^m = \prod_{i=1}^{\mu} a^{m_i} \qquad X^m = \prod_{i=1}^{\mu} (X_i)^{m_i}$$

in which a is a scalar and X a vector
μ dimension vibrational space

Define Ω as diagonal matrix with elements
$\Omega_{ii} = \omega_i/\hbar$

Define Q as μ–dimensional column vector of normal coordinates

The vibrational wavefunctions can now be written as

$$\chi_g^m(Q_g) = \left(\frac{\det(\Omega_g)}{\pi^\mu}\right)^{1/4} \cdot (2^m \cdot m!)^{-1/2} \cdot H_m(\Omega_g^{1/2} Q_g) \cdot \exp\{-\tfrac{1}{2} Q_g^\dagger \Omega_g Q_g\}$$

$$\chi_e^n(Q_e) = \left(\frac{\det(\Omega_e)}{\pi^\mu}\right)^{1/4} \cdot (2^n \cdot n!)^{-1/2} \cdot H_n(\Omega_e^{1/2} Q_e) \cdot \exp\{-\tfrac{1}{2} Q_e^\dagger \Omega_e Q_e\}$$

in which m and n indicate how many quanta are in each mode

$$m = (m_1, m_2, \ldots, m_\mu)$$

↳ number of quanta in mode 1 state g

↳ number of quanta in mode 2 state g

Calculation of vibrational overlap integral thus amounts to calculation of

$$I(m,n) = \int \chi_g^m(Q_g)\, \chi_e^n(Q_e)\, dQ_e$$

N.B. Integration variable can be either Q_g or Q_e.
Both form complete set within
vibrational space

It is clear that vibrational overlap will be determined by form of potential energy surfaces

If frequencies and geometry remain the same on electronic excitation, there will be no change in vibrational wavefunctions (m=n)

On the other hand: if there is vibrational structure in absorption or emission spectra, this indicates the presence of changes in frequency and, in particular, geometry. A quantitative interpretation of the intensity distribution thus provides valuable information on these changes, which in turn can be related directly to the electronic characteristics of initial and final states

There are two fundamental problems in the calculation of $I(m,n) = \int \chi_g^m (Q_g)\, \chi_e^n (Q_e)\, dQ_e$

1. χ_g and χ_e are functions of two different variables (Q_g and Q_e)

2. Q_g is defined with respect to Q_g^0, Q_e with respect to Q_e^0

Look for transformation between Q_g and Q_e that takes both aspects into account

F. Duschinsky, Acta Physicochim. URSS **7**, 551 (1937)

$$Q_g = J Q_e + \Delta$$

in which J is an orthogonal matrix that describes a rotation in hyperspace defined by the normal coordinates, while Δ describes a translation resulting from the difference in equilibrium geometry

Problems are in calculating the Duschinky matrix J

Many methods based on assumption J=1, so no difference apart from difference in origin

C. Manneback, Physica **17**, 1001 (1951)

Complete calculation diatomics

T.E. Sharp and H.M. Rosenstock, J. Chem. Phys. **41**, 3453 (1964)

Calculation polyatomics in terms of internal coordinates

$$S_g \triangleq S_e + R \quad \text{met} \quad R = R_e^0 - R_g^0$$

Assumption: S=LQ with L transformation matrix between internal and normal coordinates, so no transformation between normal coordinates and Cartesian displacements

$$S_g = S_e + R \iff L_g Q_g = L_e Q_e + R$$

$$\iff Q_g = L_g^{-1} L_e Q_e + L_g^{-1} R$$

$$J = L_g^{-1} L_e \qquad \Delta = L_g^{-1} R$$

Important: S=LQ is only valid for small values of Q because transformation is not linear. Large geometry changes lead to incorrect results

A. Warshel and M. Karplus, Chem. Phys. Letters **17**, 7 (1972)

Consider problem in Cartesian coordinates. In Cartesian reference system a finite vector ΔR^P to an arbitrary point P can always be expressed in terms of Q_g or Q_e

$$M^{1/2}\,\Delta R^P = L_g Q_g - \delta/2 \qquad M^{1/2}\,\Delta R^P = L_e Q_e + \delta/2$$

in which $\delta = M^{1/2}(R_e^0 - R_g^0)$ and R are Cartesian coordinates

Because this holds for an arbitrary point we can write that:

$$L_g Q_g - \delta/2 = L_e Q_e + \delta/2 \iff L_g Q_g = L_e Q_e + \delta$$

$$\Rightarrow \quad Q_g = L_g^{\dagger} L_e Q_e + L_g^{\dagger} M^{1/2} (R_e^0 - R_g^0)$$

since L is an orthonormal matrix thus $L^{-1}=L^{\dagger}$

Duschinsky matrix $\quad J = L_g^{\dagger} L_e$

Translatie $\quad \Delta = L_g^{\dagger} M^{1/2} (R_e^0 - R_g^0)$

Problem: relation $L_gQ_g=L_eQ_e+\delta$ not uniquely defined. Molecular potential invariant with respect to rotations and translations of R_g^0 and R_e^0. Changes in geometry must be expressed in terms of **only** the normal coordinates

$$\bar{L}_g \bar{Q}_g = \bar{L}_e \bar{Q}_e + \delta$$

$\bar{L}$ and $\bar{Q}$ without rotational and translational components

a. Choose center of mass equal for R_g^0 and R_e^0

b. Meet static Eckart condition

C. Eckart, Phys. Rev. **47**, 552 (1935)

Make sure that δ does not induce angular momentum with respect to axes ground state

$$\sum_i m_i \left(y_i^g \left[z_i^e - z_i^g \right] - z_i^g \left[y_i^e - y_i^g \right] \right) = 0$$

$$\sum_i m_i \left(z_i^g \left[x_i^e - x_i^g \right] - x_i^g \left[z_i^e - z_i^g \right] \right) = 0$$

$$\sum m_i \left(x_i^g \left[y_i^e - y_i^g \right] - y_i^g \left[x_i^e - x_i^g \right] \right) = 0$$

Solving these equations gives three Euler angles over which the geometry of the excited state must be rotated

Calculation multidimensional overlap integral I(m,n)

Various approaches

a. Generating functions Hermite polynomials

Sharp and Rosenstock

P.T. Ruhoff, Chem. Phys. 186, 355 (1994)

b. Boson operators

L.S. Cederbaum and W. Domcke, J.Chem. Phys. 64, 603 (1976)

c. Dynamical symmetry group

E.V. Doktorov, I.A. Malkin, and V.I. Man'ko

J. Mol. Spectros. 64, 302 (1977)

Here we will use variation of first approach

Fundamental step within this approach:
Let I(m,n) be part of series defined by

$$\sum_{m}\sum_{n} T^{m} U^{n} \left(\frac{2^{m}\, 2^{n}}{m!\, n!}\right) I(m,n)$$

in which T and U are dummy variables

N.B. $T^{m} = \prod_{i=1}^{\mu} (T_i)^{m_i}$; $2^{m} = \prod_{i=1}^{\mu} 2^{m_i}$; $m! = \prod_{i=1}^{\mu} m_i!$

$$Q_g = L_g^{\dagger} L_e Q_e + L_g^{\dagger} M^{1/2} (R_e^0 - R_g^0)$$

$$I(m,n) = \int \chi_g^m (Q_g)\, \chi_e^n (Q_e)\, dQ_e$$

$$\chi_g^m (Q_g) = \left(\frac{\det(\Omega_g)}{\pi^{\mu}} \right)^{1/4} \cdot (2^m \cdot m!)^{-1/2} \cdot H_m (\Omega_g^{1/2} Q_g) \cdot \exp\{ -\tfrac{1}{2} Q_g^{\dagger} \Omega_g Q_g \}$$

$$\chi_e^n (Q_e) = \left(\frac{\det(\Omega_e)}{\pi^{\mu}} \right)^{1/4} \cdot (2^n \cdot n!)^{-1/2} \cdot H_n (\Omega_e^{1/2} Q_e) \cdot \exp\{ -\tfrac{1}{2} Q_e^{\dagger} \Omega_e Q_e \}$$

Step 1

Switch to frequency-adapted dimensionless coordinates

$$q = \Omega^{1/2} Q \quad \Rightarrow \quad Q = \Omega^{-1/2} q$$

This leads to relation between q_g and q_e

$$q_g = J q_e + d$$

with $J = \Omega_g^{1/2} S\, \Omega_e^{-1/2}$ $\qquad S = L_g^{\dagger} L_e$

$d = \Omega_g^{1/2} L_g^{-1} \delta$ $\qquad \delta = M^{1/2} (R_e^0 - R_g^0)$

The series now gets the following form:

$$\sum_m \sum_n T^m u^n \left(\frac{2^m 2^n}{m!\, n!} \right)^{1/2}$$

$$\int dQ_e \left(\frac{\det \Omega_g}{\pi^{\mu}} \right)^{1/4} \cdot \left(\frac{1}{2^m m!} \right)^{1/2} \cdot \exp\left(-\tfrac{1}{2} Q_g^{\dagger} \Omega_g Q_g \right) H_m (\Omega_g^{1/2} Q_g)$$

$$\left(\frac{\det \Omega_e}{\pi^{\mu}} \right)^{1/4} \cdot \left(\frac{1}{2^n n!} \right)^{1/2} \cdot \exp\left(-\tfrac{1}{2} Q_e^{\dagger} \Omega_e Q_e \right) H_n (\Omega_e^{1/2} Q_e)$$

$$= \left[\det\left(\frac{\Omega_g}{\Omega_e} \right) \cdot \frac{1}{\pi^{2\mu}} \right]^{1/4} \cdot \int dq_e \, \exp\left[-\tfrac{1}{2} (q_g^{\dagger} q_g + q_e^{\dagger} q_e) \right]$$

$$\cdot \sum_m \frac{T^m}{m!} H_m (q_g) \sum_n \frac{u^n}{n!} H_n (q_e)$$

because $\int dQ_e = (\det \Omega_e)^{-1/2} \int dq_e$

$$\left[\det\left(\frac{\Omega_g}{\Omega_e}\right)\cdot\frac{1}{\pi^{2\mu}}\right]^{1/4}\cdot\int dq_e\ \exp\left[-\tfrac{1}{2}\left(q_g^\dagger q_g+q_e^\dagger q_e\right)\right]$$

$$\cdot\sum_m\frac{T^m}{m!}H_m(q_g)\sum_n\frac{u^n}{n!}H_n(q_e)$$

Stap 2

Use generating function for Hermite polynomials

$$\exp\left(-s^2+2ts\right)=\sum_n\frac{s^n}{n!}H_n(t)$$

$$\Rightarrow\left[\det\left(\frac{\Omega_g}{\Omega_e}\right)\cdot\frac{1}{\pi^{2\mu}}\right]^{1/4}\cdot\int dq_e\ \exp\left[-\tfrac{1}{2}\left(q_g^\dagger q_g+q_e^\dagger q_e\right)\right]$$

$$\cdot\exp\left[-T^\dagger T+2q_g^\dagger T\right]\cdot\exp\left[-u^\dagger u+2q_e^\dagger u\right]$$

Stap 3

Use relation $q_g=Jq_e+d \Leftrightarrow q_g^\dagger=q_e^\dagger J^\dagger+d^\dagger$

$$=\left[\det\left(\frac{\Omega_g}{\Omega_e}\right)\cdot\frac{1}{\pi^{2\mu}}\right]^{1/4}\cdot\exp\left[-u^\dagger u-T^\dagger T\right]$$

$$\cdot\int dq_e\ \exp\left[-\tfrac{1}{2}\left(q_e^\dagger J^\dagger+d^\dagger\right)\left(Jq_e+d\right)-\tfrac{1}{2}q_e^\dagger q_e\right.$$

$$\left.+2\left(q_e^\dagger J^\dagger+d^\dagger\right)T+2q_e^\dagger u\right]$$

Notice that $d^\dagger J q_e$ is a scalar and thus equal to $q_e^\dagger J^\dagger d=\left(d^\dagger J q_e\right)^\dagger$

$$\left[\det\left(\frac{\Omega_g}{\Omega_e}\right)\cdot\frac{1}{\pi^{2\mu}}\right]^{1/4}\cdot\ \exp\left[-u^\dagger u - T^\dagger T\right]$$

$$\cdot\int dq_e\ \exp\left[-\tfrac{1}{2}(q_e^\dagger J^\dagger + d^\dagger)(J q_e + d) - \tfrac{1}{2} q_e^\dagger q_e + 2(q_e^\dagger J^\dagger + d^\dagger)T + 2 q_e^\dagger u\right]$$

$$= \left[\det\left(\frac{\omega_g}{\omega_e}\right)\cdot\frac{1}{\pi^{2\mu}}\right]^{1/4}\cdot \exp\cdot\left[-u^\dagger u - T^\dagger T\right]\cdot\exp\left[-\tfrac{1}{2}d^\dagger d + 2d^\dagger T\right]$$

$$\cdot\int dq_e\ \exp\left[-\tfrac{1}{2} q_e^\dagger (J^\dagger J + 1) q_e + q_e^\dagger \underbrace{(-J^\dagger d + 2u + 2J^\dagger T)}_{w}\right]$$

Stap 4

Integral appears to have quadratic form but we must first get rid of cross-terms $(q_e)_i(q_e)_j$

Use unitary transformation V that diagonalizes $(J^\dagger J+1)$

$V^\dagger(J^\dagger J+1)V = \Theta$ with Θ diagonal $(V^{-1} = V^\dagger)$

Transformation $q_e = Vx$

The integral now becomes

$$\int dx\ \exp\left[-\tfrac{1}{2}x^\dagger V^\dagger (J^\dagger J+1) V x + x^\dagger V^\dagger w\right]$$

$$= \int dx\ \exp\left[-\tfrac{1}{2}x^\dagger \Theta x + x^\dagger V^\dagger w\right]$$

N.B. Transformation V unitary so det(V) = 1

Stap 5

Make argument in exponent quadratic

$$-\tfrac{1}{2} x^\dagger \Theta x + x^\dagger v^\dagger w =$$

$$-\tfrac{1}{2}\left(x^\dagger \Theta x - 2x^\dagger (v^\dagger w) + (v^\dagger w)^\dagger \Theta^{-1} (v^\dagger w) - (v^\dagger w)^\dagger \Theta^{-1} (v^\dagger w)\right)$$

But Θ is diagonal !

$$x^\dagger \Theta x = \sum_i \Theta_{ii} x_i^2$$

$$(v^\dagger w)^\dagger \Theta^{-1} (v^\dagger w) = \sum_i \Theta_{ii}^{-1} (v^\dagger w)_i^2$$

$$x^\dagger (v^\dagger w) = \sum_i x_i^\dagger (v^\dagger w)_i = \sum_i x_i (v^\dagger w)_i$$

so argument now becomes

$$-\tfrac{1}{2} \sum_i \left(\Theta_{ii} x_i^2 - 2x_i (v^\dagger w)_i + \Theta_{ii}^{-1} (v^\dagger w)_i^2\right) + \tfrac{1}{2} (v^\dagger w)^\dagger \Theta^{-1} (v^\dagger w)$$

$$= -\tfrac{1}{2} \sum_i \left[\Theta_{ii} \left(x_i^2 - 2x_i \frac{(v^\dagger w)_i}{\Theta_{ii}} + \frac{(v^\dagger w)_i^2}{\Theta_{ii}^2}\right)\right] + \tfrac{1}{2} (v^\dagger w)^\dagger \Theta^{-1} (v^\dagger w)$$

$$= -\tfrac{1}{2} \sum_i \left[\Theta_{ii} \left(x_i - (v^\dagger w)_i \Theta_i^{-1}\right)^2\right] + \tfrac{1}{2} (v^\dagger w)^\dagger \Theta^{-1} (v^\dagger w)$$

$$-\frac{1}{2}\sum_i \left[\Theta_{ii}\left(x_i-(V^+w)_i\,\Theta_i^{-1}\right)^2\right]+\frac{1}{2}(V^+w)^+\Theta^{-1}(V^+w)$$

Stap 6

Use standard integral

$$\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \left(\frac{\pi}{a}\right)^{1/2}$$

$$\int dx\, \exp\left[-\tfrac{1}{2}x^+\Theta x + x^+V^+w\right] =$$

$$\exp\left[\tfrac{1}{2}w^+V\Theta^{-1}V^+w\right]\int dx\, \exp\left[\sum_i -\tfrac{1}{2}\Theta_{ii}\left(x_i-(V^+w)_i\Theta_{ii}^{-1}\right)^2\right]$$

$$= \exp\left[\tfrac{1}{2}w^+V\Theta^{-1}V^+w\right]\cdot$$

$$\prod_{i=1}^{\mu}\int d\left(x_i-(V^+w)_i\Theta_{ii}^{-1}\right)\exp\left[-\tfrac{1}{2}\Theta_{ii}\left(x_i-(V^+w)_i\Theta_{ii}^{-1}\right)^2\right]$$

$$= \exp\left[\tfrac{1}{2}w^+V\Theta^{-1}V^+w\right]\cdot\prod_{i=1}^{\mu}\left(2\pi/\Theta_{ii}\right)^{1/2}$$

$$= \exp\left[\tfrac{1}{2}w^+V\Theta^{-1}V^+w\right]\left[(2\pi)^{\mu}/\det\Theta\right]^{1/2}$$

N.B. $\det(\Theta) = \det\left(V^+(J^+J+1)V\right) = \det(J^+J+1)$

$$\tfrac{1}{2}w^+V\Theta^{-1}V^+w = \tfrac{1}{2}w^+(J^+J+1)^{-1}w$$

Call $(J^+J+1)^{-1} \triangleq Q$ and realize that Q is symmetric

Fill in $w = -J^+d + 2\mathcal{U} + 2J^+T$

$$\left[\det\left(\frac{w_g}{w_e}\right)\cdot\frac{1}{\pi^{2\mu}}\right]^{1/4}\cdot\exp\cdot\left[-u^\dagger u-T^\dagger T\right]\cdot\exp\left[-\tfrac{1}{2}d^\dagger d+2d^\dagger T\right]$$

$$\cdot\int dq_e\ \exp\Big[-\tfrac{1}{2}q_e^\dagger(J^\dagger J+1)q_e + q_e^\dagger\underbrace{(-J^\dagger d+2u+2J^\dagger T)}_{W}\Big]$$

$$\exp\left[\tfrac{1}{2}W^\dagger V\Theta^{-1}V^\dagger W\right]\ \left[(2\pi)^\mu/\det\Theta\right]^{1/2}$$

$$\det(\Theta)=\det(V^\dagger(J^\dagger J+1)V)=\det(J^\dagger J+1)$$

$$(J^\dagger J+1)^{-1}\triangleq Q$$

$$W=-J^\dagger d+2u+2J^\dagger T$$

In total we get now for $\sum_m\sum_n T^m u^n\left(\frac{2^m 2^n}{m!n!}\right)^{1/2} I(m,n)$

$$\left[\det\left(\frac{w_g}{w_e}\right)\right]^{1/4}\cdot 2^{\mu/2}\cdot\det Q^{1/2}$$

$$\cdot\exp\left[-u^\dagger u-T^\dagger T\right]\cdot\exp\left[-\tfrac{1}{2}d^\dagger d+2d^\dagger T\right]$$

$$\cdot\exp\left[\tfrac{1}{2}(-J^\dagger d+2u+2J^\dagger T)^\dagger\cdot Q\cdot(-J^\dagger d+2u+2J^\dagger T)\right]$$

Stap 7

Rewrite argument exponent, realizing that all terms are scalars, thus, for example $(U^\dagger Q^\dagger J^\dagger d)^\dagger = U^\dagger Q^\dagger J^\dagger d = U^\dagger QJ^\dagger d$ since Q is symmetric ($Q^\dagger=Q$)

$$\left[\det\left(\frac{w_g}{w_e}\right)\right]^{1/4}\cdot 2^{\mu/2}\cdot\det Q^{1/2}\cdot\exp\left[\tfrac{1}{2}d^\dagger(JQJ^\dagger-1)d\right]$$

$$\cdot\exp\Big[u^\dagger(2Q-1)u + u^\dagger(-2QJ^\dagger d) + T^\dagger(2JQJ^\dagger-1)T + T^\dagger(-2(JQJ^\dagger-1)d) + u^\dagger(4QJ^\dagger)T\Big]$$

Define symmetric matrix $P=JQJ^\dagger$

matrix $R=QJ^\dagger$

$$\left[\det\left(\frac{\omega_g}{\omega_e}\right)\right]^{1/4} \cdot 2^{\mu/2} \cdot \det Q^{1/2} \cdot \exp\left[\tfrac{1}{2} d^\dagger (JQJ^\dagger - 1) d\right]$$

$$\cdot \exp\Big[u^\dagger (2Q-1) u + u^\dagger (-2QJ^\dagger d)$$

$$+ T^\dagger (2JQJ^\dagger - 1) T + T^\dagger (-2(JQJ^\dagger - 1) d)$$

$$+ u^\dagger (4QJ^\dagger) T \Big]$$

$$P \hat{=} JQJ^\dagger$$
$$R \hat{=} QJ^\dagger$$

We can now write our expression as

$$2^{\mu/2} \cdot \left[\prod_{i=1}^{\mu} \left(\frac{\omega_g}{\omega_e}\right)^{1/4}\right] \cdot (\det Q)^{1/2} \cdot \exp\left[-\tfrac{1}{2} d^\dagger (1-P) d\right]$$

$$\cdot \exp\left[u^\dagger C u + u^\dagger D + T^\dagger A T + T^\dagger B + u^\dagger E T \right]$$

with

$A = 2P - 1$ $\qquad P = JQJ^\dagger$

$B = 2(1-P)d$ $\qquad Q = (J^\dagger J + 1)^{-1}$

$C = 2Q - 1$ $\qquad R = QJ^\dagger$

$D = -2Rd$ $\qquad J = \omega_g^{1/2} S \omega_e^{-1/2}$ $\qquad S = L_g^\dagger L_e$

$E = 4R$ $\qquad d = \hbar^{-1/2} \omega_g^{1/2} L_g^\dagger M^{1/2} (R_e^0 - R_g^0)$

We now have to compare this expression with our original expression

$$\sum_m \sum_n T^m u^n \left(\frac{2^m 2^n}{m!\,n!}\right) I(m,n)$$

and try to extract from this expression the coefficients $I(m,n)$

$$2^{\mu/2} \cdot \left[\prod_{i=1}^{\mu} \left(\frac{w_g}{w_e} \right)^{1/4} \right] \cdot (\det Q)^{1/2} \cdot \exp\left[-\tfrac{1}{2} d^{\dagger} (1-P) d \right]$$

$$\cdot \exp\left[u^{\dagger} C u + u^{\dagger} D + T^{\dagger} A T + T^{\dagger} B + u^{\dagger} E T \right]$$

Stap 8

Develop both sides of the equation in powers of $t_i^{m_i}$ and $u_i^{m_i}$. Because t_i and u_i are dummy variables and thus can have an arbitrary value, there will only be a solution if the coefficients for each of the terms $t_i^{m_i}$ and $u_i^{m_i}$ are equal

take $m = (m_1, m_2, \cdots, m_\mu) = (0, 0, \cdots, 0)$
$n = (n_1, n_2, \cdots, n_\mu) = (0, 0, \cdots, 0)$

$$I(0,0) = 2^{\mu/2} \cdot \left[\prod_{i=1}^{\mu} \left(\frac{w_g}{w_e} \right)^{1/4} \right] \cdot (\det Q)^{1/2} \cdot \exp\left[-\tfrac{1}{2} d^{\dagger} (1-P) d \right]$$

In this way we can also find expressions for the other overlap integrals, but it would be more useful if we could find **recursion relations**

Stap 9

Derive recursion relations by differentiation of both sides with respect to u_k or t_k

$$I_0 \cdot \exp\Big[\sum_i \sum_j t_i t_j A_{ij} + \sum_i t_i B_i + \sum_i \sum_j u_i u_j C_{ij} + \sum_i u_i D_i + \sum_i \sum_j u_i t_j E_{ij} \Big] =$$

$$\sum_{n_i=0}^{\infty} \sum_{m_j=0}^{\infty} \prod_{i=1}^{\mu} \prod_{j=1}^{\mu} \left(\frac{2^{n_i} 2^{m_j}}{n_i! \, m_j!} \right)^{1/2} u_i^{n_i} t_j^{m_j} \, (m_1, m_2, \ldots \mid n_1, n_2, \ldots)$$

$$I_0 \cdot \exp\Big[\sum_i\sum_j t_i t_j A_{ij} + \sum_i t_i B_i + \sum_i\sum_j u_i u_j C_{ij} + \sum_i u_i D_i + \sum_i\sum_j u_i t_j E_{ij}\Big] =$$

$$\sum_{n_i=0}^{\infty}\sum_{m_j=0}^{\infty}\prod_{i=1}^{\mu}\prod_{j=1}^{\mu}\left(\frac{2^{n_i}2^{m_j}}{n_i!\,m_j!}\right)^{1/2} u_i^{n_i} t_j^{m_j}\,(m_1,m_2,\dots\,|\,n_1,n_2,\dots)$$

$$\sum_m\sum_n T^m u^n\left(\frac{2^m 2^n}{m!\,n!}\right) I(m,n)$$

Differentiate with respect to u_k

$$I_0\cdot\Big[\sum_j u_j C_{kj} + \sum_i u_i C_{ik} + D_k + \sum_\ell t_\ell E_{k\ell}\Big]\cdot\exp[\dots] =$$

$$\sum_{n_i=0}^{\infty}\sum_{m_j=0}^{\infty}\prod_{i\neq k}\prod_j\left(\frac{2^{n_i}2^{m_j}}{n_i!\,m_j!}\right)^{1/2}\cdot\left(\frac{2^{n_k}}{n_k!}\right)^{1/2}\cdot n_k u_k^{n_k-1}\, u_i^{n_i} t_j^{m_j}\cdot(m_1,m_2,\dots\,|\,n_1,n_2,\dots)$$

1. Matrix C symmetric

$$\sum_j u_j C_{kj} + \sum_i u_i C_{ik} = 2\sum_j u_j C_{jk}$$

2. I_0 exp[…] is original power series

$$\Big[2\sum_j u_j C_{jk} + D_k + \sum_\ell t_\ell E_{k\ell}\Big]\cdot\sum_{n_i}\sum_{m_j}\prod_i\prod_j\left(\frac{2^{n_i}2^{m_j}}{n_i!\,m_j!}\right)^{1/2} u_i^{n_i} t_j^{m_j}\,(m_1,m_2,\dots\,|\,n_1,n_2,\dots) =$$

$$\sum_{n_i}\sum_{m_j}\prod_{i\neq k}\prod_j\left(\frac{2^{n_i}2^{m_j}}{n_i!\,m_j!}\right)^{1/2}\left(\frac{2^{n_k}}{n_k!}\right)^{1/2} n_k u_k^{n_k-1}\, u_i^{n_i} t_j^{m_j}\,(m_1,m_2,\dots\,|\,n_1,n_2,\dots)$$

We must now find on both sides the same power, so we are going to look at terms of the form $u_i^{n_i} t_i^{m_j}$

On right side we find as coefficient

$$(n_k+1)\cdot\left(\frac{2^{n_k+1}}{(n_k+1)!}\right)^{1/2}(m_1,m_2,\dots\,|\,n_1,n_2,\dots,(n_k+1),\dots) =$$

$$[2(n_k+1)]^{1/2}\cdot\left(\frac{2^{n_k}}{n_k!}\right)^{1/2}\cdot(m_1,m_2,\dots\,|\,n_1,n_2,\dots,(n_k+1),\dots)$$

$$\left[2\sum_j u_j C_{jk} + D_k + \sum_e t_e E_{ke}\right] \cdot$$

$$\sum_{n_i}\sum_{m_j}\prod_i\prod_j \left(\frac{2^{n_i}2^{m_j}}{n_i!\,m_j!}\right)^{1/2} u_i^{n_i} t_j^{m_j} \; (m_1, m_2, \dots \mid n_1, n_2, \dots)$$

On left side we have three terms

1. Term with D_k gives $D_k\,(m_1, m_2, \dots \mid n_1, n_2, \dots)$
2. Term with $\sum_j u_j C_{jk}$ raises $u_j^{n_j}$ to $u_j^{n_j+1}$

   $u_j^{n_j}$ has now as coefficient $\left(\frac{2^{n_j-1}}{(n_j-1)!}\right)^{1/2} (m_1, m_2, \dots \mid n_1, n_2, \dots (n_j-1) \dots)$

   $$= \left(\frac{n_j}{2}\right)^{1/2} \cdot \left(\frac{2^{n_j}}{n_j!}\right)^{1/2} \cdot (m_1, m_2, \dots \mid n_1, n_2, \dots, (n_j-1), \dots)$$

   $$\Rightarrow\; 2\sum_j C_{jk}\left(\frac{n_j}{2}\right)^{1/2} (m_1, m_2, \dots \mid n_1, n_2, \dots, (n_j-1), \dots)$$

3. Term with $\sum_e t_e E_{ke}$ raises $t_e^{m_e}$ to $t_e^{m_e+1}$

   $t_e^{m_e}$ has now as coefficient

   $$\left(\frac{m_e}{2}\right)^{1/2}\left(\frac{2^{m_e}}{m_e!}\right)^{1/2} (m_1, m_2, \dots, (m_e-1), \dots \mid n_1, n_2, \dots)$$

   $$\Rightarrow\; \sum_e E_{ke}\left(\frac{m_e}{2}\right)^{1/2} (m_1, m_2, \dots, (m_e-1), \dots \mid n_1, n_2, \dots)$$

We can now equate terms with $u_i^{n_i} t_i^{m_j}$ and find the recursion relation

$$[2(n_k+1)]^{1/2} \cdot \left(\frac{2^{n_k}}{n_k!}\right)^{1/2} \cdot (m_1, m_2, \cdots \mid n_1, n_2, \cdots, (n_k+1), \cdots)$$

$$D_k\,(m_1, m_2, \cdots \mid n_1, n_2, \cdots)$$

$$2 \sum_j C_{jk} \left(\frac{n_j}{2}\right)^{1/2} (m_1, m_2, \cdots \mid n_1, n_2, \cdots, (n_j-1), \cdots)$$

$$\sum_l E_{kl} \left(\frac{m_l}{2}\right)^{1/2} (m_1, m_2, \cdots, (m_l-1), \cdots \mid n_1, n_2, \cdots)$$

$A = 2P-1$

$B = 2(1-P)d$

$C = 2Q-1$

$D = -2Rd$

$E = 4R$

$$(m \mid n_1, \cdots, (n_k+1), \cdots) =$$

$$2 \sum_l R_{kl} \left(\frac{m_l}{n_k+1}\right)^{1/2} (m_1, \cdots, (m_l-1), \cdots \mid n)$$

$$+ \sum_j (2Q-1)_{jk} \left(\frac{n_j}{n_k+1}\right)^{1/2} (m \mid n_1, \cdots, (n_j-1), \cdots)$$

$$- \left(\frac{2}{n_k+1}\right)^{1/2} (Rd)_k \, (m \mid n)$$

N.B. $(m| = (m_1, m_2, \cdots, m_l, \cdots)$
$|n) = (n_1, n_2, \cdots, n_k, \cdots)$

Differentiation with respect to t_k gives analogously the following recursion relation

$$(m_1, \cdots, (m_k+1), \cdots \mid n) =$$

$$2 \sum_l R_{lk} \left(\frac{n_l}{m_k+1}\right)^{1/2} (m \mid n_1, \cdots, (n_l-1), \cdots)$$

$$+ \sum_j (2P-1)_{kj} \left(\frac{m_j}{m_k+1}\right)^{1/2} (m_1, \cdots, (m_j-1), \cdots \mid n)$$

$$+ \left(\frac{2}{m_k+1}\right)^{1/2} [(1-P)d]_k \, (m \mid n)$$

Consider limiting situation that frequencies and normal coordinates are nearly the same, in which case

$$S = L_g^{+} L_e = 1 \qquad ; \qquad J = \omega_g^{1/2}\, S\, \omega_e^{-1/2} = 1$$

For absorption experiments from the vibrationless ground state only (2Q-1) and (Rd) are important

$$Q = (J^{+}J + 1)^{-1} = \tfrac{1}{2}\cdot 1 \Rightarrow 2Q - 1 = 0$$

$$R = Q J^{+} = \tfrac{1}{2}\cdot 1$$

Transitions determined by d, the projection of the geometry change on the frequency-weighted normal coordinates

$$(0|n_1,\cdots,(n_i+1),\cdots) = -(Rd)_i \left(\frac{2}{n_i+1}\right)^{1/2} (0|n_1,\cdots,n_i,\cdots)$$

If frequencies and normal coordinates change, but there is no change in geometry (d=0) then we find

$$(0|n_1,\cdots,(n_i+1),\cdots) = \sum_j (2Q-1)_{ji} \left(\frac{n_j}{n_i+1}\right)^{1/2} (0|n_1,\cdots,(n_j-1),\cdots)$$

Fundamental transitions $(0|0_1,0_2,\cdots,1_i\cdots)$ thus require changes in geometry

The role of symmetry

- The Duschinsky matrix $L_g^{\dagger}L_e$ and its frequency-weighted analogue will be blocked on the basis of the lemma of Schur
- If symmetry does not change on transition, Δ and its frequency-weighted analogue will only have components in the totally-symmetric coordinates

As a result, the matrices J, Q, R and P will become block-diagonal while the vectors Rd and (1-P)d will only have components in the totally-symmetric vibrations

$\Rightarrow$

1. The recursion relations connect overlap integrals within the same symmetry
2. The recursion relations for nontotally-symmetric vibrations do not have contributions from terms involving Rd and (1-P)d
3. Two-dimensional overlap integrals in which two vibrations of different symmetry are involved are given by the product of the corresponding one-dimensional overlap integrals

$$(0|\cdots n_i, n_j \cdots) = (0|\cdots n_i\, 0_j \cdots)\,(0|\cdots 0_i\, n_j \cdots)$$

Determination geometry changes from absorption and emission spectra

Consider absorption from the vibrationless ground state to fundamental vibrations (N.B. for symmetric molecules limited to totally-symmetric vibrations

$$\frac{(0_g | 0_1, \cdots, 1_i, \cdots)}{(0|0)} = -\sqrt{2}\,(Rd)_i = (I_i^a)^{1/2}$$

For transitions in emission

$$\frac{(0_1, \cdots, 1_k, \cdots | 0_e)}{(0|0)} = \sqrt{2}\,[(1-P)d]_k = (I_k^e)^{1/2}$$

Previously we concluded that intensity is mainly determined by changes in geometry, and that it is less sensitive to changes in frequencies and normal coordinates. Consider latter therefore as exact and try to get agreement between experiment and theory by adjusting the geometry

$$d = \hbar^{-1/2}\,\omega_g^{1/2}\,L_g^{\dagger}\,M^{1/2}\,(R_e^{\circ} - R_g^{\circ}) \quad \Rightarrow$$

$$(R_e^{\circ} - R_g^{\circ}) = M^{-1/2}\,L_g\,\omega_g^{-1/2}\,\hbar^{1/2}\,d$$

$$= \hbar^{1/2}\,M^{-1/2}\,L_g\,\omega_g^{-1/2}\,R^{-1}R\,d$$

$$R^{-1} = (QJ^{\dagger})^{-1} = (J^{\dagger})^{-1}Q^{-1} = (J^{\dagger})^{-1}(1 + J^{\dagger}J)$$

$$= [(J^{\dagger})^{-1} + J]$$

$$(R_e^o - R_g^o) = \hbar^{1/2} M^{-1/2} L_g \omega_g^{-1/2} [(J^+)^{-1} + J] (Rd)$$

$$= \pm \hbar^{1/2} M^{-1/2} L_g \omega_g^{-1/2} [(J^+)^{-1} + J] \left(\frac{I^a}{2}\right)^{1/2}$$

in which I^a is the vector of experimentally measured relative intensities of fundamental transitions with respect to intensity (0|0) transition

The same can be done for emissive transitions
(use $(1-P)^{-1}(1-P)$ instead of $R^{-1}R$)

$$(R_e^o - R_g^o) = \pm \hbar^{1/2} M^{-1/2} L_g \omega_g^{-1/2} (1-P)^{-1} \left(\frac{I^e}{2}\right)^{1/2}$$

N.B. Because experimental intensities are used that are proportional to the square of the overlap integral, the direction of the geometry change is not uniquely defined

For the determination of the absolute geometry change use can be made of the intensity of combination bands

$$(0_g | 0_1, \cdots, 1_i, 1_j, \cdots) = (2Q-1)_{ij} (0|0) - (Rd)_i \sqrt{2}\, (0|1_j)$$

$$= (2Q-1)_{ij} (0|0) + 2 (Rd)_i (Rd)_j (0|0)$$

Choice of sign will therefore work through in intensity of for example combination bands

If it is assumed that intensities are only determined by geometry changes, for example in absence of reliable normal coordinates for electronically excited states, then experiment and theory can be connected by the relations

$$(R_e^0 - R_g^0) = \pm \hbar^{1/2} M^{-1/2} L_g \omega_g^{-1/2} (1+1) \left(\frac{I_a}{2}\right)^{1/2}$$

$$= \pm \hbar^{1/2} M^{-1/2} L_g \omega_g^{-1/2} (2 I_a)^{1/2}$$

$$= \pm \hbar^{1/2} M^{-1/2} L_g \omega_g^{-1/2} (2 I_e)^{1/2}$$

Notice that measurement of transition intensities in principle also enables one to determine (in part) the Duschinsky matrix. Formally, it is even so that, for example, measurement of $(\ldots 1_k \ldots | 0)$, $(\ldots 2_k \ldots | 0)$ and $(\ldots 1_k 1_l \ldots | 0)$ for all k and l reconstructs the matrix P

Reconstruction Duschinsky matrix from experimental data

$$(1_k|0) = \sqrt{2}\,[(1-P)d]_k\,(0|0)$$

$$I(1_k|0) = \left[\frac{(1_k|0)}{(0|0)}\right]^2 = 2\,[(1-P)d]_k^2$$

$$(2_k|0) = \frac{1}{\sqrt{2}}\,(2P-1)_{kk}\,(0|0) + \sqrt{2}\,[(1-P)d]_k^2\,(0|0)$$

$$= \frac{1}{\sqrt{2}}\,(2P-1)_{kk}\,(0|0) + \frac{1}{\sqrt{2}}\,I(1_k|0)\,(0|0)$$

$$I(2_k|0) = \frac{1}{2}\left[(2P-1)_{kk} + I(1_k|0)\right]^2$$

$$P_{kk} = \frac{1}{2}\left[1 \pm \sqrt{2}\,I(2_k|0)^{1/2} - I(1_k|0)\right]$$

$$(1_k1_\ell|0) = (2P-1)_{k\ell}\,(0|0) + 2\,[(1-P)d]_k\,[(1-P)d]_\ell\,(0|0)$$

$$= (2P-1)_{k\ell}\,(0|0) \pm I(1_k|0)^{1/2}\,I(1_\ell|0)^{1/2}\,(0|0)$$

$$I(1_k1_\ell|0) = \left[(2P-1)_{k\ell} \pm I(1_k|0)^{1/2}\,I(1_\ell|0)^{1/2}\right]^2$$

$$P_{k\ell} = \pm\frac{1}{2}\left[I(1_k1_\ell|0)^{1/2} \pm I(1_k|0)^{1/2}\,I(1_\ell|0)^{1/2}\right]$$

$$P^{-1} = (J^\dagger)^{-1}(1 + J^\dagger J)J^{-1}$$

$$= (J^\dagger)^{-1}J^{-1} + 1 = \omega_g^{-1/2}\, S\, \omega_e\, S^\dagger\, \omega_g^{-1/2} + 1 \quad \Leftrightarrow$$

$$\omega_g^{1/2}\,(P^{-1} - 1)\,\omega_g^{1/2} = S\,\omega_e\, S^\dagger$$

This is equivalent to finding matrix S that diagonalizes the matrix $W' = \omega_g^{1/2}(P^{-1} - 1)\omega_g^{1/2}$

$$S^\dagger W' S = \omega_e$$

Same kind of derivations can be made for measurements in absorption

Conclusion: absorption and emission data provide in principle the possibility to determine geometry changes but also the Duschkinsky matrix

Vibronic coupling

So far transition probability assumed to be proportional to

$$\int \chi_g(\vec{R}) \left[\int \psi_g(\vec{r};\vec{R})\, \vec{\mu}^{el}\, \psi_e(\vec{r};\vec{R})\, d\vec{r} \right] \chi_e(\vec{R})\, d\vec{R} \simeq$$

$$\vec{\mu}^{el}_{ge}(\vec{R}_0) \int \chi_g(\vec{R})\, \chi_e(\vec{R})\, d\vec{R}$$

If $\psi_g \otimes \mu^{el} \otimes \psi_e$ is not totally-symmetric we are dealing with a forbidden transition

Experimentally it turns out that in many cases these transitions can still be observed. Reason is found in $\vec{R}$ dependence of $\int \psi_g(\vec{r};\vec{R})\, \vec{\mu}^{el} \psi_e(\vec{r};\vec{R}) d\vec{r}$

For $\vec{R} = \vec{R}_0$ transition moment can be 0, but for $\vec{R} \neq \vec{R}_0$ it is possible that integral is not equal to 0. We then talk about vibronically induced transitions. For such transitions it must be true that

$$\left(\psi_g(\vec{r};\vec{R}_0)\, \chi_g(\vec{R})\right) \otimes \vec{\mu}^{el} \otimes \left(\psi_e(\vec{r};\vec{R}_0)\, \chi_e(\vec{R})\right)$$

contains the totally-symmetric representation

“Breakdown” Born-Oppenheimer approximation

Complete Schrödinger equation is given by

$$H(q,Q)\,\Psi(q,Q) = \varepsilon\,\Psi(q,Q)$$

with $H(q,Q) = T(q) + T(Q) + U(q,Q) + V(Q)$
$U(q,Q) = V_{Ne}(q,Q) + V_{ee}(q)$

$$H(q,Q) = H_e(q,Q) + T(Q) + V(Q)$$
$$H_e(q,Q) = T(q) + U(q,Q)$$

Use solutions of the electronic Schrödinger equation to solve this equation

$$H_e(q;Q)\,\psi_n(q;Q) = E_n(Q)\,\psi_n(q;Q)$$

by $\Psi(q,Q)$ expansion in these $\Psi_i(q,Q) = \sum_n \psi_n(q;Q)\,\chi_{ni}(Q)$

$$H(q,Q)\sum_n \psi_n(q;Q)\,\chi_{ni}(Q) = \varepsilon_i \sum_n \psi_n(q;Q)\,\chi_{ni}(Q)$$

$$T(Q)\left[\psi_n(q;Q)\,\chi_{ni}(Q)\right] = -\frac{\hbar^2}{2}\sum_k \frac{\partial^2}{\partial Q_k^2}\left[\psi_n(q;Q)\,\chi_{ni}(Q)\right]$$

$$= -\frac{\hbar^2}{2}\sum_k \left[\frac{\partial^2 \psi_n(q;Q)}{\partial Q_k^2}\chi_{ni}(Q) + 2\,\frac{\partial \psi_n(q;Q)}{\partial Q_k}\frac{\partial \chi_{ni}(Q)}{\partial Q_k} + \psi_n(q;Q)\,\frac{\partial^2 \chi_{ni}(Q)}{\partial Q_k^2}\right]$$

$$= \left[T(Q)\,\psi_n(q;Q)\right]\chi_{ni}(Q) + \psi_n(q;Q)\,T(Q)\,\chi_{ni}(Q) - \hbar^2\sum_k\left[\frac{\partial \psi_n(q;Q)}{\partial Q_k}\,\frac{\partial \chi_{ni}(Q)}{\partial Q_k}\right]$$

$$\sum_n \left(\left\{ \psi_n(q;Q) \left[T(Q) + V(Q) + E_n(Q) \right] + \left[T(Q)\, \psi_n(q;Q) \right] \right\} \chi_{ni}(Q) \right.$$

$$\left. - \hbar^2 \sum_k \left[\frac{\partial \psi_n(q;Q)}{\partial Q_k} \frac{\partial \chi_{ni}(q;Q)}{\partial Q_k} \right] \right) = \varepsilon_i \sum_n \psi_n(q;Q)\, \chi_{ni}(Q)$$

Multiply with $\psi_n^*(q;Q)$ and integrate over q

$$\left[T(Q) + V(Q) + E_n(Q) + \langle \psi_n(q;Q) | T(Q) | \psi_n(q;Q) \rangle - \varepsilon_i \right] \chi_{ni}(Q)$$

$$+ \sum_{m \neq n} \left[\langle \psi_n(q;Q) | T(Q) | \psi_m(q;Q) \rangle \right.$$

$$\left. - \sum_k \hbar^2 \langle \psi_n(q;Q) | \frac{\partial}{\partial Q_k} | \psi_m(q;Q) \rangle \frac{\partial}{\partial Q_k} \right] \chi_{mi}(Q) = 0$$

Neglecting non-diagonal terms leads to

$$\Psi_{ni}^A(q,Q) = \psi_n(q;Q)\, \chi_{ni}^A(Q)$$

$$\left[T(Q) + V(Q) + E_n(Q) + \langle \psi_n(q;Q) | T(Q) | \psi_n(q;Q) \rangle - \varepsilon_{ni}^A \right] \chi_{ni}^A(Q) = 0$$

Separation of electronic and nuclear coordinates

N.B. Within what is called Born-Oppenheimer approximation also $\langle \psi_n(q;Q) | T(Q) | \psi_n(q;Q) \rangle$ is neglected

The crude spectroscopic approach

Make use of molecular symmetry by expansion of electronic wavefunctions at **one** particular nuclear configuration $\mathbf{Q_0}$

$$\Psi_i(q,Q) = \sum_n \psi_n(q;Q_0)\,\chi_{ni}(Q)$$

with $H_e(q,Q_0)\,\psi_n(q;Q_0) = E_n(Q_0)\,\psi_n(q;Q_0)$

$H_e(q,Q)$ and $H_e(q,Q_0)$ are related by

$$\begin{aligned} H_e(q,Q) &= T(q) + U(q,Q) = T(q) + U(q,Q_0) + \Delta U(q,Q) \\ &= H_e(q,Q_0) + \Delta U(q,Q) \end{aligned}$$

Schrödinger equation now becomes

$$\left[H_e(q,Q_0) + \Delta U(q,Q) + V(Q) + T(Q)\right] \sum_n \psi_n(q;Q_0)\,\chi_{ni}(Q) = \varepsilon_i \sum_n \psi_n(q;Q_0)\,\chi_{ni}(Q)$$

which leads to

$$\left[T(Q) + V(Q) + E_n(Q_0) + \langle \psi_n(q;Q_0) | \Delta U(q,Q) | \psi_n(q;Q_0)\rangle - \varepsilon_i\right] \chi_{ni}(Q) + \sum_{m\neq n} \langle \psi_n(q;Q_0) | \Delta U(q,Q) | \psi_m(q;Q_0)\rangle\, \chi_{mi}(Q) = 0$$

Neglect of non-diagonal terms leads to

$$\Psi_{ni}^{CA}(q,Q) = \psi_n(q;Q_0)\,\chi_{ni}^{CA}(Q)$$

$$\left[T(Q) + V(Q) + E_n(Q_0) + \langle \psi_n(q;Q_0)|\Delta U(q,Q)|\psi_n(q;Q_0)\rangle - \varepsilon_{ni}^{CA}\right]\chi_{ni}^{CA}(Q) = 0$$

Herzberg-Teller expansion

The electronic wavefunctions $\psi_n(q;Q_0)$ are independent of Q. Try to incorporate Q-dependence of real wavefunction using perturbation theory

$$\Delta U(q,Q) = U(q,Q) - U(q,Q_0)$$

$$= \sum_k \left(\frac{\partial U(q,Q)}{\partial Q_k}\right)_{Q_0} \cdot Q_k + \frac{1}{2}\sum_{l,m}\left(\frac{\partial^2 U(q,Q)}{\partial Q_l\,\partial Q_m}\right)_{Q_0} \cdot Q_l Q_m + \cdots$$

$$\psi_n^{HT}(q;Q) = \psi_n(q;Q_0) + \sum_{m\neq n} a_{mn}(Q)\,\psi_m(q;Q_0)$$

$$a_{mn}(Q) = \frac{\langle m|\Delta U|n\rangle}{(E_n - E_m)} + \sum_{l\neq n}\frac{\langle m|\Delta U|l\rangle\langle l|\Delta U|n\rangle}{(E_n - E_m)\,(E_n - E_l)} + \cdots$$

N.B. $|n\rangle \mathrel{\hat{=}} \psi_n(q;Q_0)$ $\quad E_n \mathrel{\hat{=}} E_n(Q_0)$ $\quad \Delta U \mathrel{\hat{=}} \Delta U(q,Q)$

If we now use the expression for ΔU in $a_{mn}(Q)$ and restrict ourselves to the first term, we find

$$\psi_n^{HT}(q;Q) = \psi_n(q;Q_0) + \sum_k \sum_{m\neq n}\left[\frac{\langle m|\left(\frac{\partial U}{\partial Q_k}\right)_{Q_0}|n\rangle}{E_n - E_m} \cdot Q_k\right]\psi_m(q;Q_0)$$

The complete wavefunction is given by

$$\Psi_{ni}^{HT}(q,Q) = \psi_n^{HT}(q;Q)\,\chi_{ni}(Q)$$

$$= \left[\psi_n^{CA}(q;Q_0) + \sum_{m\neq n} a_{mn}(Q)\,\psi_m^{CA}(q;Q_0)\right]\chi_{ni}(Q)$$

This expansion is called the Herzberg-Teller expansion, and the use of Q-dependent electronic wavefunctions the breakdown of the Condon-approximation. Strictly speaking this is not vibronic coupling because electronic and nuclear coordinates are still separated

Transition probability between $\Psi_{gi}^{HT}(q,Q)$ and $\Psi_{ej}^{HT}(q,Q)$ given by

$$(\langle \Psi_{gi}^{HT}(q,Q) | \mu | \Psi_{ej}^{HT}(q,Q)\rangle)$$

$$(\langle [g + \sum_{\ell\neq g} a_{\ell g}(Q)\,\ell\,| i_g | \mu | [e + \sum_{n\neq e} b_{ne}(Q)\,n]\, j_e\rangle) =$$

$$(i_g | \langle g | \mu | e\rangle\, j_e) +$$

$$\sum_k \sum_{\ell\neq g} \frac{\langle e | \left(\frac{\partial u}{\partial Q_k}\right)_{Q_0} | g\rangle}{E_g - E_\ell} \langle \ell | \mu | e\rangle\,(i_g | Q_k | j_e) +$$

$$\sum_m \sum_{n\neq e} \frac{\langle n | \left(\frac{\partial u}{\partial Q_m}\right)_{Q_0} | e\rangle}{E_e - E_n} \langle g | \mu | n\rangle\,(i_g | Q_m | j_e) + \cdots$$

Transition probability by mixing in of ground state

Transition probability by mixing in of electronically excited state

$$(i_g|\langle g|\mu|e\rangle j_e) +$$

$$\sum_k \sum_{\ell\neq g} \frac{\langle e|\left(\frac{\partial u}{\partial Q_k}\right)_{Q_0}|g\rangle}{E_g - E_e} \langle e|\mu|e\rangle (i_g|Q_k|j_e) +$$

$$\sum_m \sum_{n\neq e} \frac{\langle n|\left(\frac{\partial u}{\partial Q_m}\right)_{Q_0}|e\rangle}{E_e - E_n} \langle g|\mu|n\rangle (i_g|Q_m|j_e) + \cdots$$

Herzberg-Teller expansion ground state:

$$\psi_g^{HT}(q;Q) \simeq \psi_g(q;Q_0) + \sum_k \sum_{\ell\neq g} \left[\frac{\langle e|\left(\frac{\partial u}{\partial Q_k}\right)_{Q_0}|g\rangle}{E_g - E_e} \cdot Q_k\right] \psi_e(q;Q_0)$$

$$\frac{\partial \psi_g^{HT}(q;Q)}{\partial Q_k} \simeq \sum_{\ell\neq g} \left[\frac{\langle e|\left(\frac{\partial u}{\partial Q_k}\right)_{Q_0}|g\rangle}{E_g - E_e}\right] \psi_e(q;Q_0)$$

The expression for the transition probability can therefore also be written as

$$\langle g|\mu|e\rangle (i_g|j_e) +$$

$$\sum_k \left\langle \frac{\partial \psi_g^{HT}(q;Q)}{\partial Q_k} |\mu| \psi_e(q;Q_0)\right\rangle (i_g|Q_k|j_e) +$$

$$\sum_m \left\langle \psi_g(q;Q_0) |\mu| \frac{\partial \psi_e^{HT}(q;Q)}{\partial Q_m}\right\rangle (i_g|Q_m|j_e) + \cdots =$$

$$\left(i_g \middle| M_{ge}(Q_0) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \cdot Q_k + \cdots \middle| j_e\right) =$$

because $\left(\frac{\partial \mu}{\partial Q}\right)_{Q_0} \neq 0$ for electronic transitions, this equals

$$(i_g|M_{ge}(Q)|j_e)$$

An equivalent treatment to incorporate a Q-dependence into $\psi(q;Q_0)$ is to incorporate a Q-dependence into $M_{ge}(Q_0)$ using a Taylor expansion

$$M(Q) = M(Q_0) + \sum_i \left(\frac{\partial M(Q)}{\partial Q_i}\right)_{Q_0} \cdot Q_i + \frac{1}{2}\sum_i\sum_j \left(\frac{\partial^2 M(Q)}{\partial Q_i \partial Q_j}\right)_{Q_0} \cdot Q_i Q_j + \cdots$$

$$(\langle \Psi_{gi}(q,Q) | \mu | \Psi_{ej}(q,Q) \rangle =$$

$$M_{ge}(Q_0)\,(i_g|j_e) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} (i_g|Q_k|j_e)$$

$$+ \frac{1}{2}\sum_k \sum_l \left(\frac{\partial^2 M_{ge}(Q)}{\partial Q_k \partial Q_l}\right)_{Q_0} (i_g|Q_k Q_l|j_e) + \cdots$$

This approach offers a number of significant advantages:

- Not all electronic coupling elements need to be calculated
- Initial and final states are treated equivalently
- Calculation derivatives numerically simple

$$\left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} = \frac{M_{ge}(Q_0+\Delta Q_k) - M_{ge}(Q_0-\Delta Q_k)}{2\Delta Q_k}$$

Only additional information we need concerns

$$Q_k|n_1,n_2,\cdots,n_k,\cdots) = \left(\frac{\hbar}{2\omega_k}\right)^{1/2}\Big[n_k^{1/2}|n_1,\cdots(n_k-1),\cdots)$$

$$+ (n_k+1)^{1/2}|n_1,\cdots,(n_k+1),\cdots)\Big]$$

Without Duschinsky rotation and frequency changes the matrix element $(i_g|Q_k|j_e)$ will only be different from zero if

$$m_k\,(\text{grond}) = (n_k \pm 1)\,(\text{aangeslagen})$$

Spectroscopic implications for excitation from vibrationless ground state

We specify Q_0 as Q_0 (ground state) and denote with $M_{ge}^{01_p}$ excitation of mode p in state e

$$M_{ge}^{01_p} = M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} (0_g|Q_k|1_{p,e}) + \sum_k \sum_l \left(\frac{\partial^2 M_{ge}(Q)}{\partial Q_k\,\partial Q_l}\right)_{Q_0} (0_g|Q_k Q_l|1_{p,e}) + \cdots$$

in which Q_k are normal coordinates of the ground state

$$= M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e}) + \cdots$$

For 0-0 transition we find analogously

$$M_{ge}^{00} = M_{ge}(Q_0)\,(0_g|0_e) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|0_e) + \cdots$$

$$M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})$$

a) $M_{ge}(Q_0) = 0$, transition induced via asymmetric vibrations

$$M_{ge}^{01_p} = \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})$$

$$M_{ge}^{00} = 0$$

No influence geometry changes, but Duschinsky rotatation is important $(1_{k,g}|1_{p,e}) = 2R_{pk}\,(0|0)$

What about the intensity of symmetric vibrations ?

$$(0_g|\langle\psi_g(q,Q)|\mu|\psi_e(q,Q)\rangle|1_{p,e}1_{s,e}) =$$

$$\sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} (0_g|Q_k|1_{p,e}1_{s,e}) =$$

$$\sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})\,(0_g^s|1_{s,e}) =$$

$$(0_g^s|1_{s,e})\,M_{ge}^{01_p}$$

Multiplication of Franck-Condon factor with induced intensity

What about the role of higher derivatives in transitions mentioned above ?

$$\sum_{k\in a}\sum_{l\in s} \left(\frac{\partial^2 M_{ge}(Q)}{\partial Q_k \partial Q_l}\right)_{Q_0} \begin{matrix}(0_g|Q_k Q_l|1_{p,e}) \\ (0_g|Q_k Q_l|1_{p,e}1_{s,e})\end{matrix}$$

$$M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})$$

$$\sum_{k\in A}\sum_{l\in S} \left(\frac{\partial^2 M_{ge}(Q)}{\partial Q_k \partial Q_l}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} \left(\frac{\hbar}{2\omega_{l,g}}\right)^{1/2} (1_{k,g}|1_{p,e})(1_{l,g}|0_e^s)$$

$$\left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} \left(\frac{\hbar}{2\omega_{l,g}}\right)^{1/2} (1_{k,g}|1_{p,e})(1_{l,g}|1_{s,e})$$

Especially in the case of large geometry changes the second derivatives can influence significantly the ratio of intensities

N.B. By second derivatives it is also possible that intensity is induced in combination bands of asymmetric vibrations

Benzeen F.M. Garforth and C.K. Ingold, J. Chem. Soc., 417 (1948)
Octatetraeen W.J. Buma and F. Zerbetto, J. Am. Chem. Soc. 118, 9178 (1996)

B $M_{ge}(Q_0) \neq 0$, vibronic coupling via asymmetric vibrations

$$M_{ge}^{0 1_p} = M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} (0_g|Q_k|1_{p,e})$$

$$= \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})$$

$$M_{ge}^{00} = M_{ge}(Q_0)\,(0_g|0_e)$$

$$M_{ge}^{0 1_s} = M_{ge}(Q_0)\,(0_g|1_{s,e})$$

$$M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})$$

$$\psi_n^{HT}(q;Q) = \psi_n(q;Q_0) + \sum_k \sum_{m\neq n} \left[\frac{\langle m|\left(\frac{\partial u}{\partial Q_k}\right)_{Q_0}|n\rangle}{E_n - E_m}\cdot Q_k\right] \psi_m(q;Q_0)$$

(c) $M_{ge}(Q_0) \neq 0$, vibronic coupling via symmetric vibrations

$$M_{ge}^{0,p} = M_{ge}(Q_0)\,(0_g|1_{p,e}) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|1_{p,e})$$

$$M_{ge}^{00} = M_{ge}(Q_0)\,(0_g|0_e) + \sum_k \left(\frac{\partial M_{ge}(Q)}{\partial Q_k}\right)_{Q_0} \left(\frac{\hbar}{2\omega_{k,g}}\right)^{1/2} (1_{k,g}|0_e)$$

In this case we will get interference between parts that depend strongly on geometry changes and vibronically induced contributions

Calculation vibronic matrix elements

Previously we have seen that:

$$\frac{\partial \psi_n^{HT}(q;Q)}{\partial Q_k} = \sum_{e\neq n} \left[\frac{\langle e|\left(\frac{\partial u}{\partial Q_k}\right)_{Q_0}|n\rangle}{E_n - E_e}\right] \psi_e(q;Q_0)$$

From this it immediately follows that:

$$\langle \psi_m(q;Q)|\frac{\partial}{\partial Q_k}|\psi_n(q;Q)\rangle_{Q_0} = \frac{\langle \psi_m(q;Q_0)|\left(\frac{\partial u}{\partial Q_k}\right)_{Q_0}|\psi_n(q;Q_0)\rangle}{E_n(Q_0) - E_m(Q_0)}$$

For a number of applications, such as dominant vibronic coupling with a limited number of states, it is useful to calculate such matrix elements. This can be done for example with the methods that have been discussed for CI wavefunctions

Nice example of such an approach can be found in the theoretical treatment of single level emission spectra of naphthalene

F. Negri and M.Z. Zgierski, J. Chem. Phys. 104, 3486 (1996)

Non-adiabatic corrections

We consider the influence of T_N via perturbation theory starting from the Herzberg-Teller electronic wavefunctions

$$\Psi_{ni}^{HT}(q,Q) = \left[\psi_n(q;Q_0) + \sum_{m\neq n} a_{mn}(Q)\,\psi_m(q;Q_0)\right]\chi_{ni}(Q)$$

Incorporate influence $-\hbar^2\left(\frac{\partial \psi_n(q;Q)}{\partial Q_k}\right)\frac{\partial}{\partial Q_k}$ and $-\frac{\hbar^2}{2}\left(\frac{\partial^2 \psi_n(q;Q)}{\partial Q_k^2}\right)$

with perturbation theory

$$\Psi_{ni}^{NA}(q,Q) = \Psi_{ni}^{HT}(q,Q)$$

$$+\sum_m \sum_j \frac{\left(\langle \Psi_{mj}^{HT}(q,Q)\,|\,T_N\,|\,\Psi_{ni}^{HT}(q,Q)\rangle\right)}{E_{ni}-E_{mj}}\Psi_{mj}(q,Q)$$

Consider following situation:

1. Ground state $\Psi_{gi}(q,Q) = \psi_g(q;Q_0)\,\chi_{gi}(Q)$
2. Excited state $\Psi_{ej}(q,Q)$ which can only mix with state $\Psi_{nk}(q,Q)$ Mixing only occurs via coordinate Q_a

$$\Psi^{NA}_{ni}(q,Q) = \Psi^{HT}_{ni}(q,Q) + \sum_m \sum_j \frac{(\langle \Psi^{HT}_{mj}(q,Q) | T_N | \Psi^{HT}_{ni}(q,Q)\rangle)}{E_{ni}-E_{mj}} \Psi_{mj}(q,Q)$$

$$\Psi^{HT}_{ej}(q,Q) = \left[\psi_e(q;Q_0) + \frac{\langle n | \left(\frac{\partial u}{\partial Q_a}\right)_{Q_0} | e\rangle}{E_e - E_n} \cdot Q_a \cdot \psi_n(q;Q_0)\right] \chi_{ej}(Q)$$

$$= \left[\psi_e(q;Q_0) + \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot Q_a \psi_n(q;Q_0)\right] \chi_{ej}(Q)$$

$$\Psi^{HT}_{nk}(q,Q) = \left[\psi_n(q;Q_0) - \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot Q_a \psi_e(q;Q_0)\right] \chi_{nk}(Q)$$

For $\Psi^{NA}_{ej}(q,Q)$ we get now

$$\Psi^{NA}_{ej}(q,Q) = \Psi^{HT}_{ej}(q,Q) + \frac{(\langle \Psi^{HT}_{nk}(q,Q) | T_N | \Psi^{HT}_{ej}(q,Q)\rangle)}{E_{ej}-E_{nk}} \Psi^{HT}_{nk}(q,Q)$$

$$\frac{\partial \psi^{HT}_e(q;Q)}{\partial Q_a} = \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \psi_n(q;Q_0) \qquad \frac{\partial^2 \psi^{HT}_e(q;Q)}{\partial Q_a^2} = 0$$

$$(\langle \Psi^{HT}_{nk}(q,Q) | T_N | \Psi^{HT}_{ej}(q,Q)\rangle) =$$

$$-\hbar^2 \left(\left\langle \left[\psi_n(q;Q_0) - \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot Q_a \psi_e(q;Q_0)\right] \chi_{nk}(Q) \right| \right.$$

$$\left.\left. \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot \psi_n(q;Q_0) \cdot \frac{\partial \chi_{ej}(Q)}{\partial Q_a} \right\rangle\right)$$

$$= -\hbar^2 \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot \left(\chi_{nk}(Q) \left| \frac{\partial}{\partial Q_a} \right| \chi_{ej}(Q)\right)$$

$$\Psi_{ej}^{NA}(q,Q) = \Psi_{ej}^{HT}(q,Q) + \frac{(\langle \Psi_{nk}^{HT}(q,Q) | T_N | \Psi_{ej}^{HT}(q,Q)\rangle)}{E_{ej} - E_{nk}} \Psi_{nk}^{HT}(q,Q)$$

$$\left[\psi_e(q;Q_0) + \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot Q_a \psi_n(q;Q_0)\right] \chi_{ej}(Q)$$

$$-\hbar^2 \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot \left(\chi_{nk}(Q) \left| \frac{\partial}{\partial Q_a} \right| \chi_{ej}(Q)\right)$$

$$\Psi_{ej}^{NA}(q,Q) = \left[\psi_e(q;Q_0) + \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot Q_a \cdot \psi_n(q;Q_0)\right] \chi_{ej}(Q)$$

$$-\hbar^2 \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot \frac{1}{E_{ej} - E_{nk}} \cdot \left(\chi_{nk}(Q) \left| \frac{\partial}{\partial Q_a} \right| \chi_{ej}(Q)\right)$$

$$\cdot \left[\psi_n(q;Q_0) - \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot Q_a \cdot \psi_e(q;Q_0)\right] \chi_{nk}(Q)$$

We now consider the situation that $\langle \psi_g(q;Q_0) | \mu | \psi_e(q;Q_0)\rangle$ is equal to zero and that the transition probability is induced by mixing with state nk

Based on HT wavefunctions we find:

$$(\langle \Psi_{gi}^{HT}(q,Q) | \mu | \Psi_{ej}^{HT}(q,Q)\rangle)$$

$$= \langle \psi_g(q;Q_0) | \mu | \psi_n(q;Q_0)\rangle \cdot \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot (\chi_{gi}(Q) | Q_a | \chi_{ej}(Q))$$

Based on NA wavefunctions we find:

$$(\langle \Psi_{gi}^{NA}(q,Q) | \mu | \Psi_{ej}^{NA}(q,Q)\rangle)$$

$$= \langle \psi_g(q;Q_0) | \mu | \psi_n(q;Q_0)\rangle \cdot \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot (\chi_{gi}(Q) | Q_a | \chi_{ej}(Q))$$

$$-\hbar^2 \langle \psi_g(q;Q_0) | \mu | \psi_n(q;Q_0)\rangle \cdot \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot \frac{1}{E_{ej} - E_{nk}}$$

$$\cdot \left(\chi_{nk}(Q) \left| \frac{\partial}{\partial Q_a} \right| \chi_{ej}(Q)\right) (\chi_{gi}(Q) | \chi_{nk}(Q))$$

$$\langle \psi_g(q;Q_0)|\mu|\psi_n(q;Q_0)\rangle \cdot \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot (\chi_{gi}(Q)|Q_a|\chi_{ej}(Q))$$

$$-\hbar^2 \langle \psi_g(q;Q_0)|\mu|\psi_n(q;Q_0)\rangle \cdot \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot \frac{1}{E_{ej}-E_{nk}}$$

$$\cdot (\chi_{nk}(Q)|\tfrac{\partial}{\partial Q_a}|\chi_{ej}(Q))(\chi_{gi}(Q)|\chi_{nk}(Q))$$

$$= \langle \psi_g(q;Q_0)|\mu|\psi_n(q;Q_0)\rangle \cdot \frac{V_{ne}(Q_0)}{\Delta E_{en}(Q_0)} \cdot$$

$$\left[(\chi_{gi}(Q)|Q_a|\chi_{ej}(Q)) - \hbar^2 \frac{(\chi_{nk}(Q)|\frac{\partial}{\partial Q_a}|\chi_{ej}(Q))(\chi_{gi}|\chi_{nk})}{E_{ej}-E_{nk}} \right]$$

Assume no Duschinsky mixing, no frequency changes and transition from vibrationless ground state to excited state with $n_a = 1$

$$\psi_g\, 0_a \rightarrow \psi_e\, 1_a \leftrightarrow \psi_n\, 0_a \text{ of } \psi_n\, 2_a$$

$$(0_a|Q_a|1_a) = \left(\frac{\hbar}{2\omega}\right)^{1/2} \qquad (0_a|\tfrac{\partial}{\partial Q_a}|1_a) = \left(\frac{\omega}{2\hbar}\right)^{1/2}$$

$$M^{NA} = M^{HT}\left[1 - \hbar^2 \frac{(\chi_{nk}|\frac{\partial}{\partial Q_a}|\chi_{ej})}{(\chi_{gi}|Q_a|\chi_{ej})} \cdot \frac{(\chi_{gi}|\chi_{nk})}{E_{ej}-E_{nk}}\right]$$

$$= M^{HT}\left[1 - \frac{\hbar\omega}{E_{ej}-E_{nk}}\right]$$

Contribution non-adiabatic term small, unless energy difference between vibronic state ej and nk becomes of the order of vibrational frequency inducing mode