Marcus Theory of Electron Transfer

- From a molecular perspective, Marcus theory is typically applied to *outer sphere* ET between an electron donor (D) and an electron acceptor (A).
- For convenience in this discussion we will assume D and A are neutral molecules so that electrostatic forces may be ignored.
- It is also worth considering that either D or A may be in a photoexcited state *(photoinduced electron transfer aka PET)*.
- Other than a change in the starting stage energies, the principles of Marcus' model apply equally well to both ground and excited state electron transfer.

For second-order reactions between a homogenous mixture of D and A the reaction can be broken down into three steps:

1.Precursor complex

D and A diffuse together with a rate constant k_a to form an outer sphere precursor complex D|A. Dissociation of the precursor complex without ET is described by k_d .

$$\mathrm{D} + \mathrm{A} \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} \mathrm{D|A}$$

2.Successor complex

The precursor complex D|A undergoes reorganization toward a transition state in which ET takes place to form a successor complex $D^+|A^-$.

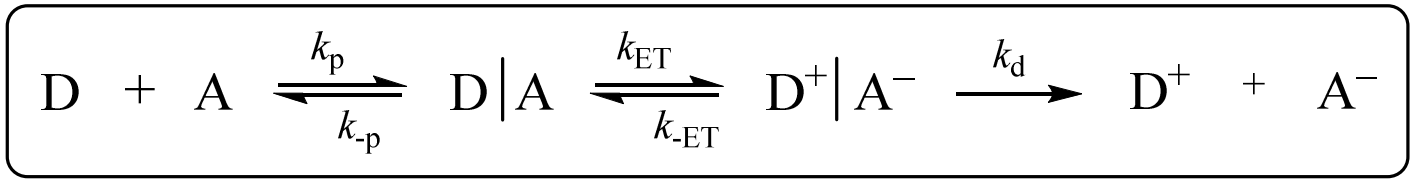
$$\mathrm{D|A} \underset{k_{-ET}}{\overset{k_{ET}}{\rightleftharpoons}} \mathrm{D^+|A^-}$$

The nuclear-configuration of the precursor and successor complexes at the transition state must be identical for successor complex to form.

3.Dissociation

Finally, the successor complex dissociates forming the independent D^+ cation and A^- anion.

$$\mathrm{D^+|A^-} \xrightarrow{k_d} \mathrm{D^+} + \mathrm{A^-}$$



- Using a steady-state approximation k_{obs} can be estimated as

$$k_{obs} = \frac{k_p}{1 + \frac{k_{-p}}{k_{ET}} + \frac{k_{-p}k_{-ET}}{k_d k_{ET}}} \qquad \text{eqn. 1}$$

which can be rearranged to

$$\frac{1}{k_{obs}} = \frac{1}{k_p} + \frac{k_{-p}}{k_p k_{ET}}\left[1 + \frac{k_{-ET}}{k_d}\right] \qquad \text{eqn. 2}$$

- If $k_d >> k_{-ET}$ eqn. 2 reduces to

$$\frac{1}{k_{obs}} = \frac{1}{k_p} + \frac{k_{-p}}{k_p k_{ET}} \qquad \text{eqn. 3}$$

a) If $k_{-p} >> k_{ET}$ eqn. 3 reduces to

$$k_{obs} \cong \frac{k_p k_{ET}}{k_{-p}} \qquad \text{eqn. 3a}$$

b) Conversely, if $k_{-p} << k_{ET}$

$$k_{obs} \cong k_p \qquad \text{eqn. 3b}$$

and the second order ET rate constant will contain no information about k_{ET}

- If D and A are covalently linked, or even fixed within a close distance (e.g. H-bonding, protein matrix) only the ET step need be considered.

$$\mathrm{D}\,|\,\mathrm{A} \underset{k_{\text{-ET}}}{\overset{k_{\text{ET}}}{\rightleftharpoons}} \mathrm{D}^{+}\,|\,\mathrm{A}^{-}$$

  k_{ET} and $k_{\text{-ET}}$ can then, in principle at least, be directly observed.

- Knowledge of the various state energies is critical for the interpretation of kinetic data for electron transfer with Marcus theory.

- This is particularly true for PET. For example, the first singlet excited state S_1 energy may be estimated by the point of overlap for normalized absorption ($S_0 \rightarrow S_1$) and emission ($S_0 \leftarrow S_1$) bands.

- With the $S_0 \rightarrow T_1$ transition typically absent, the T_1 energy is usually estimated by the blue edge of the low-temperature phosphorescence spectrum (assuming a negligible Stokes shift between $S_0 \rightarrow T_1$ and $S_0 \leftarrow T_1$).

- The energies of D^+ and A^- can be easily obtained by electrochemical methods, e.g. linear and cyclic voltammetry, differential pulse and square wave voltammetries.

- The Gibbs energy difference under standard conditions between the "D + A" and "$D^+ + A^-$" states can be approximated as

$$\Delta G^o = e\left(E^o_{D+/D} + E^o_{A/A-}\right) + \omega^p - \omega^r$$

e = electronic charge

E^o = standard reduction potential

ω = work, i.e. energy used in bringing reactants (-tive) and products (-tive) together.

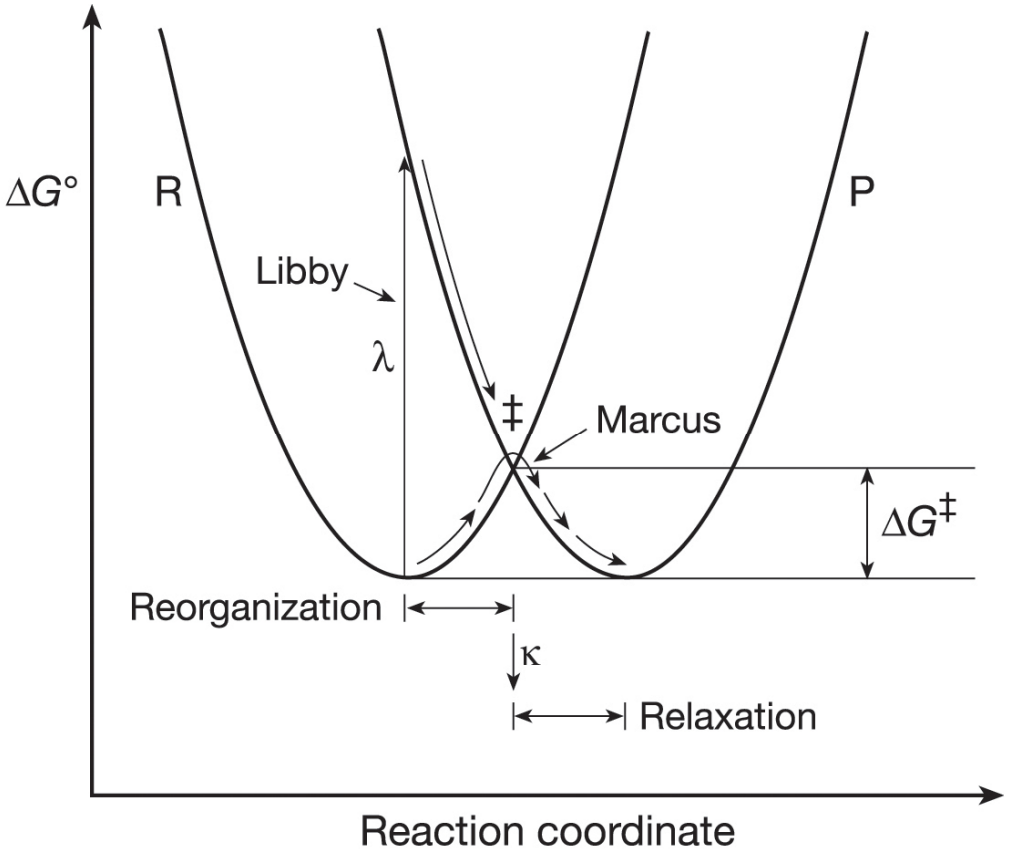
- From here on we will assume only covalently linked D-A supramolecular species where

$$\Delta G^o = e\left(E^o_{D+/D} + E^o_{A/A-}\right)$$

- The potential energies of ground, excited, transition and product states are all dependent upon the many nuclear coordinates involved inclusive of the solvation cage and its associated energies.
- In transition state theory a *reaction coordinate* is introduced so that the potential energy surface can be reduced to a one-dimensional profile.

- Curve R represents the reactant state $D|A$ while curve P represents the product state $D^+|A^-$
- For ET to occur the reactant state must distort from its equilibrium energy state to reach a transition state geometry ‡ which also exists as a distorted form of the product state.
- Electron transfer occurs at the point along the reaction coordinate as the transition state has a 50% probability of producing the $D^+|A^-$ product state (at least in this ideal symmetrical case with $\Delta G^o = 0$)

[note: Marcus theory assumes R and P curves are of equal shape. This model neglects external solvation effects, when included give a more accurate non-parabolic picture]



$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^{o})^2}{4\lambda}$$

- According to classical transition state theory

$$k_{\mathrm{ET}} = \kappa_{\mathrm{el}}\, \upsilon_{\mathrm{n}} \exp\left(\frac{-\Delta G^{\ddagger}}{k_{\mathrm{B}}\mathrm{T}}\right)$$

κ_{el} = electron transmission coefficient (~1)

ν_n = vibrational frequency of the transition state $(D \mid A)^{\ddagger}$ (~10^{13} s^{-1})

k_B = Boltzmann constant

T = temperature (K)

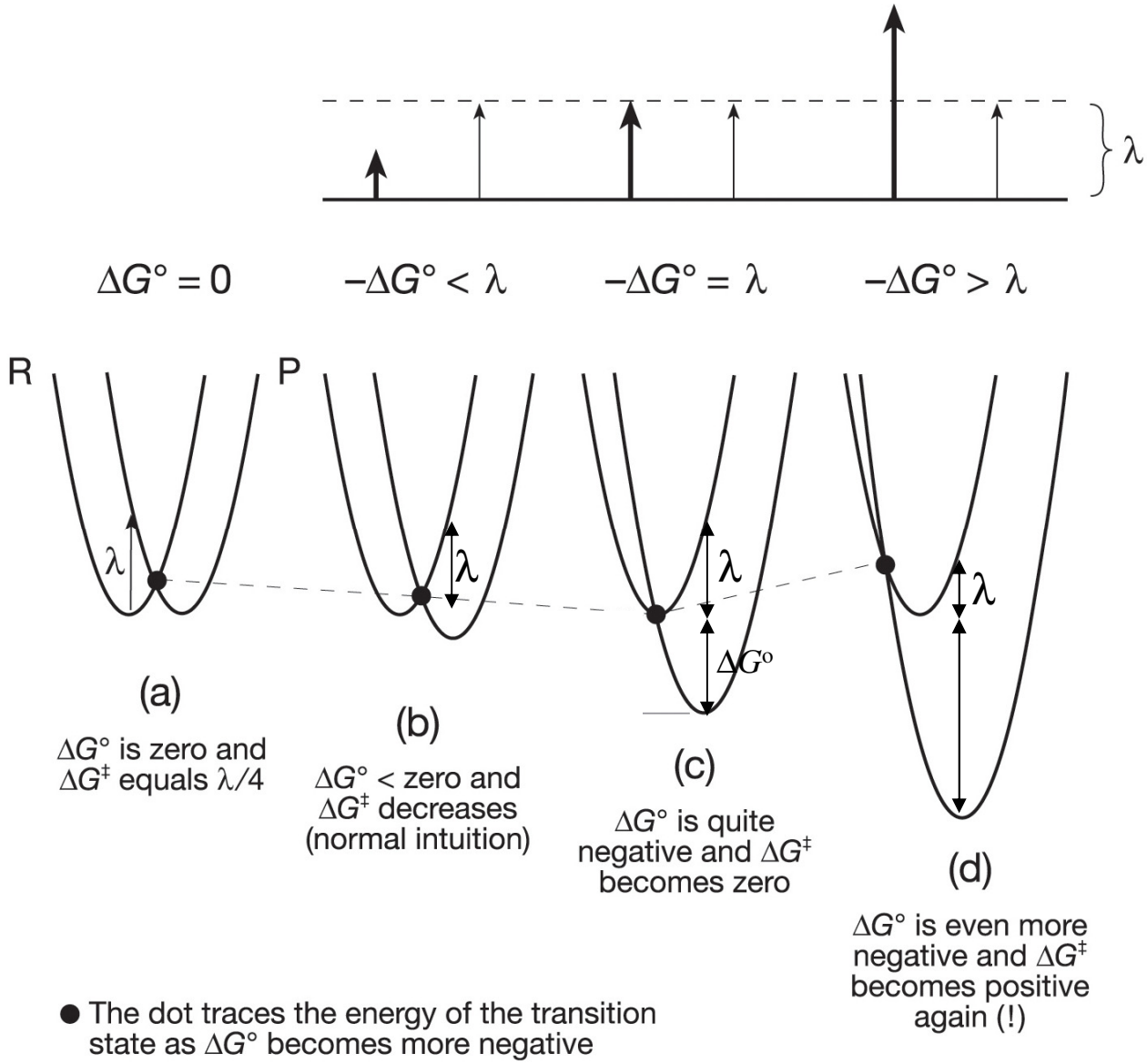
$\Delta G^{\ddagger}$ = Gibbs free energy of activation

- Thus, following the mathematical description of parabolic curves where

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^{\mathrm{o}})^2}{4\lambda}$$

the classical Marcus equation can be written as:

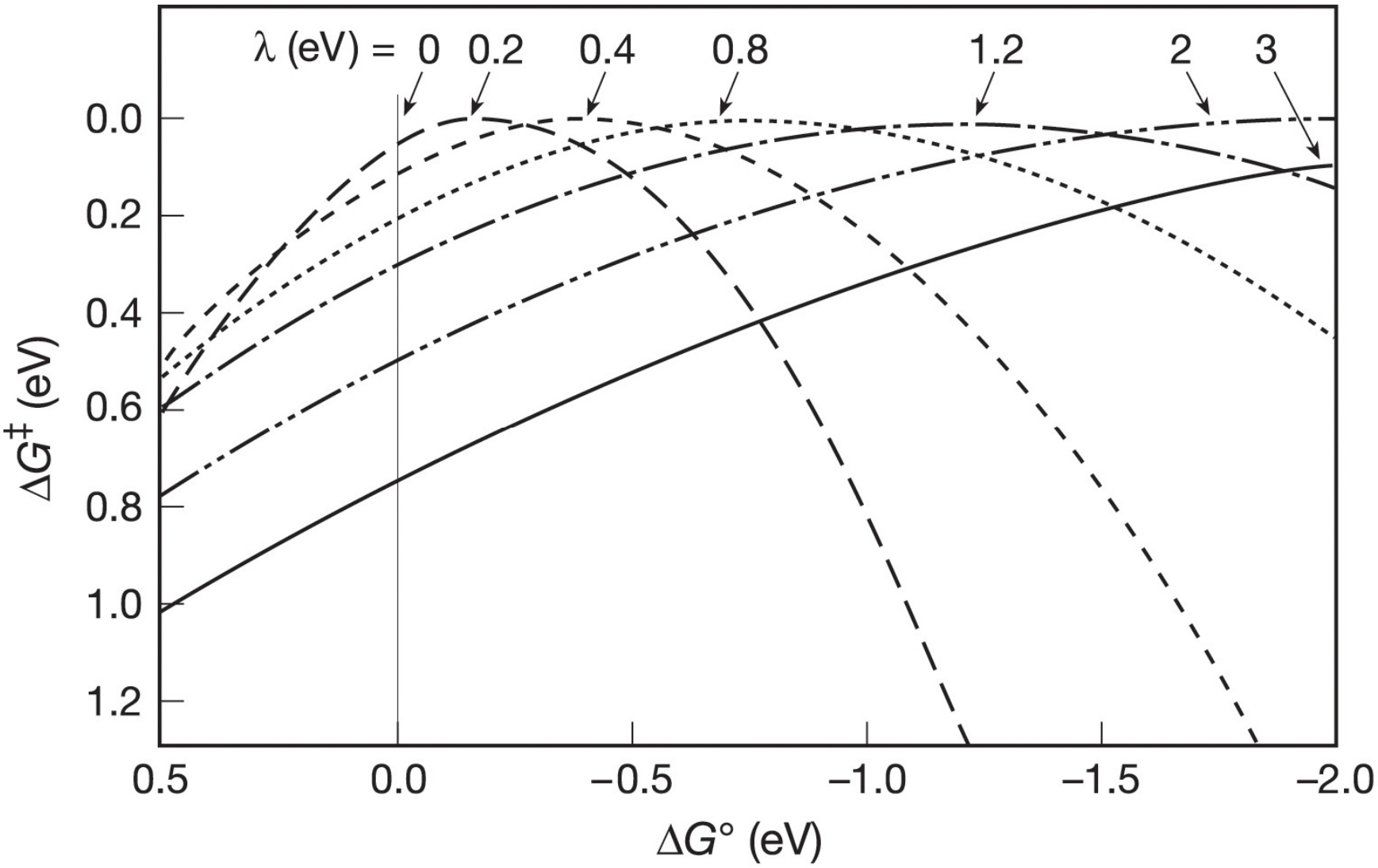
$$k_{\mathrm{ET}} = \kappa_{\mathrm{el}}\, \upsilon_{\mathrm{n}} \exp\left[\frac{-(\lambda + \Delta G^{\mathrm{o}})^2}{4\lambda\, k_{\mathrm{B}}\, \mathrm{T}}\right]$$



The ***reorganization energy (λ)*** is defined as the change in Gibbs energy if the reactant state ($D|A$) were to distort to the equilibrium conformation of the product state ($D^+|A^-$) without transfer of an electron.

$$k_{ET} = \kappa_{el}\, \upsilon_n \exp\left[\frac{-(\lambda + \Delta G^o)^2}{4\lambda\, k_B\, T}\right]$$

- The Marcus equation implies that for moderately exergonic reactions $\Delta G^{\ddagger}$ will decrease while k_{ET} will increase as ΔG^o becomes more negative.
- When $\Delta G^{\ddagger} = 0$ and $-\Delta G^o = \lambda$, k_{ET} reaches its maximum value of $\kappa_{el}\, \nu_n$
- However, as $-\Delta G^o$ becomes more negative in a highly exergonic reaction, the intersection point of R and P surfaces moves to the left causing $\Delta G^{\ddagger}$ to increase again realizing that k_{ET} will actually begin to decrease as the reaction becomes highly exergonic.
- This “contradictory” observation is know as the **Marcus inverted region**.


λ (eV) = 0 0.2 0.4 0.8 1.2 2 3
0.0
0.2
0.4
0.6
0.8
1.0
1.2
ΔG‡ (eV)
0.5
0.0
−0.5
−1.0
−1.5
−2.0
ΔG° (eV)

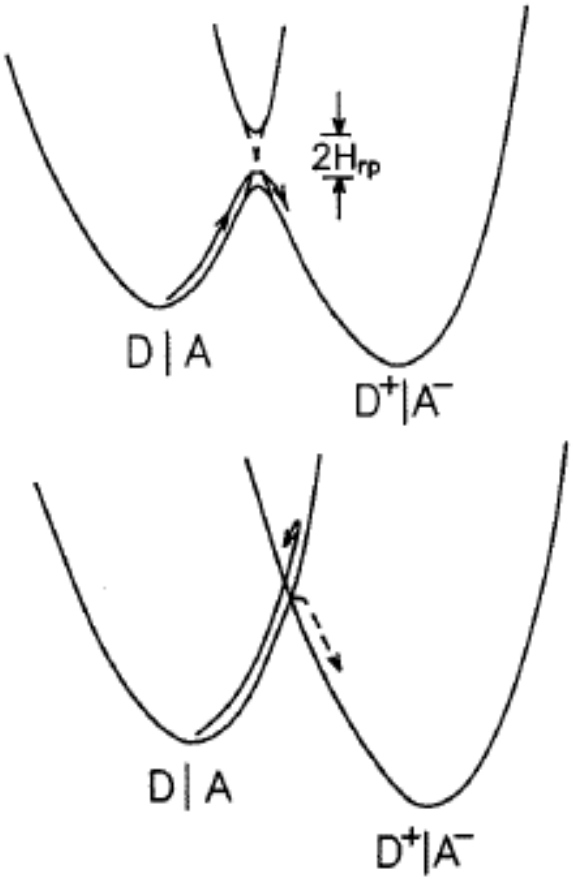
Adiabatic vs. non-adiabatic electron transfer

- Two types of electron transfer reactions can be distinguished according to the magnitude of the *electronic coupling factor* H_{rp} between the reactant and product states.

$$H_{rp} = \langle \psi_r^o | \mathcal{H}_{el} | \psi_p^o \rangle$$

ψ^o = electronic wavefunction for reactant and product states

$\mathcal{H}_{el}$ = the Born-Oppenheimer electronic Hamiltonian for the system.

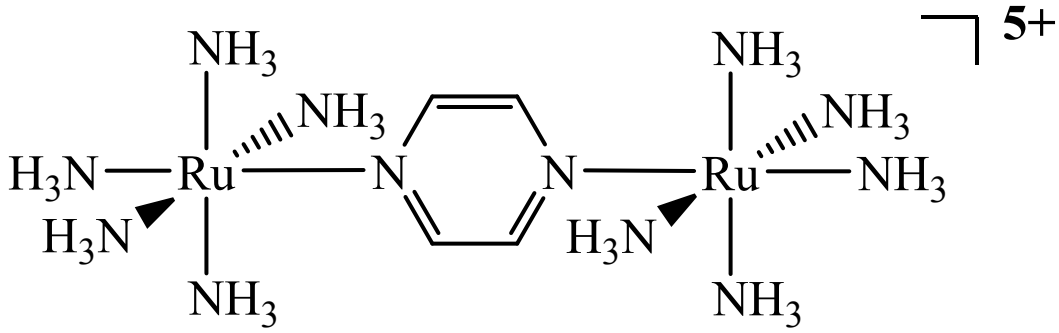


- **Large H_{rp} = adiabatic (κ_{el} ~1)**
- **Small H_{rp} = non-adiabatic (κ_{el} << 1)**

- For transition metal redox reactions the point of demarcation between adiabatic and non-adiabatic is where $H_{rp} \sim 0.025$ eV.
- H_{rp} decreases exponentially with distance between D and A

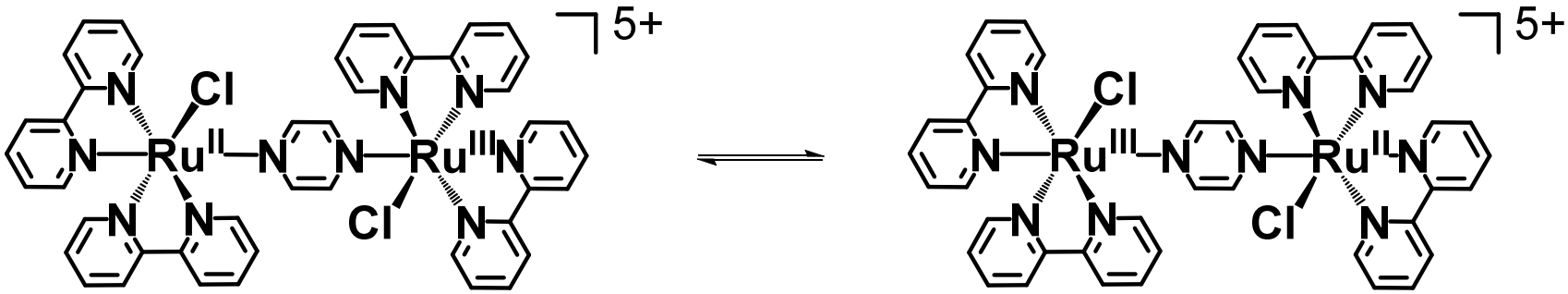
Mixed valence transition metal complexes

- Mixed-valence compounds contain an element which, at least in a formal sense, exists in more than one oxidation state.
- This is a common phenomenon, e.g. Prussian blue which has a cyanide-bridged Fe(II)-Fe(III) structure, was one of the first chemical materials to be described.
- In the 1970s the first designed mixed-valence complexes were prepared, the μ-pyrazine-bridged dimer $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ by Carol Creutz and Henry Taube.



- One of the reasons for interest in mixed-valence molecules was the possibility that they could be used to measure rate constants and activation barriers for intramolecular electron transfer

- These reactions have proven difficult to study by direct measurement, but the analogous light-driven process can often be observed as a broad, solvent-dependent absorption band.
- For symmetrical mixed-valence complexes these bands typically appear in low-energy visible or near-infrared spectra.
- They are typically called intervalence transfer (IT), metal-metal charge transfer (MMCT), or intervalence charge transfer (IVCT) bands.
- Hush provided an analysis of IT band shapes based on parameters that also define the electron-transfer barrier.
- The barrier arises from nuclear motions whose equilibrium displacements are affected by the difference in electron content between oxidation states.
- This includes both intramolecular structural changes and the solvent where there are changes in the orientations of local solvent dipoles.



- In the above example, the geometrical distance between the metal centers (6.9 Å) is sufficiently large that direct overlap of the electronic wave functions is negligible.
- Electronic coupling occurs indirectly by mixing of metal-based donor and acceptor orbitals of appropriate symmetry in the bridge.
- The electronic coupling matrix element arising from donor-acceptor coupling is often called H_{ab} (as reactant is indistinguishable from the product state)
- As H_{ab} increases, the discrete oxidation-state character of the local sites decreases and with it structural differences and dipole orientational changes in the solvent.
- It also mixes the donor and acceptor orbitals along the ligand bridge or organic spacer, which has the effect of decreasing the electron transfer distance.

- A linear combination of the initial, zero-order, diabatic (noninteracting) wave functions for the electron transfer reactants [Ψ_a for Ru(III)-Ru(II)] and products [Ψ_b for Ru(II)-Ru(III)], including the interaction between them, gives rise to two new adiabatic states of energies E_1 and E_2 .
- The associated wave functions, Ψ_1 and Ψ_2, are linear combinations of Ψ_a and Ψ_b.
- Energies of the unperturbed initial and final diabatic states are described by

$$H_{aa} = \langle \psi_a | \mathcal{H}_{el} | \psi_a \rangle \qquad\qquad H_{bb} = \langle \psi_b | \mathcal{H}_{el} | \psi_b \rangle$$

- Mixing between states is described by the electronic coupling matrix element

$$H_{ab} = \langle \psi_a | \mathcal{H}_{el} | \psi_b \rangle$$

$$E_1 = \frac{(H_{aa} + H_{bb})}{2} - \frac{\left[(H_{aa} - H_{bb})^2 + 4H_{ab}^2\right]^{1/2}}{2}$$

$$E_1 = \frac{(H_{aa} + H_{bb})}{2} + \frac{\left[(H_{aa} - H_{bb})^2 + 4H_{ab}^2\right]^{1/2}}{2}$$

- These expressions assume a symmetrical mixed-valence molecule with zero driving force for electron transfer.

$$\Delta G^o = 0 \; (H^o_{aa} = H^o_{bb})$$

- The coordinate x, is the displacement from the energy minimum at x = 0.

- The displacement difference between the minima before and after electron transfer is a. The corresponding energies at the minima are H^o_{aa} and H^o_{bb}.

- Equal force constants (f) are assumed for the electron transfer reactants and products. The following equations describe an average of the coupled vibrational and solvent modes assumed to be harmonic.

- When a coupled nuclear motion is included as an harmonic oscillator, H_{aa} and H_{bb} vary with the coordinate for this motion

$$H_{\mathrm{aa}} = H^o_{aa} + fx^2/2$$

$$H_{\mathrm{bb}} = H^o_{bb} + f(x-a)^2/2$$

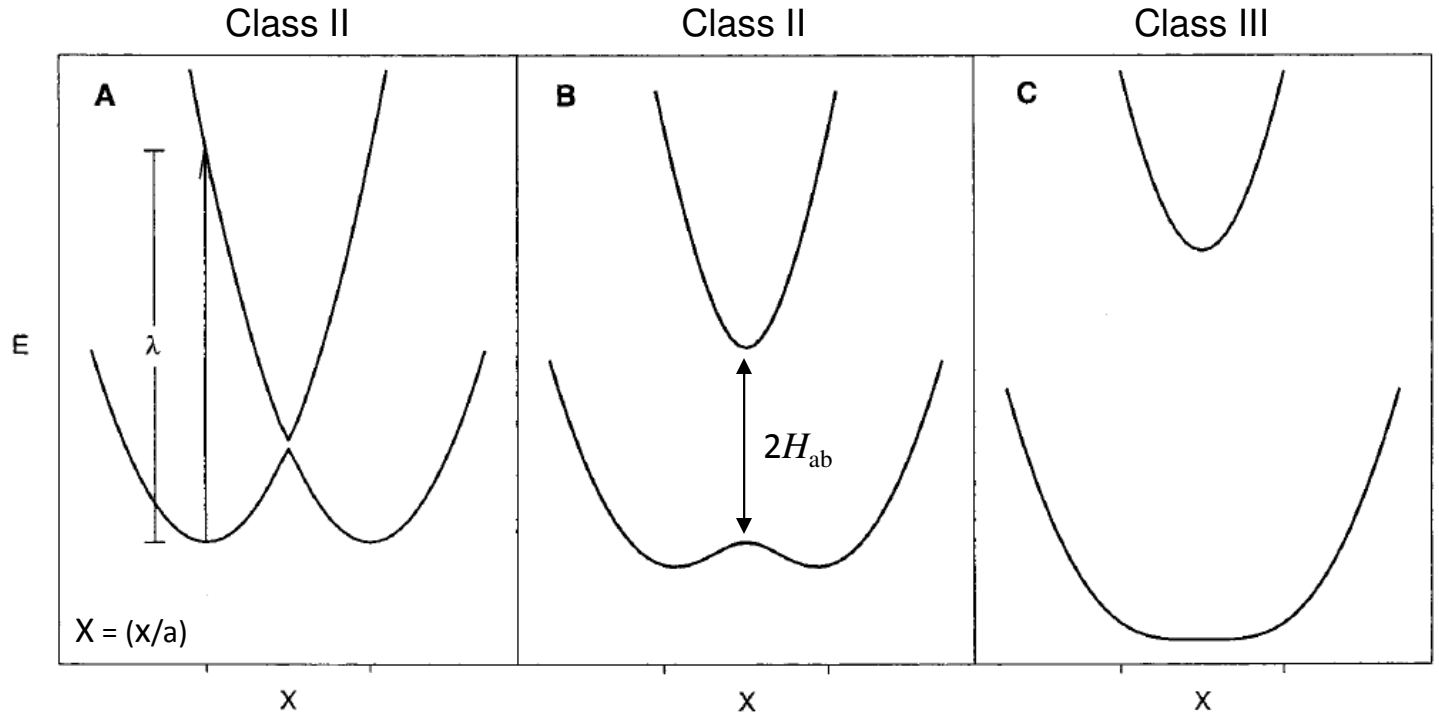
- With the dependence of H_{aa} and H_{bb} on x included, the potential energy curves E_1 and E_2 are generated.

$$E_1 = \frac{\lambda(2X^2 - 2X + 1)}{2} - \frac{\{[\lambda(2X-1)]^2 + 4H_{ab}^2\}^{1/2}}{2}$$

$$E_2 = \frac{\lambda(2X^2 - 2X + 1)}{2} + \frac{\{[\lambda(2X-1)]^2 + 4H_{ab}^2\}^{1/2}}{2}$$

- E_1 and E_2 describe how the energies of the ground and excited state vary with the reduced nuclear coordinate $X = (x/a)$ where $\lambda = f a^2/2$.

- Depdending upon the magnitude of H_{ab} supramolecular systems are typically classified according to the Robin and Day scheme, i.e. Class I, II or III systems.



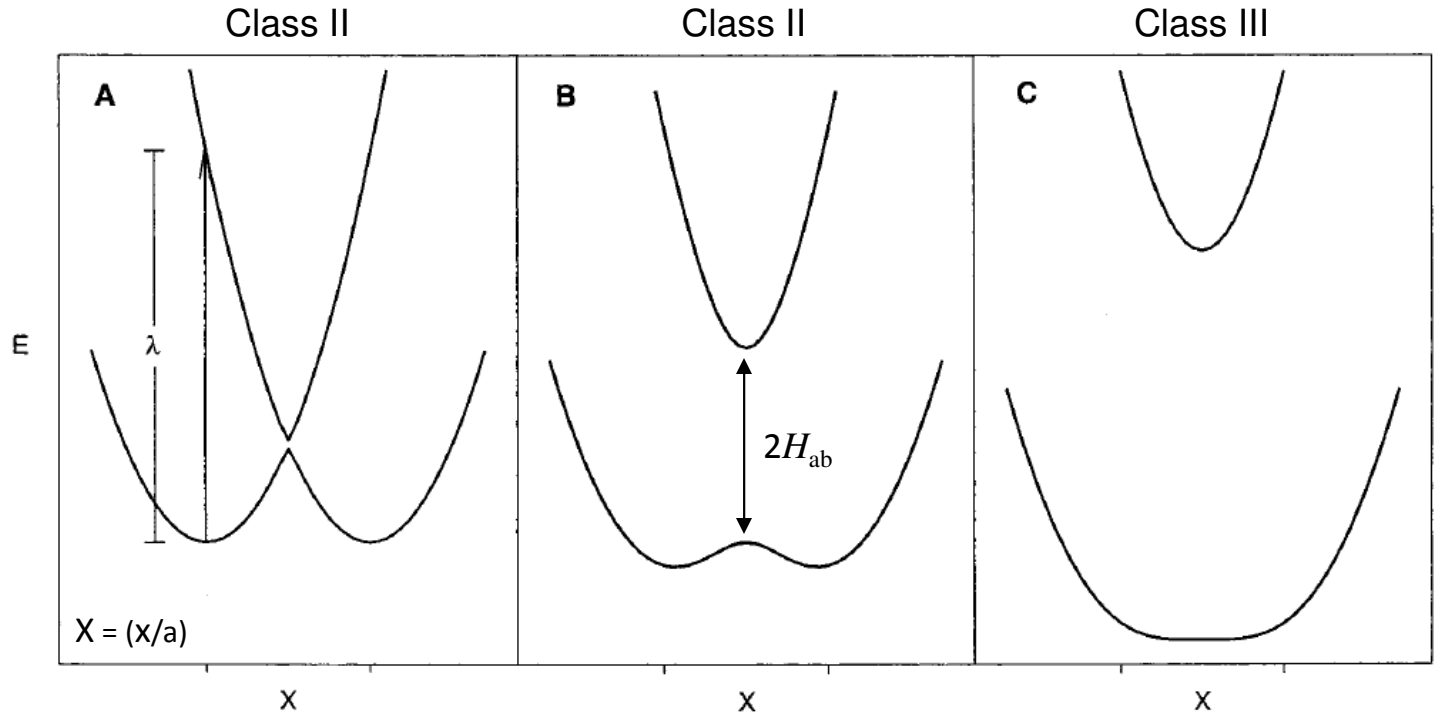
Energy-coordinate diagrams for E_1 and E_2 calculated using the following eqns.

$$E_1 = \frac{\lambda(2X^2 - 2X + 1)}{2} - \frac{\{[\lambda(2X-1)]^2 + 4H_{ab}^2\}^{1/2}}{2}$$

$$E_2 = \frac{\lambda(2X^2 - 2X + 1)}{2} + \frac{\{[\lambda(2X-1)]^2 + 4H_{ab}^2\}^{1/2}}{2}$$

Where λ = 8000 cm^{-1} (all cases) and (A) H_{ab} = 100 cm^{-1} (B) H_{ab} = 2000 cm^{-1} (C) H_{ab} = 4000 cm-1.

The coordinate axis is the reduced coordinate $X = (x/a)$



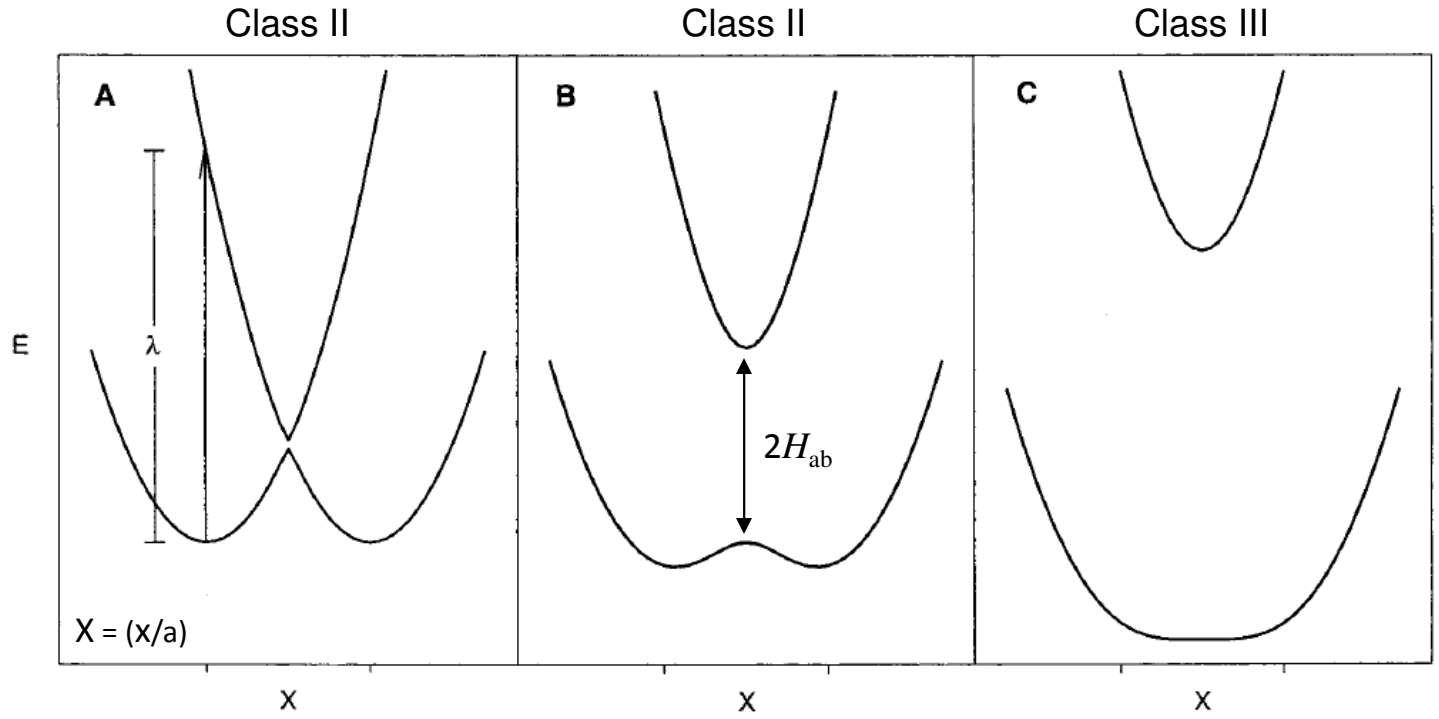
A - When H_{ab} = 0 both minima in the energy coordinate curve occur at $X_{min} = 0$ and $X_{min} = 0$.

B and **C** - With electronic coupling, the minima occur at $E_{min} = \frac{-H_{ab}^2}{\lambda}$

where $X_{min} = \left\{1 \pm \left(1 - \left(4H_{ab}^2/\lambda^2\right)\right)\right\}^{1/2}/2$

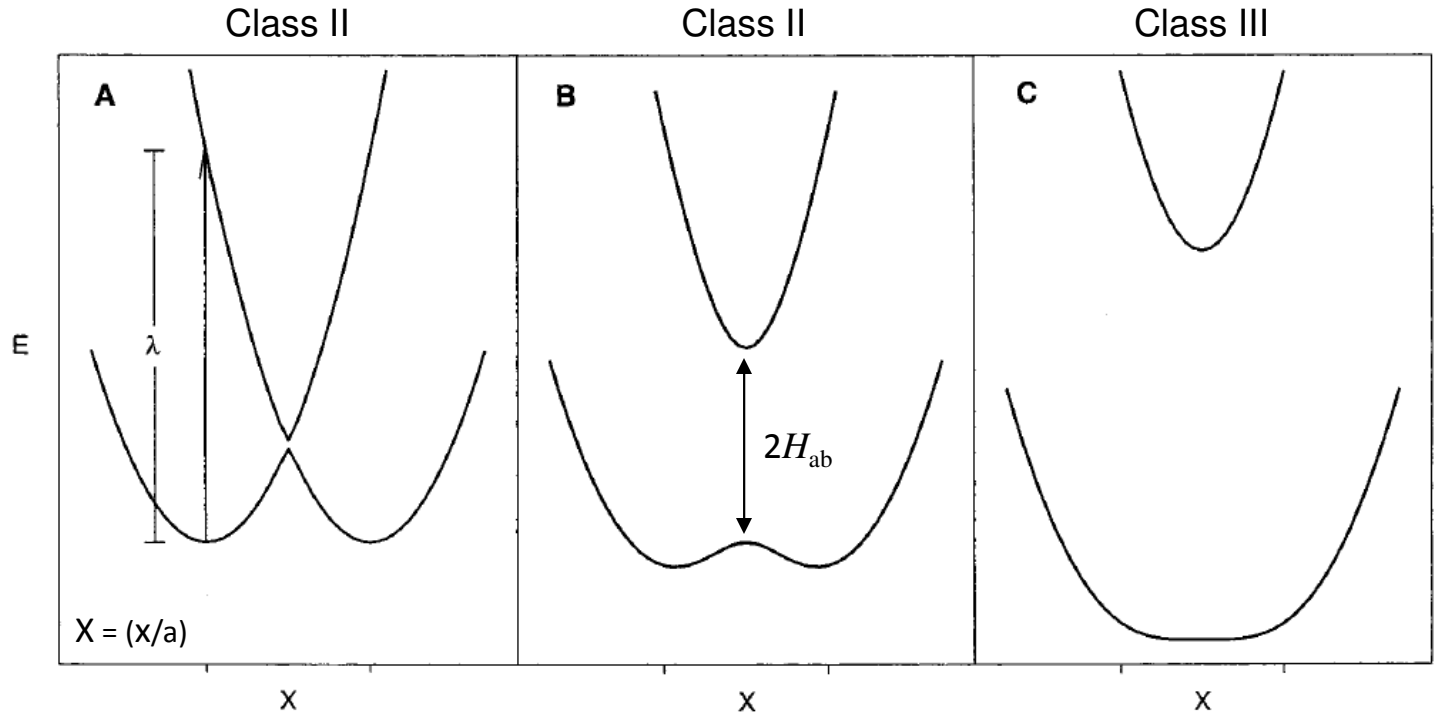
and the vertical difference between minima in **A** and **B** is

$$E_2 - E_1 = \left\{[\lambda(2X - 1)]^2 + 4H_{ab}^{1/2}\right\}^{1/2}$$



- The intervalence transfer absorption maximum corresponds to the vertical transition at X_{min} with E_{IT} = λ if H_{ab} = 0.

- In the classical limit with H_{ab} << λ there is a Gaussian distribution of energies in the ground-state centered at X = 0 which varies with x as exp $-(f\,x^2/2k_BT)$ resulting in a nearly Gaussian shaped absorption band with a maximum at X = 0 and E_{IT} = λ = $f\,a^2/2$



- Expressions for the absorption band maximum E_{IT} and bandwidth $\Delta\bar{\nu}_{IT}$ are

$$E_{IT} = \lambda \qquad (\Delta\bar{\upsilon}_{IT})^2 = 16k_B T\lambda \ln 2$$

- At the top of the activation energy barrier $x = a/2$ $(X = ½)$ $E_{IT} = \lambda/4 - |H_{ab}|$

- The energy difference from the minimum, $E_{min} = -(H_{ab}^2/\lambda)$, then gives the classical energy of activation term

$$E_a = (\lambda/4) - |H_{ab}| + (H_{ab}^2/\lambda)$$

- Expressions for the absorption band maximum E_{IT} and bandwidth $\Delta\bar{\nu}_{IT}$ are

$$E_{IT} = \lambda \text{ if } H_{ab} = 0 \qquad\qquad (\Delta\bar{\nu}_{IT})^2 = 16 k_B T \lambda \ln 2$$

- At the top of the activation energy barrier $x = a/2$ $(X = ½)$ and $E_{IT} = \lambda/4 - |H_{ab}|$

- The energy difference from the minimum, $E_{min} = -(H_{ab}^2/\lambda)$, then gives the classical energy of activation term

$$E_a = (\lambda/4) - |H_{ab}| + (H_{ab}^2/\lambda)$$

- For a Gaussian-shaped IT absorption band, H_{ab} can be calculated from characteristic band shape parameters knowing E_{IT} and λ

$$H_{ab}\,(\text{cm}^{-1}) = [(4.2 \times 10^{-4})\, \varepsilon\, \Delta\bar{\nu}_{IT}\, E_{IT}]^{1/2} / d$$

where ε is the molar extinction coefficient at E_{IT} and d is the e-transfer distance.

- H_{ab} is related to the absorption band regardless of shape by the relationship

$$H_{ab}^2 = [(4.2 \times 10^{-4})\, E_{IT} \int \varepsilon(\bar{\nu})\, d\bar{\nu}\,] / d^2$$

$$H_{ab}\,(\mathrm{cm}^{-1}) = [(4.2 \times 10^{-4})\,\varepsilon\,\Delta\bar{\upsilon}_{IT}\,E_{IT}]^{1/2} / d$$

- The electron transfer distance can be considerably different from the *center-to-center* distance if H_{ab} with the bridging ligand orbitals is significant.
- As such electron delocalization often results in a lower-limit for H_{ab} when the center-to-center distance is used.
- An added complication for transition metal systems is the presence of multiple IT bands. Assuming a single IT and results in an upper-limit estimate of H_{ab}. If resolved enough, the lowest energy IT band may be used to inform more accurately on H_{ab} .
- In case **B** , with H_{ab} being quanitatively significant relative to λ, and as E_{IT} approaches $k_B T$ (~ 500 cm^{-1}), the fraction of molecules at the top of the activation energy barrier $x = a/2\ (X = ½)$ $E_{IT} = \lambda/4 - |H_{ab}|$ approaches 10 %.
- Further evolution past the activation energy barrier at $x = a/2\ (X = ½)$ results in electron transfer and the IT band intensity should drop to zero, leading to a sharp cut off on the low-energy side of the IT absorption band.
- Spectral analysis here allows direct insight to the top of the electron transfer barrier.

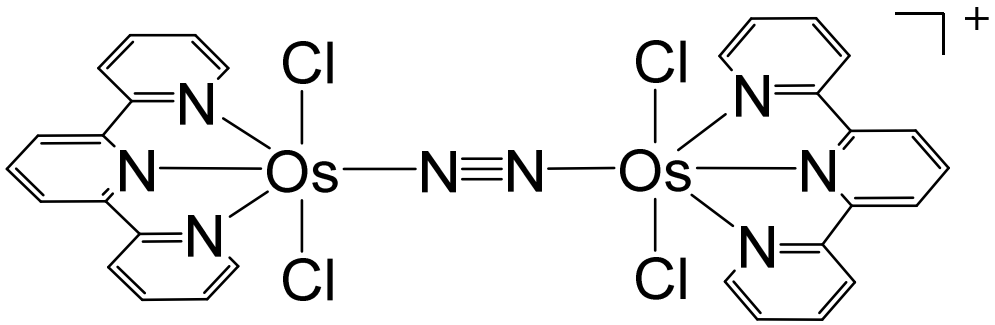
- The IT transition results in intramolecular electron transfer, e.g.,

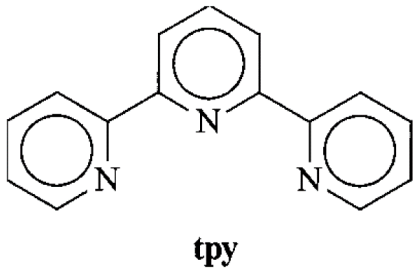
$$Ru_a(II)\text{-}Ru_b(III) \rightarrow \{Ru_a(III)\text{-}Ru_b(II)\}$$

- The electron-transfer product, $\{Ru_a(III)\text{-}Ru_b(II)\}$, formed in excited levels of the solvent and vibrational modes coupled to the transition.
- Subsequent relaxation occurs to the intersection region at X = 1/2, where further relaxation or intramolecular electron transfer give a distribution of $Ru_a(II)\text{-}Ru_b(III)$ and $Ru_a(III)\text{-}Ru_b(II)$.
- In Class II there are localized valences (oxidation states) and measurable electronic coupling ($H_{ab} > 0$).
- Class I is the limiting case with $H_{ab} = 0$.
- Class III occurs when $2H_{ab}^2/\lambda \geq 1$ and there is no longer a barrier to electron transfer and the absorption band arises from a transition between delocalized electronic levels ($\Psi_a \pm \Psi_b$). Solvent coupling and λ_o is far less than for intervalence transfer since there is no net charge transfer in the transition.

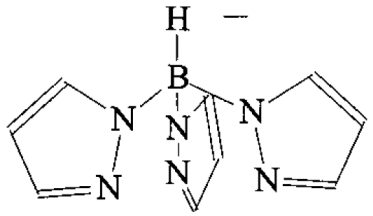
Ligand bridged Osmium complexes

- The mixed-valence N_2 bridged osmium compounds below show strong behavior characteristic of Class II complexes.

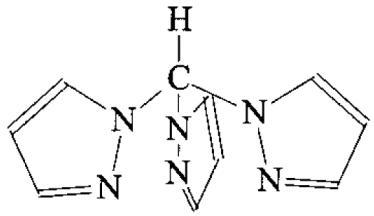




tpy

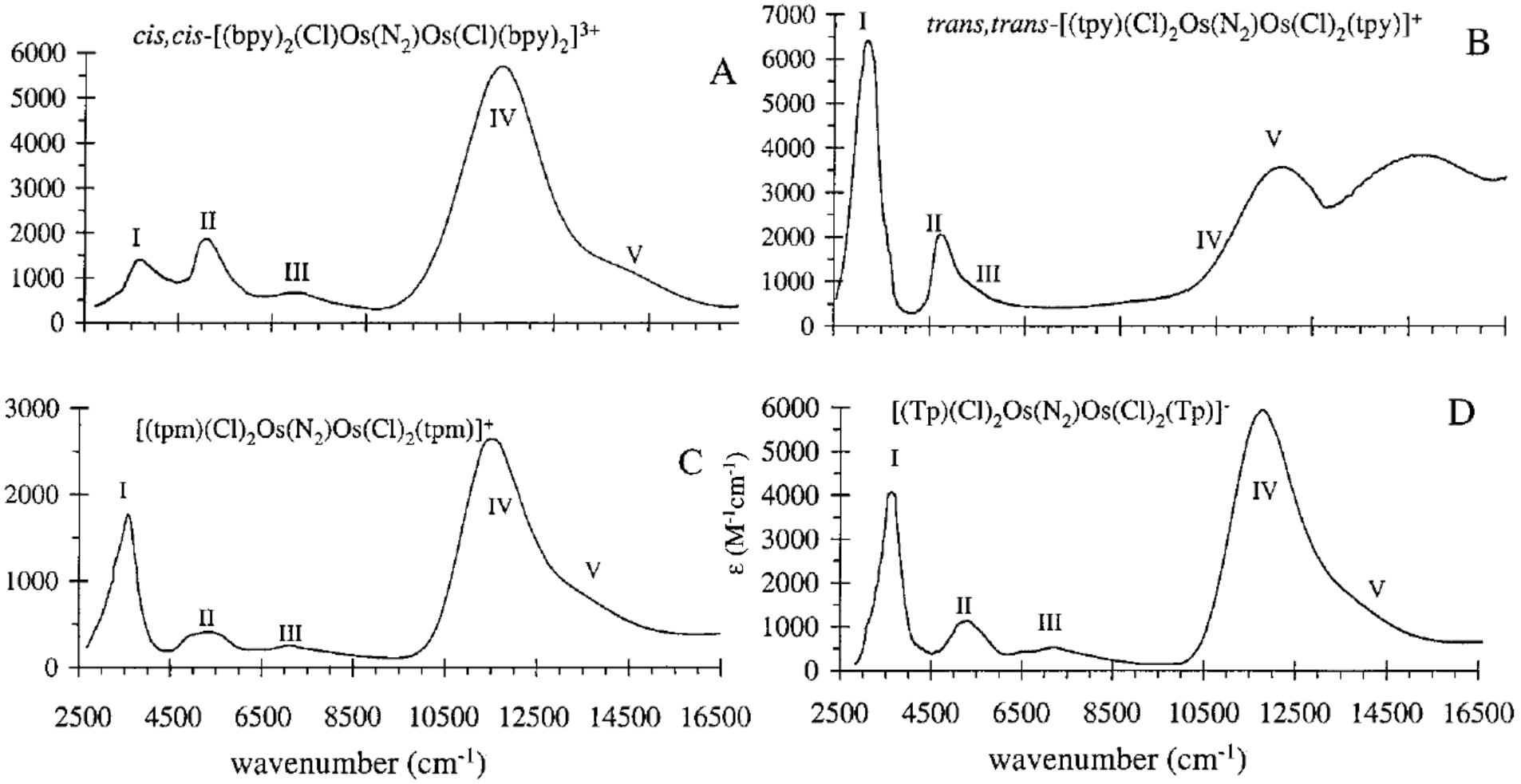


Tp

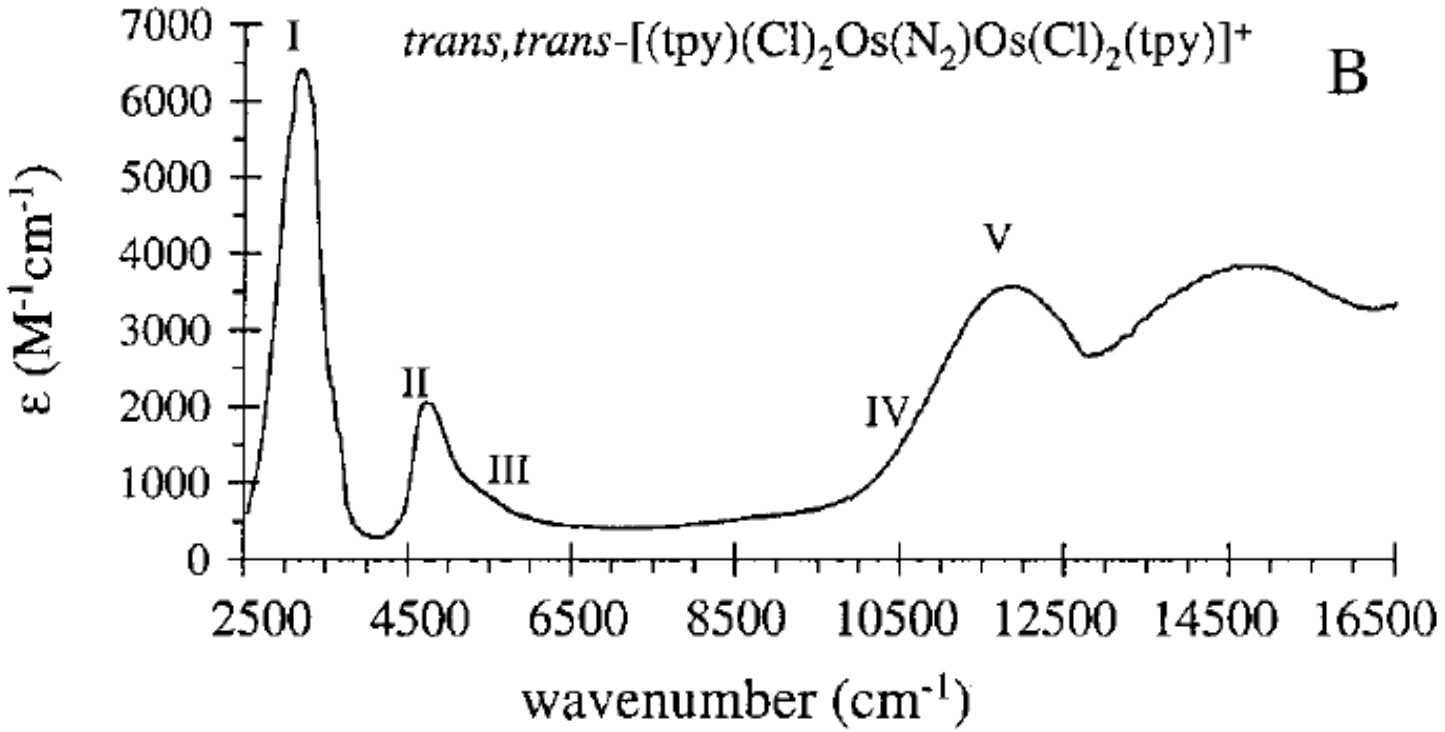


tpm

- Intense $\nu(N_2)$ stretches appear at 2007 cm^{-1} for **tpy** and 2029 cm^{-1} for **tpm** consistent with electronic asymmetry on the time scale of the IR absorption response (recorded in KBr pellets)



- IR-NIR spectra for a series of N_2 bridged mixed valence osmium complexes recorded in acetonitrile.

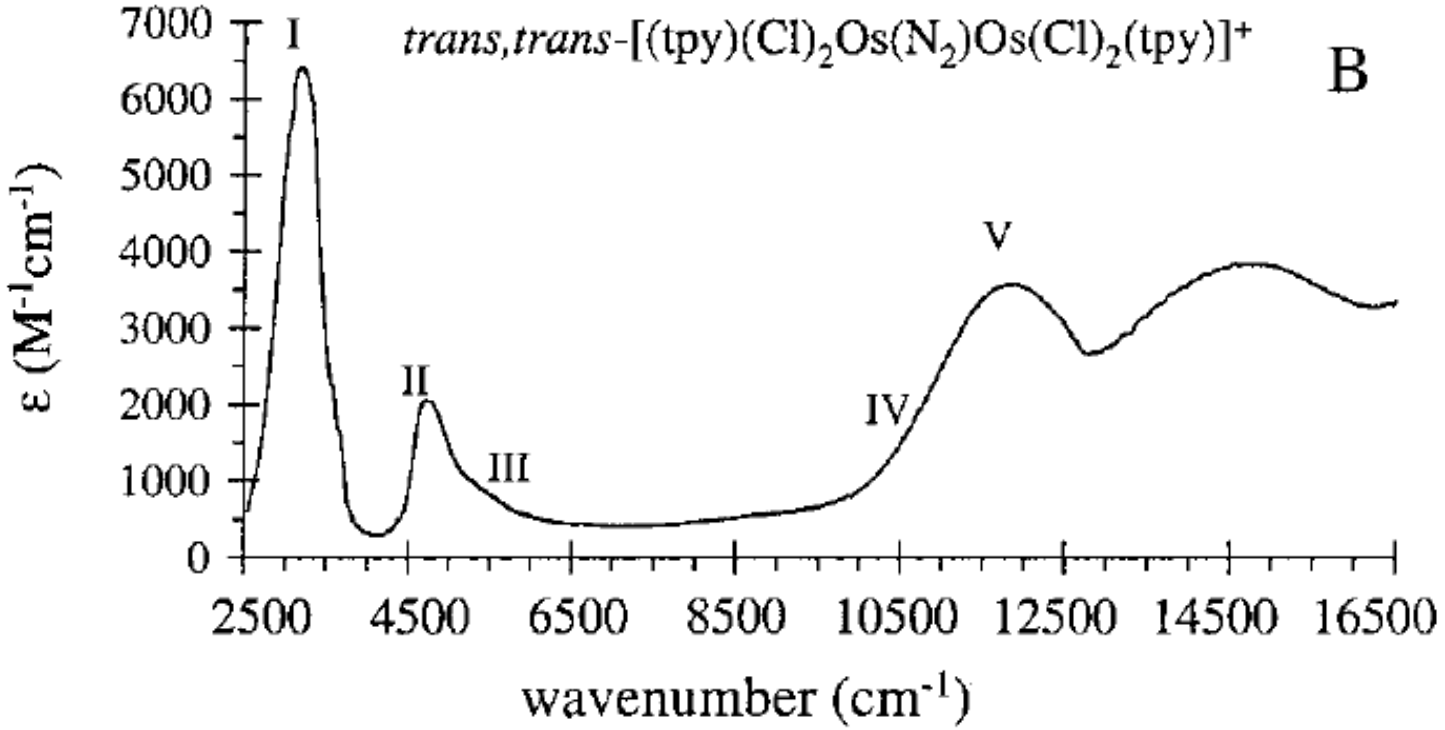


- Bands I and II provide an oxidation-state marker for Os(III).
- Due to low symmetry, extensive metal-ligand overlap, and spin-orbit coupling [χ = 3 000 cm^{-1} for Os(III)] the d^5 Os(III) core is split into three Kramer's doublets (E_1' , E_2' , E_3') separated by thousands of cm^{-1}.

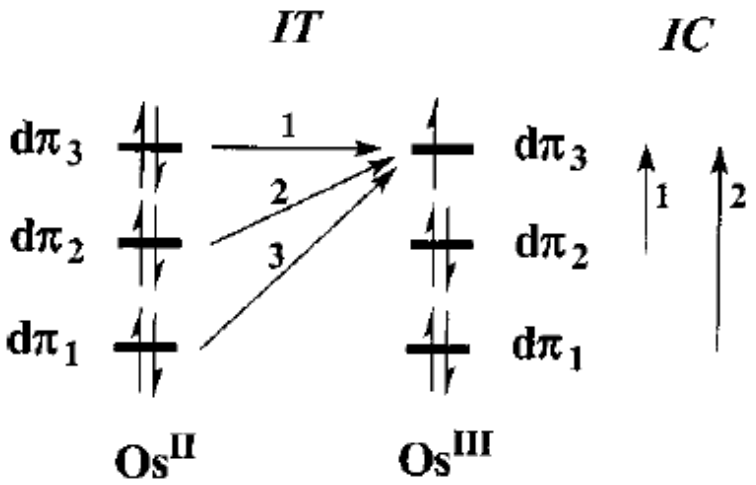
$$E_3' = d\pi_1^{\,1}\, d\pi_2^{\,2}\, d\pi_3^{\,2} \quad \text{(IC-2)}$$

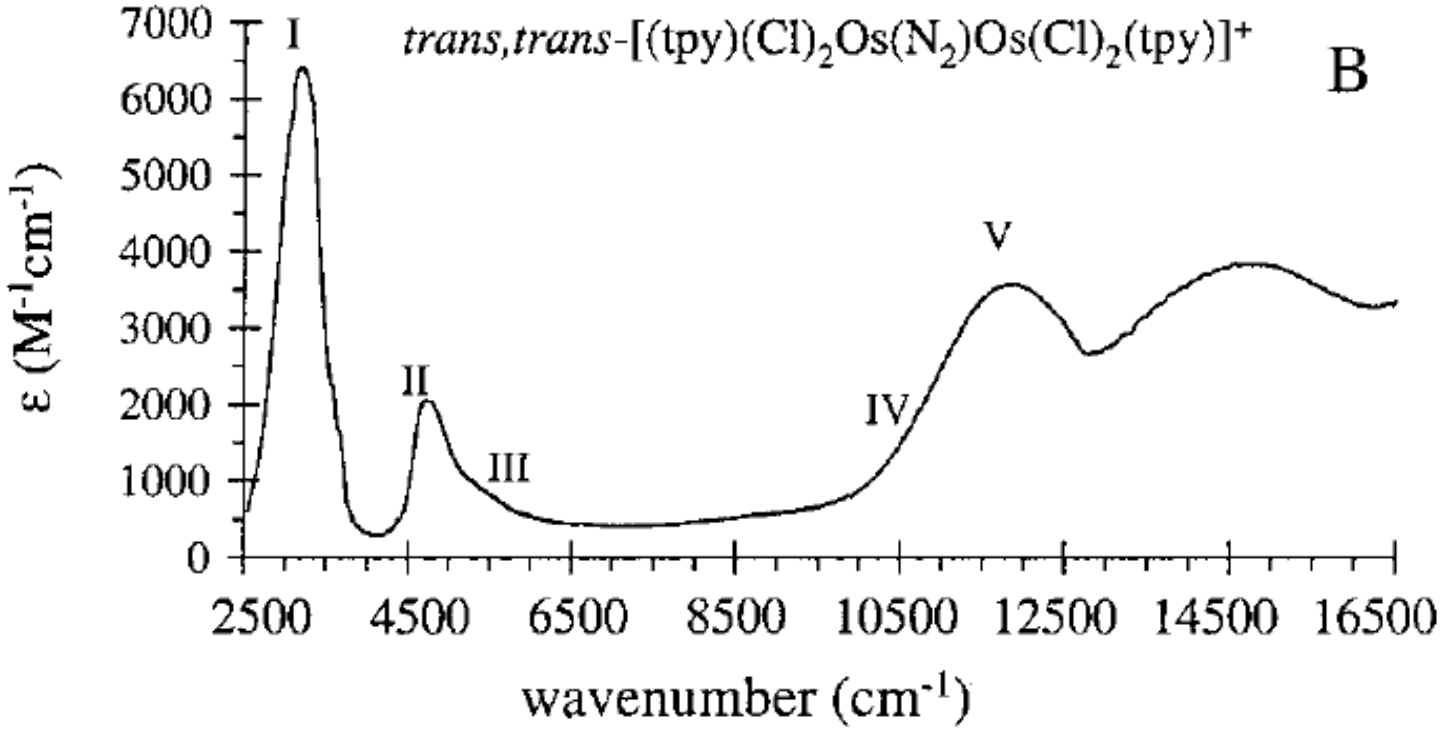
$$E_2' = d\pi_1^{\,2}\, d\pi_2^{\,1}\, d\pi_3^{\,2} \quad \text{(IC-1)}$$

$$E_1' = d\pi_1^{\,2}\, d\pi_2^{\,2}\, d\pi_3^{\,1} \quad \text{(GS)}$$

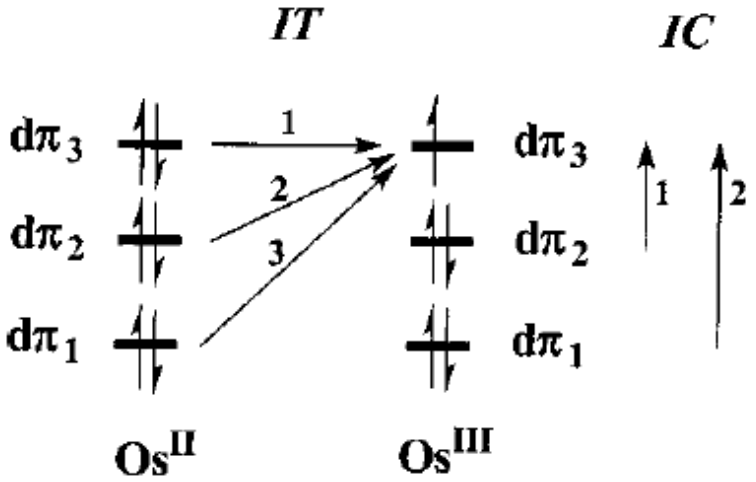


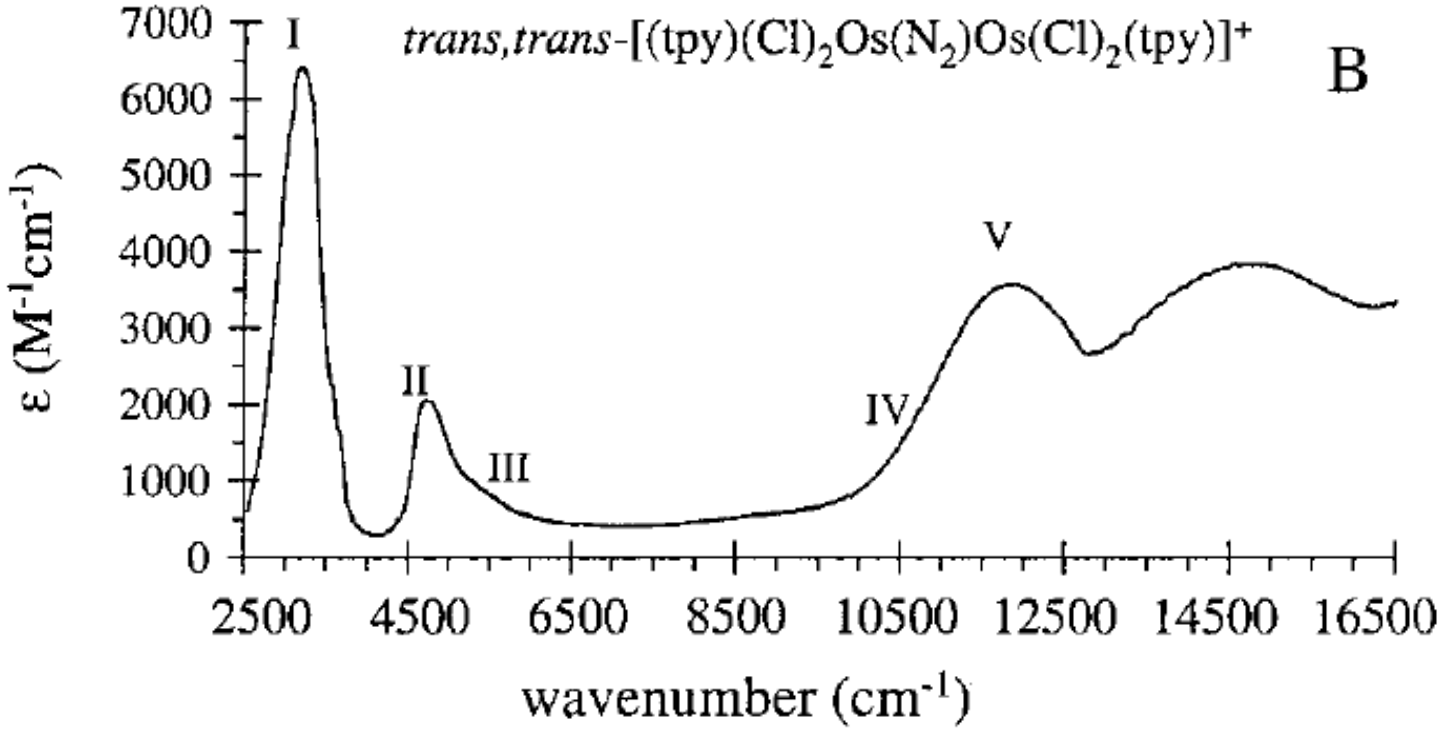
- Bands I (IC-1) and II (IC-2), are called interconfigurational (IC) transitions, assigned to transitions between the Kramer's doublets.
- They are LaPorte forbidden but gain intensity through spin-orbit coupling and M-L mixing.
- IC bands are less commonly observed for Fe(III), $\chi \sim 500\ cm^{-1}$, or for Ru(III), $\chi \sim 1000\ cm^{-1}$.



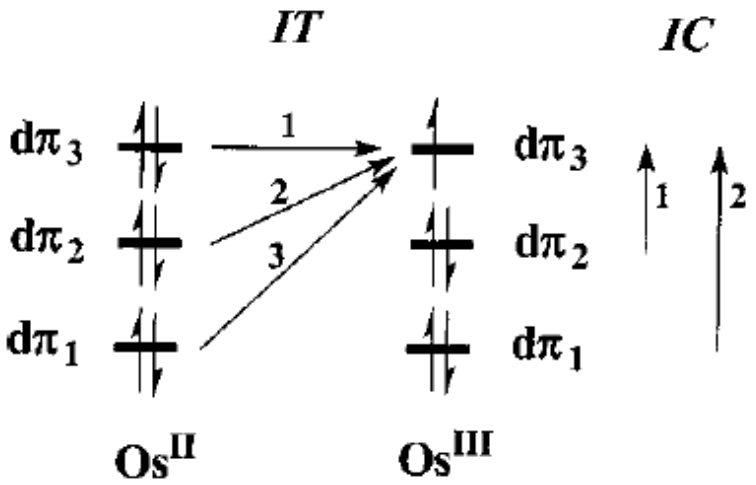


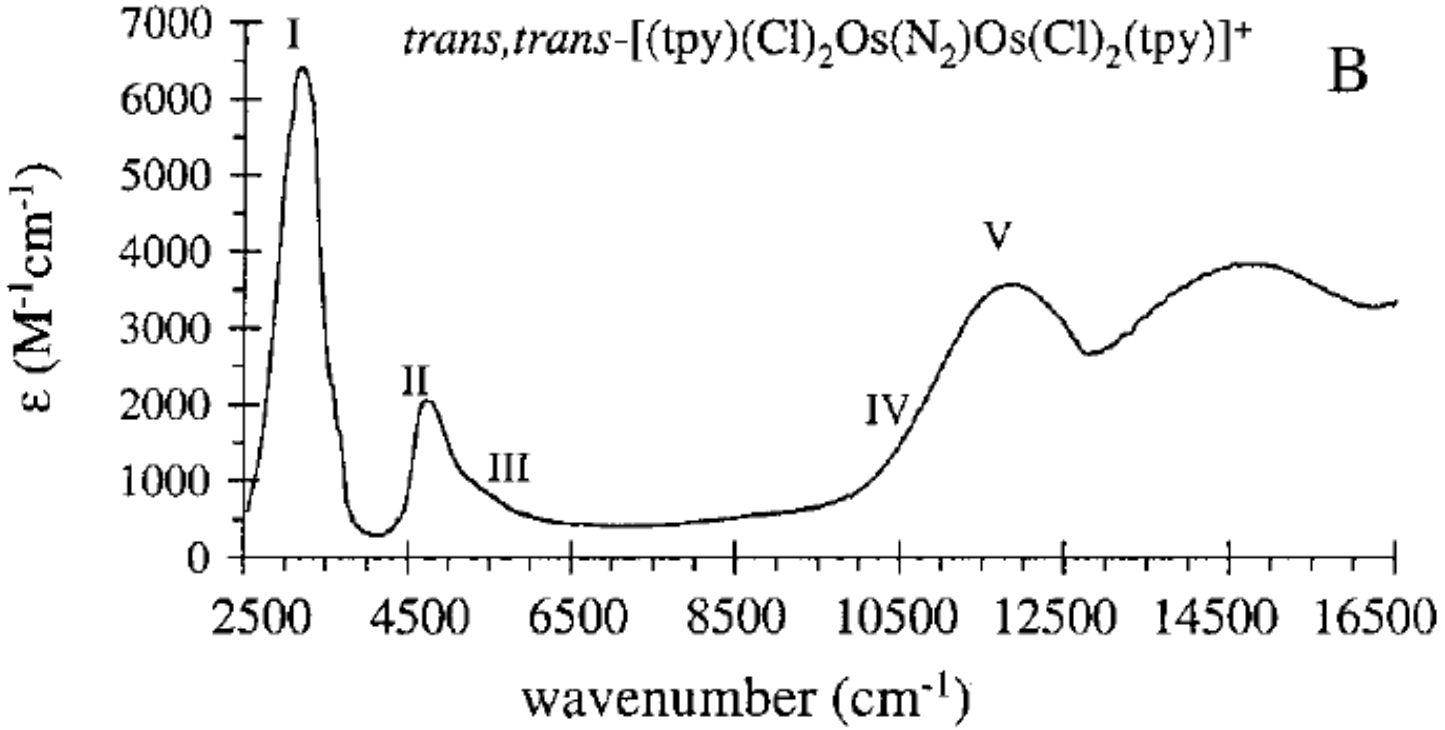
- The remaining three bands (III, IV, V) can be assigned to IT transitions arising from separate electronic excitations across the bridge from the three $d\pi$ orbitals at Os(II) to the hole at Os(III).
- These bands are also narrow but slightly broader than the IC bands, which helps to distinguish them in making band assignments.





- With weaker ligand field splitting in first and second row transition metals the IT transitions typically merge into a single broad overlapping absorption band.
- Transitions IT-2 and IT-3 generate E_2' and E_3' Kramer's doublet configurations at the new Os(III) center.



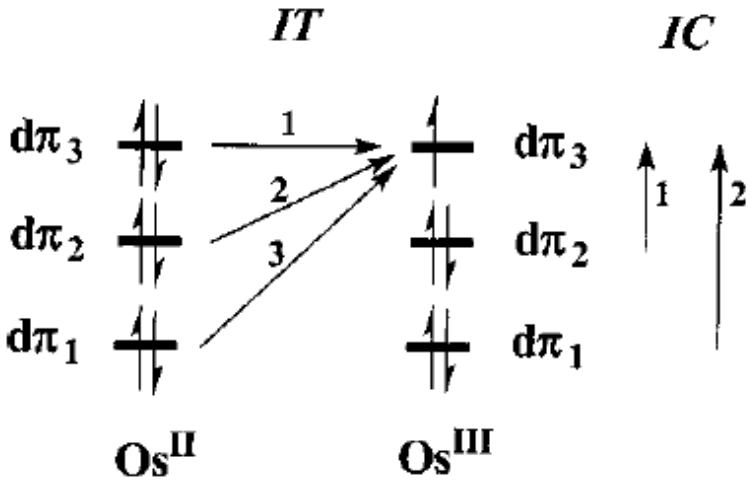


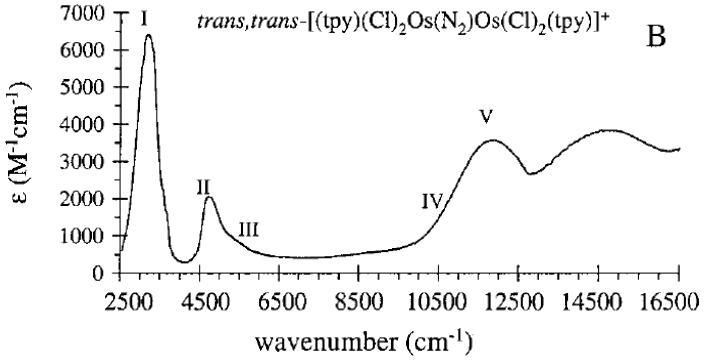
- Assuming the classical limit and a constant λ, the energies of the IC and IT bands are related as

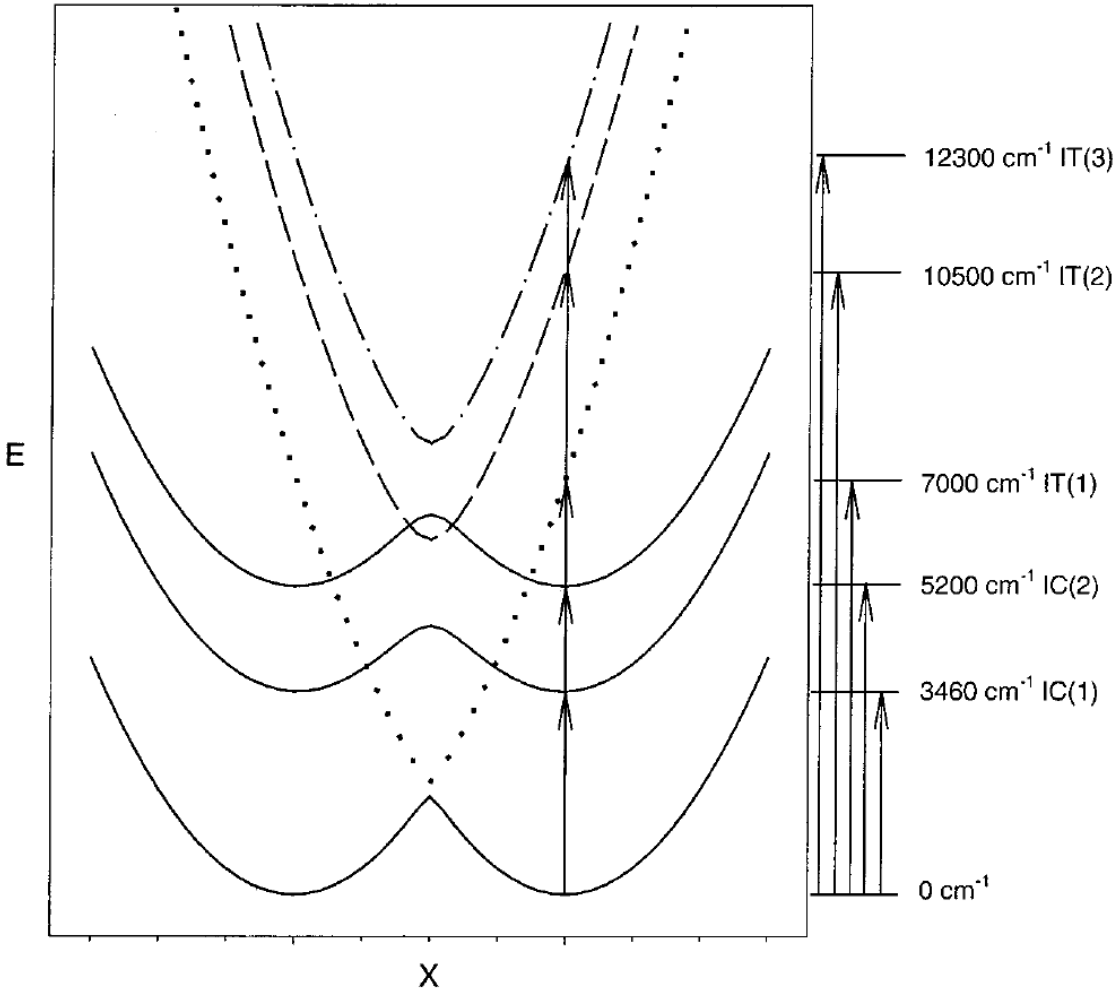
$$E_{IT}\,(1) = \lambda$$

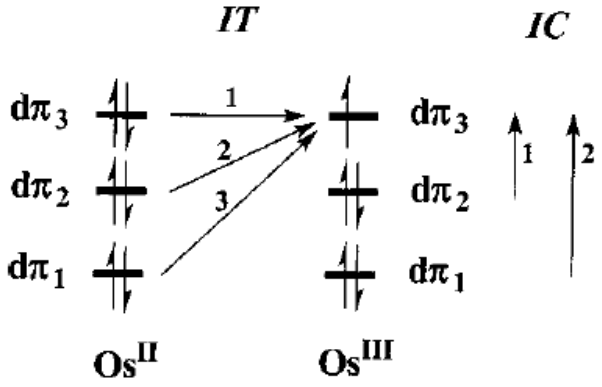
$$E_{IT}\,(2) = \Delta G_1^{\circ} + \lambda \approx E_{IT}\,(1) + \lambda$$

$$E_{IT}\,(3) = \Delta G_2^{\circ} + \lambda \approx E_{IT}\,(2) + \lambda$$









Energy-coordinate diagrams for E_1 and E_2 calculated using the following eqns.

$$E_1 = \frac{\lambda(2X^2 - 2X + 1)}{2} - \frac{\{[\lambda(2X-1)]^2 + 4H_{ab}^2\}^{1/2}}{2}$$

$$E_2 = \frac{\lambda(2X^2 - 2X + 1)}{2} + \frac{\{[\lambda(2X-1)]^2 + 4H_{ab}^2\}^{1/2}}{2}$$

$\lambda = 7000\ cm^{-1}$

$H_{ab}(1) = 118\ cm^{-1}$

The upper two sets of curves were calculated similarly but offsetting by

$E_{IC}\ (1) = 3460\ cm^{-1}$

$E_{IC}\ (1) = 5200\ cm^{-1}$

with

$H_{ab}(2) = 723\ cm^{-1}$

and $H_{ab}(3) = 595\ cm^{-1}$