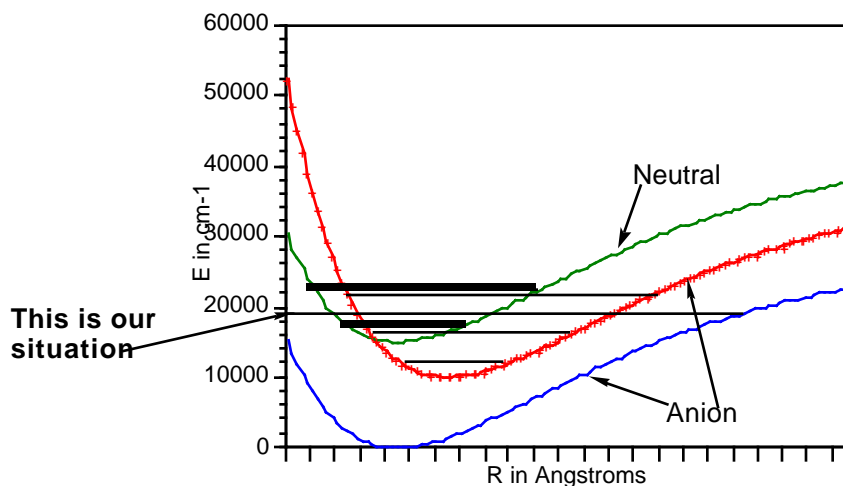


Vibration, Rotation, and Collision Induced Electron Ejection in Molecular Anions

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Molecular anions **with excess vibrational, rotational, or collisional energy** may **convert some of this energy into electronic energy** and thus eject the “extra” electron. Such events can be induced by **non Born-Oppenheimer couplings** or **by a crossing** of the anion and neutral energy surfaces.



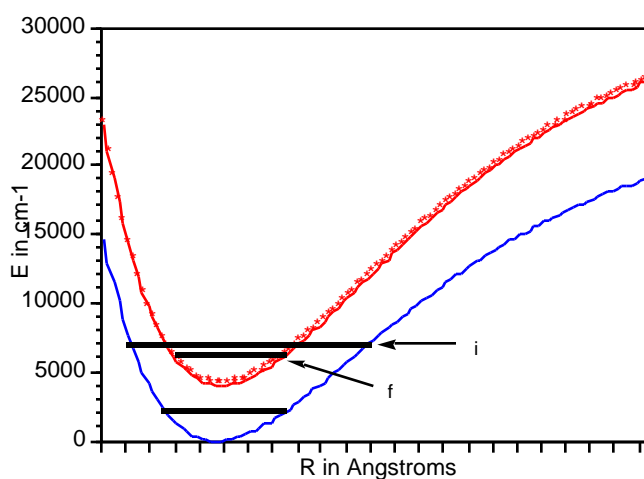
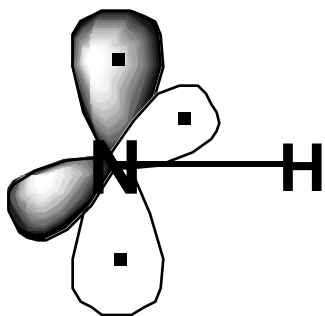
In the cases we have studied, the **anion's electronic energy lies below the neutral's for all geometries.**

1. Dipole-bound anions (Rotations

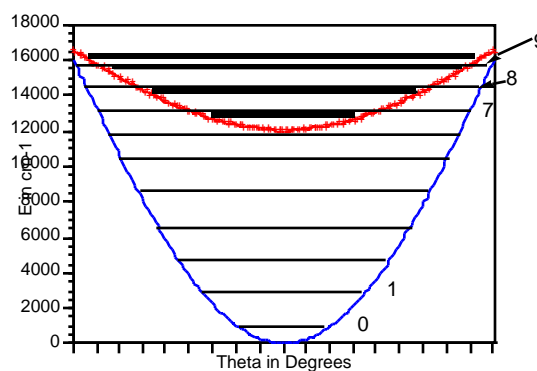
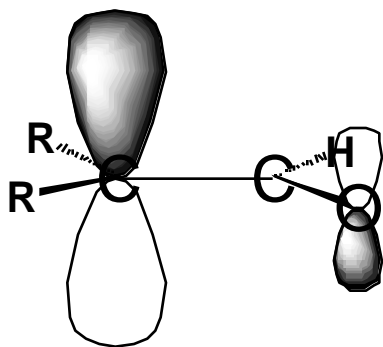
induce; EA 100 cm^{-1})



2. NH^- (Rotations $>$ vibrations; EA 0.4 eV)



3. Enolate anions ($\text{H}_2\text{C}-\text{C}$ twisting induces; EA 1 eV)



The **rate R of transitions** from the **bound anion** state $\psi_i = \psi_i^-$ to the **neutral plus free electron** state $\psi_f = \psi_f^0 + \psi_f^-$

$$R = \frac{2\pi}{\hbar} |\langle \psi_i | \langle \psi_i | \mathbf{P} | \psi_f \rangle (P/\mu) | \psi_f \rangle|^2 \delta(E_f - E_i) dE_f$$

$$\{ (P/\mu) | \psi_f \rangle = \langle \psi_i | (-i\hbar \nabla / R_a) (-i\hbar \nabla / R_a) / m_a \}$$

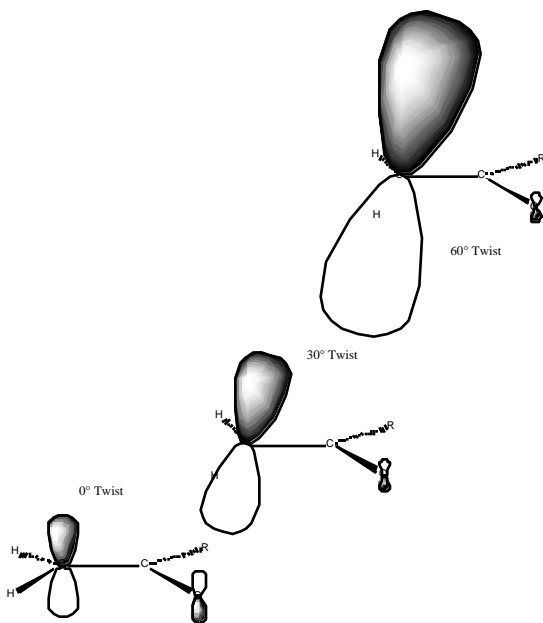
Electronic Non BO Matrix Elements

$m_{i,f} = \langle \psi_f | \mathbf{P} | \psi_i \rangle$ vanish if the **symmetry** of ψ_i and $d\psi/dQ$, and of ψ_f do not match; they can be large when

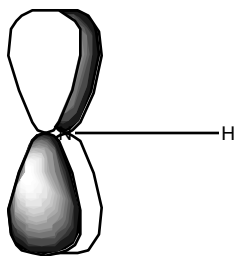
1. The anion's **HOMO** is strongly modulated by movement of the molecule- so $d\psi_i/dQ$ must be significant.
2. The energy $E = E_i - E_f$ of the ejected electron **is not too large** (else ψ_f is too oscillatory to overlap well with ψ_i).

What are derivatives of the anion's orbitals i/Q ?

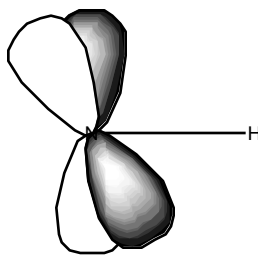
1. The orbital's **LCAO-MO coefficients** (and thus its size, orientation, and stability) vary with Q



2. The **atomic orbitals** (AO) themselves jiggle under motions of the atomic centers



$d/dR = (R^+ - R^-) / R^2$
causes $2p_x$ to acquire d character



$d/d = (R^+ + R^-) / R^2$
causes $2p_x$ to acquire $2p_z$ character

Time Domain Rate Expression

$$R = (2/\hbar) \int |\langle f | \langle i | P | f \rangle (P/\mu) | f \rangle|^2 (E_f + E_i - E) dE$$

Introduce $m_{i,f} = \langle f | P | i \rangle$ and $\tau = dt$

$$R_T = (2/\hbar) \int \langle f | (1/2 \hbar) \exp[it(E_f - E_i + E)/\hbar] \langle m_{i,f} (P/\mu) | i \rangle \langle f | m_{i,f} (P/\mu) | i \rangle dt (E) dE.$$

Replace $(E_f + E) \langle f |$ by $\langle f | (T + V_f + E)$,
 $(E_i) | i \rangle$ by $|(T + V_i) | i \rangle$, and $\langle f | f \rangle \langle f | = 1$

$$R_T = (2/\hbar) \int (1/2 \hbar) (E) \exp(itE/\hbar)$$

$$\langle m_{i,f} (P/\mu) \exp(it(T + V_i)/\hbar) | i \rangle$$

$$\exp(it(T + V_f)/\hbar) m_{i,f} (P/\mu) | i \rangle dt dE$$

R_T is the Fourier transform of the overlap of two time propagated functions.

In the more familiar the **Optical Spectroscopy** case

$$R = (2/\hbar) |\langle \psi_i | V | \psi_f \rangle|^2 (\omega_f - \omega_i - \hbar)^{-2}$$

Defining $\mu_{i,f} = \langle \psi_f | V | \psi_i \rangle$, and using

$$H_{e_{i,f}} = V_{i,f}(Q) \psi_{i,f}, [T + V_{i,f}(Q)] \psi_{i,f} = \omega_{i,f} \psi_{i,f}$$

$\langle \psi_f | \psi_f \rangle = 1$, gives

$$R_T = (2/\hbar) (1/2\hbar) \int_{-\infty}^{\infty} \exp[-it(\omega_f - \omega_i - \hbar)]$$

$$\langle \mu_{i,f} \exp(it\omega_f/\hbar) \psi_i | \exp(it\omega_i/\hbar) \mu_{i,f} | \psi_i \rangle dt$$

Again, a **Fourier transform of the overlap of two time-propagated wavefunctions:**

(a) $\mu_{i,f} | \psi_i \rangle$ propagated using the **excited-state** propagator

$$\exp(it\omega_f/\hbar)$$

(b) $| \psi_i \rangle$ propagated using the **ground-state** propagator

$\exp(it\omega_i/\hbar)$, after which $\mu_{i,f}$ acts

Let's Compare and Contrast

Photon Case: $R_T = (2/\hbar) (1/2 \hbar) \exp[-it]$

$$\langle \mu_{i,f} \exp(i\hbar/\hbar) | \exp(i\hbar_f/\hbar) \mu_{i,f} | \rangle dt$$

Short-time propagation because is large.

Non BO Case: $R_T = (2/\hbar) (1/2 \hbar) (E) \exp(itE/\hbar)$

$$\langle m_{i,f} (P/\mu) \exp(it(T + V_i)/\hbar) |$$

$$\exp(it(T + V_f)/\hbar) m_{i,f} (P/\mu) \rangle dt dE.$$

Long-time propagation because **E** is small.

Classical Approximation: $\exp(it\hbar_{i,f}/\hbar) \exp(itT/\hbar)$

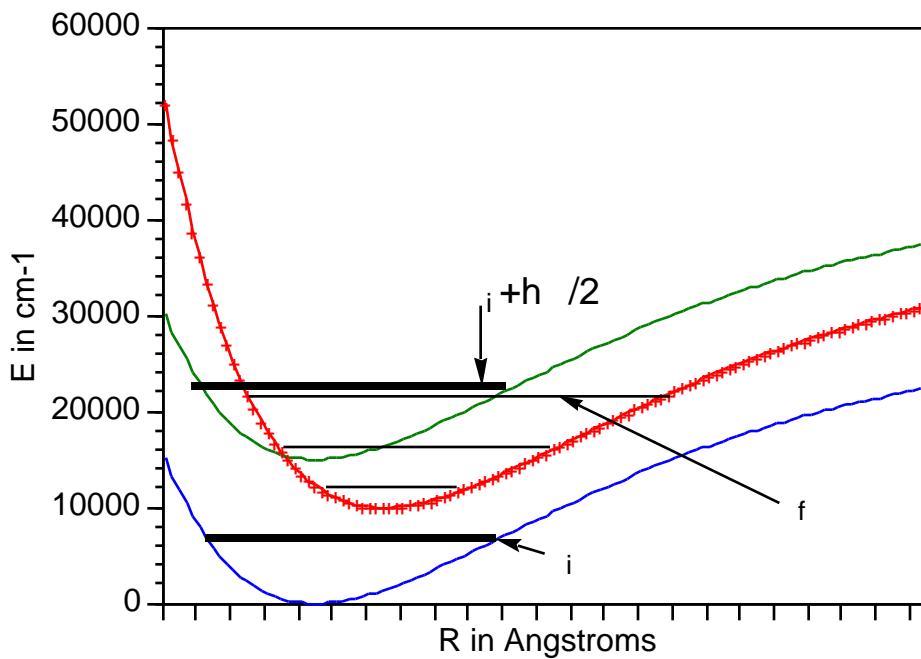
$\exp(itV_{i,f}/\hbar)$

Photon Case: $R_T = (2/\hbar) \langle \mu_{i,f} | \exp(itV_f/\hbar) | \mu_{i,f} \rangle \exp[-it]$

$$\langle \mu_{i,f} | \exp(itV_i/\hbar) | \mu_{i,f} \rangle \exp(itV_f/\hbar) | \mu_{i,f} \rangle dt$$

$$= (2/\hbar) \langle \mu_{i,f} | \mu_{i,f}^* (V_f - V_i - \hbar) | \mu_{i,f} \rangle$$

Says all of the photon energy goes into electronic energy; nuclear kinetic energy is conserved.



Non BO Case:

$$R_T = \frac{2}{\hbar} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dE \exp(it(E + V_f)/\hbar) \langle m_{i,f} | P/\mu | m_i \rangle \exp(it(V_i)/\hbar)$$

$$\exp(it(E + V_f)/\hbar) \langle m_{i,f} | P/\mu | m_i \rangle \int_{-\infty}^{\infty} dt dE$$

$$= \frac{2}{\hbar} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dE \exp(it(E + V_f + V_i)/\hbar) \langle m_{i,f} | P/\mu | m_i \rangle$$

$$\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dE \exp(it(E + V_f + V_i)/\hbar) \langle m_{i,f} | P/\mu | m_i \rangle$$

However, $V_i(Q)$ lies below $V_f(Q)$ for all geometries, so **there are no geometries** where the argument of the delta function vanishes, so **R_T is predicted to vanish** in the classical approximation to nuclear motions.

An Approximation that Works for Non BO

$$M = \langle m_{i,f}(P/\mu) \exp(it(T + V_i)/\hbar) \mid_i \rangle \exp(it(T + V_f)/\hbar) \mid_i \rangle m_{i,f}(P/\mu)$$

replace (exact) $\exp(it(T + V_i)/\hbar) \mid_i \rangle$ by $\exp(it(T) / \hbar) \mid_i \rangle$

approximate $\exp(it(T + V_f)/\hbar)$ by $\exp(it(T) / \hbar) \exp(it(V_f)/\hbar)$

introduce $\int dp \mid p \rangle \langle p \mid = 1$ and $\int dQ \mid Q \rangle \langle Q \mid = 1$

$$M = \int dQ' \int dQ \int dp \langle m_{i,f}(P/\mu) \exp(it(T) / \hbar) \mid_i \rangle \mid Q' \rangle \langle Q' \mid p \rangle \exp(it(T_{\text{class}}) / \hbar) \langle p \mid Q \rangle \langle Q \mid \exp(it(V_f(Q)/\hbar)) \mid_i \rangle m_{i,f}(P/\mu)$$

$$T_{\text{class}} = (p^2 / 2\mu_Q) \quad \text{and} \quad \langle Q' \mid p \rangle = (2\hbar)^{-1/2} \exp(ipQ' / \hbar)$$

The integration over time can be carried out

$$R_T = (2/\hbar) \int (E) dQ' dQ dp$$

$$\langle m_{i,f}(P/\mu) | Q' \rangle \langle Q' | p \rangle$$

$$(\mathcal{T}_{\text{class}} + E + V_f(Q) - \epsilon_i) \langle p|Q \rangle \langle Q| m_{i,f}(P/\mu) | \epsilon_i \rangle dE$$

Since $E = \epsilon_i - \epsilon_f$, the integral over dE can be replaced by a sum multiplied by $dE_f = \epsilon_f - \epsilon_{f-1}$:

$$R_T = (2/\hbar) \sum_f (\epsilon_i - \epsilon_f) dE_f dQ' dQ dp$$

$$\langle (P/\mu) | \epsilon_i | Q' \rangle m_{i,f}(Q') \langle Q' | p \rangle$$

$$(\mathcal{T}_{\text{class}} + V_f(Q) - \epsilon_f) \langle p|Q \rangle m_{i,f}(Q) \langle Q| (P/\mu) | \epsilon_i \rangle$$

The integral over p can also be carried out.

Defining

$$f(p) = (2\hbar)^{-1/2} \exp(-ipQ/\hbar) (2\hbar)^{-1/2} \exp(ipQ'/\hbar)$$

$$\begin{aligned} & \int_{-\infty}^{\infty} (p^2/2\mu_Q - E_f + V_f(Q)) f(p) dp \\ &= \frac{1}{2\hbar} \int_{-\infty}^{\infty} 2 \cos\{[Q' - Q] \sqrt{2\mu_Q (E_f - V_f(Q))} / \hbar\} \\ & \quad \frac{\mu_Q}{\sqrt{2\mu_Q (E_f - V_f(Q))}} \end{aligned}$$

Substituting this result back into R_T gives

$$\begin{aligned} R_T &= (2/\hbar) \int_{-\infty}^{\infty} \langle i | \dots | f \rangle dE_f \int dQ' \int dQ \langle m_{i,f}(P/\mu) | Q' \rangle \\ & \quad \frac{1}{\hbar} \cos\{[Q' - Q] \sqrt{2\mu_Q (E_f - V_f(Q))} / \hbar\} \\ & \quad \frac{\mu_Q}{\sqrt{2\mu_Q (E_f - V_f(Q))}} \langle Q | m_{i,f}(P/\mu) | i \rangle \end{aligned}$$

Bearing in mind the nature of the electronic non BO matrix elements $m_{i,f}(Q)$, Q' and Q can often be constrained to the region $Q' = Q = Q_0$ where the anion and neutral surfaces approach most closely:

$$m_{i,f}(Q) = (Q - Q_0)m^*$$

and so

$$R_T = (2/\hbar) \int_{i-f} dE_f \{ (P/\mu)_{i(Q_0)} \}^2 > |m^*|^2 \frac{1}{\hbar v_0}$$

where

$$v_0 = \frac{\sqrt{2\mu_Q (E_f - V_f(Q_0))}}{\mu_Q}$$

Summary of Primary Non BO Eqns.

Quantum Mechanical Time Fourier Transform

$$R_T = (2/\hbar) \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dE \exp(itE/\hbar)$$

$$\langle m_{i,f}(P/\mu) \exp(it(T + V_i)/\hbar) |$$

$$\exp(it(T + V_f)/\hbar) | m_{i,f}(P/\mu) \rangle dt dE$$

Semi-classical

$$R_T = (2/\hbar) \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dE_f \int_{-\infty}^{\infty} dQ \langle m_{i,f}(P/\mu) | Q \rangle \frac{1}{\hbar}$$

$$\cos\{[Q - Q_0 \sqrt{2\mu_Q (E_f - V_f(Q))}]/\hbar\} \frac{\mu_Q}{\sqrt{2\mu_Q (E_f - V_f(Q))}} \langle Q | m_{i,f}(P/\mu) \rangle$$

if $m_{i,f}(Q)$ is localized

$$R_T = (2/\hbar) \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dE_f \{ \langle m_{i,f}(P/\mu) | Q_0 \rangle \}^2 > |m^*|^2 \frac{1}{\hbar v_0}$$

Vibration, Rotation, and Collision Induced Electron Ejection in Molecular Anions

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Abstract

Molecular anions that possess excess internal vibrational and/or rotational energy can eject their “extra” electron through a radiationless transition event involving non Born-Oppenheimer coupling. In such processes, there is an interplay between the nuclear motions (i.e., vibrations and rotations) and the electronic motions that allows energy to be transferred from the former to the latter and that permits momentum and/or angular momentum to also be transferred in a manner that preserves total energy, momentum, and angular momentum. There are well established quantum mechanical expressions for the rates of this kind of radiationless process, and these expressions have been used successfully to compute electron ejection rates. In this paper, we recast the quantum rate equation into more physically clear and easy-to-understand forms by making use of semi-classical approximations that have proven useful in rewriting the quantum expressions for rates of other processes (e.g., photon absorption) in a more classical manner. It is hoped that by achieving alternative and clearer interpretations of the electron ejection rate equation, it will be possible to more readily predict when such rates will be significant.

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