Semi-Classical Pictures of Non-Adiabatic Induced Electron Ejection in Molecular Anions

Jack Simons

Henry Eyring Center for Theoretical Chemistry
Chemistry Department
University of Utah
Salt Lake City, Utah 84112

ADVANCES IN QUANTUM CHEMISTRY, VOLUME 35

0065-3276/99 $30.00

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 and 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 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.

1. INTRODUCTION

1.1 Relation to Experiments

There exist a series of beautiful spectroscopy experiments that have been carried out over a number of years in the Lineberger (1), Brauman (2), and Beauchamp (3) laboratories in which electronically stable negative molecular ions prepared in excited vibrational-rotational states are observed to eject their "extra" electron. For the anions considered in those experiments, it is unlikely that the anion and neutral-molecule potential energy surfaces undergo crossings at geometries accessed by their vibrational motions in these experiments, so it is believed that the mechanism of electron ejection must involve vibration-rotation to electronic energy flow. That is, the couplings between nuclear motions and electronic motions known as non Born-Oppenheimer (BO) couplings have been postulated to cause the electron ejection rather than curve crossings in which the anion's energy surface intersects that of the neutral at some geometries.

In earlier works (4), we and others (5) have formulated and computed such non BO coupling strengths for several of the anion systems that have been studied experimentally including:

1. Dipole-bound anions (5a, 4f) in which the extra electron is attracted primarily by the dipole force field of the polar molecule and for which rotation-to-electronic coupling is most important in inducing electron ejection.
2. NH^- ($X^2\Pi$) for which (4d) vibration of the N-H bond couples only weakly to the non-bonding $2p_\pi$ orbital and for which rotation-to-electronic coupling can be dominant in causing electron ejection for high rotational levels.
3. Enolate anions (4e) that have been "heated" by infrared multiple photon absorption for which torsional motion about the H_2C-C bond, which destabilizes the π orbital containing the extra electron, is the mode contributing most to vibration-to-electronic energy transfer and thus to ejection.

Our calculations have been successful in interpreting trends that are seen in the experimentally observed rates of electron ejection. However, until now, we have not had a clear physical picture of the energy and momentum (or angular momentum) balancing events that accompany such non BO processes. It is the purpose of this paper to enhance our understanding of these events by recasting the rate equations in ways that are more classical in nature (and hence hopefully more physically clear). This is done by

1. starting with the rigorous state-to-state quantum expression for non BO transition rates (4g),
2. including what is known from past experience (4) about the magnitudes and geometry dependencies of the electronic non BO matrix elements arising in these rate expressions, to

3. make the simplest reasonable semi-classical approximation to the nuclear motion (7) (i.e., vibration-rotation) and its coupling to the electronic motions. By so doing, we are able to arrive at expressions for rates of electron ejection that, in our opinion, offer better physical insight into these radiationless processes and thus offer the potential for predicting when such rates will be significant in other systems.

1.2 State-to-State Quantum Rate Expression

Within the Born-Oppenheimer approximation to molecular structure, the electronic Schrödinger equation

$$h_e\,(r|Q)\ \psi_K(r|Q) = E_K(Q)\ \psi_K(r|Q) \qquad (1)$$

is solved to obtain electronic wavefunctions $\psi_K(r|Q)$, which are functions of the molecule's electronic coordinates (collectively denoted r) and atomic coordinates (denoted Q), and the corresponding electronic energies $E_K(Q)$, which are functions of the Q coordinates. The electronic Hamiltonian

$$h_e(r|Q) = \Sigma_i \{-\hbar^2/2m_e \nabla_i^2 + 1/2\ \Sigma_{j \neq i}\ e^2/r_{i,j}\ - \Sigma_a Z_a e^2 / r_{i,a}$$

$$+ 1/2\ \Sigma_{a \neq b}\ Z_a Z_b\ e^2/R_{a,b}\ \} \qquad (2)$$

contains, respectively, the sum of the kinetic energies of the electrons, the electron-electron repulsion, the electron-nuclear Coulomb attraction, and the nuclear-nuclear repulsion energy. In h_e, second-order differential operators involving the coordinates of the electrons appear, but the coordinates of the atomic centers appear only parametrically in the various Coulomb potentials. Hence, the solutions $\{\psi_K$ and $E_K\}$ depend only parametrically on the nuclear positions.

Given the solutions to the electronic Schrödinger equation, the solutions of the full Schrödinger equation (i.e., the equation in which all nuclei and electrons are moving)

$$H(r|Q)\,\Psi(r,Q) = E\,\Psi(r,Q) \tag{3}$$

are expressed as sums over the (complete set of functions of the electronic coordinates r) electronic functions $\{\psi_k(r|Q)\}$

$$\Psi(r,Q) = \Sigma_k\, \psi_k(r|Q)\, \chi_k(Q), \tag{4}$$

with the "expansion coefficients" $\chi_k(Q)$ carrying the remaining Q-dependence. When substituted into the full Schrödinger equation, this expansion of Ψ gives equations which are to be solved for these $\{\chi_k\}$ functions:

$$(H - E)\Sigma_k\, \psi_k(r|Q)\, \chi_k(Q) = 0. \tag{5}$$

Using the fact that the full Hamiltonian H is h_e plus the kinetic energy operator for nuclear motion T

$$H = h_e + T = h_e + \Sigma_a\,(-\hbar^2/2m_a\, \nabla_a^{\,2}), \tag{6}$$

and premultiplying the above Schrödinger equation by ψ_n and integrating over the electronic coordinates gives the set of coupled equations that need to be solved for the $\{\chi_k\}$:

$$\begin{aligned}
&\Sigma_k \int \psi_n^*(r|Q)\, \{h_e + T - E\}\, \psi_k(r|Q)\, \chi_k(Q)\, dr \\
&= \{E_n(Q) - E\}\, \chi_n(Q) + T\, \chi_n(Q) \\
&+ \Sigma_a \Sigma_k\, \{\int \psi_n^*(r|Q)\, (-i\hbar\,\partial\psi_k/\partial R_a)(-i\hbar\,\partial\chi_k/\partial R_a)/m_a\, dr \\
&+ \int \psi_n^*(r|Q)\, (-\hbar^2\partial^2\, \psi_k/\partial R_a^{\,2})/2m_a\, dr\, \chi_k\} = 0.
\end{aligned} \tag{7}$$

The expression

$$\{E_n(Q) - E\} \chi_n(Q) + T \chi_n(Q) = 0 \tag{8a}$$

is, within the Born-Oppenheimer model, the equation governing the nuclear motion functions $\{\chi_{k\,L}(Q)\}$ in the absence of the so-called non Born-Oppenheimer (non BO) coupling terms (i.e., the latter two terms in Eq.(7)). Within this model, the vibration-rotation functions $\{\chi_k(Q)\}$ of each specific electronic state labeled k are found by solving the vibration-rotation Schrödinger equation

$$\{T + E_k(Q)\} \chi_{k,L}(Q) = \varepsilon_{k,L} \chi_{k,L}(Q). \tag{8b}$$

There are a complete set of functions of Q (i.e., the $\{\chi_{k,L}\}$ for each electronic state k.

In the theory of radiationless transitions as covered in this paper (6,4g), the two non BO terms are treated as perturbations (not externally applied, but arising as imperfections within this model of molecular structure) that can induce transitions between unperturbed states each of which is taken to be a specific Born-Oppenheimer product state:

$$\Psi_{k,L}(r,Q) \equiv \psi_k(r|Q) \chi_{k,L}(Q). \tag{9}$$

It is reasonably well established that the non BO coupling term involving second derivatives of the electronic wavefunction contributes less to the coupling than does the term $(-i\hbar\partial\psi_k/\partial R_a)(-i\hbar\partial\chi_k/\partial R_a)/m_a$ having first derivatives of the electronic and vibration-rotation functions. Hence, it is only the latter terms that will be discussed further in this paper.

With this background, it should not be surprising that it has been shown that the rate R ($\sec^{-1}$) at which transitions from a Born-Oppenheimer initial state $\Psi_i = \psi_i \chi_i$ to a final state $\Psi_f = \psi_f \chi_f$ is given, via first-order perturbation theory, as:

$$R = (2\pi/\hbar) \int |\langle\chi_i| \langle\psi_i |P| \psi_f\rangle(P/\mu)\chi_f\rangle|^2\, \delta(\varepsilon_f + E - \varepsilon_i)\, \rho(E)\, dE. \quad (10)$$

Here, $\varepsilon_{i,f}$ are the vibration-rotation energies of the initial (anion) and final (neutral) states, and E denotes the kinetic energy carried away by the ejected electron (e.g., the initial state corresponds to an anion and the final state to a neutral molecule plus an ejected electron). The density of translational energy states of the ejected electron is $\rho(E) = 4\pi m_e L^3(2meE)^{1/2}/h^2$. We have used the short-hand notation involving P P/μ to symbolize the multidimensional derivative operators that arise in the non BO couplings as discussed above:

$$(P\psi_f)(P/\mu\chi_f) = \Sigma_a (-i\hbar\partial\psi_f/\partial R_a)(-i\hbar\partial\chi_f/\partial R_a)/m_a , \quad (11)$$

where R_a runs over the Cartesian coordinates (X_a, Y_a, Z_a) of the a^{th} atom whose mass is m_a. In Eq. (10), the product ρ dE is unitless, $\delta(\varepsilon_f + E - \varepsilon_i)$ has units of $sec^2/(gm\ cm^2)$, the square of the P matrix element has units of $(gm\ cm/sec)^2$, the square of the P/μ matrix element has units of $(cm/sec)^2$, and $2\pi/\hbar$ has units of $(sec/(gm\ cm^2))$. Hence the product has units of sec^{-1} .

1.3 The Electronic Non BO Matrix Elements

The integrals over the anion and neutral-plus-free-electron electronic states

$$m_{i,f} = \langle\psi_f |P| \psi_i\rangle \quad (12)$$

are known to be large in magnitude only under special circumstances:

1. The orbital of the anion from which an electron is ejected to form the state ψf of the neutral (usually the anion's highest occupied molecular orbital (HOMO)) must be strongly modulated or affected by movement of the molecule in one or more directions (Q). That is $\partial\psi_i/\partial Q$, which appears in $P\psi_i$, must be significant.

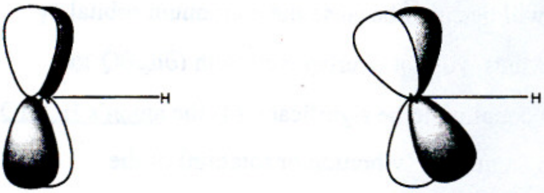
2. The state-to-state energy gap $\varepsilon_i - \varepsilon_f$, which is equal to the energy E of the ejected electron, must not be too large; otherwise, the oscillations in the ejected

electron's wavefunction ψ_f will be so rapid as to render overlap with $\partial\psi_i/\partial Q$ negligible.

Moreover, symmetry can cause $m_{i,f} = <\psi_f |P| \psi_i>$ to vanish. In particular, if the direct product of the symmetry of ψ_i and of $\partial/\partial Q$ do not match that of ψ_f, then $m_{i,f}$ will vanish.

Let us consider these conditions in more detail before proceeding further because they form the basis for approximations that are introduced later. The derivatives or responses of the anion's orbitals to nuclear motions $\partial\psi_i/\partial Q$ arise from two sources:

1. The orbital's LCAO-MO coefficients depend on the positions of the atoms (or, equivalently, on bond lengths and internal angles). For example, the π^* orbital of an olefin anion that contains the "extra" electron is affected by stretching or twisting the C-C bond involving this orbital because the LCAO-MO coefficients depend on the bond length and twist angle. As the bond stretches or twists, the π^* orbital's LCAO-MO coefficients vary, as a result of which the orbital's energy, radial extent, and other properties also vary.
2. The atomic orbitals (AO) themselves respond to the motions of the atomic centers. For example, vibration of the $X^2\Pi$ NH^- anion's N-H bond induces d_π character into the $2p_\pi$ orbital containing the extra electron as shown in Fig. 1. Alternatively, rotation of this anion's N-H bond axis causes the $2p_\pi$ HOMO to acquire some $2p_\sigma$ character (see Fig. 1 again). Such AO responses can be evaluated using the same analytical derivative methods that have made computation of potential energy gradients and Hessians powerful tools in quantum chemistry.



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

$d\Psi/d\theta = (\Psi(\theta+\delta) - \Psi(\theta))/\delta$ causes $2p_x$ to acquire $2p_z$ character

Figure 1. Orbital response of NH^- 's $2p_\pi$ orbital to (a) vibratation of the N-H bond (left) and (b) rotation of the N-H bond (right).

Another view of how the LCAO-MO coefficients vary with geometry can be achieved by differentiating $h_e \psi_i = E_i \psi_i$ with respect to Q (an arbitrary molecular motion) and then premultiplying by the anion-plus-free-electron function ψ_f and integrating over the electronic coordinates r to obtain:

$$<\psi_f|\partial h_e/\partial Q|\psi_i>/(E_i - E_f - E) = <\psi_f|\partial/\partial Q \psi_i>. \tag{13}$$

In this form, one sees that the response of the anion's electronic state, when projected against the neutral-plus-free-electron state to which it will decay, will be enhanced at geometries where the anion and neutral potential surfaces approach closely (so the denominator in Eq. (13) is small). Enhancement is also effected when the initial and final states have a strong matrix element of the "force operator" $\partial h_e/\partial Q$. The latter is effectively a one-electron operator involving derivatives of the electron-nuclear Coulomb attraction potential $\Sigma_i \Sigma_a Z_a e^2 / r_{ii,a}$, so the matrix element $<\psi_f|\partial h_e/\partial Q|\psi_i>$ can be visualized as $<\phi_f|\partial h_e/\partial Q|\phi_i>$, where ϕ_i is the anion's HOMO and ϕ_f is the continuum orbital of the ejected electron. At geometries where the anion-neutral energy surfaces are far removed, the denominator in Eq.(13) will attenuate the coupling. If the state-to-state energy difference $\varepsilon_i - \varepsilon_f = E$ accompanying the electron ejection is large, the integral $<\phi_f|\partial h_e/\partial Q|\phi_i>$ will be small because the continuum orbital ϕ_f will be highly oscillatory and thus will not overlap well with $(\partial h_e/\partial Q)\phi_i$.

In summary, for non BO coupling to be significant (4) the anion's HOMO must be strongly modulated by a motion (vibration or rotation) of the molecule's nuclear framework and the state-to-state energy gap must not be too large as to render the HOMO-to-continuum-orbital overlap insignificant. For the HOMO to be strongly modulated, it is helpful if the anion and neutral energy surfaces approach closely (n.b., this is not the same as requiring that the state-to-state energy gap $\varepsilon_i - \varepsilon_f$ be small) at some accessible geometries.

It should be emphasized that it is necessary but not sufficient for $E_f(Q) - E_i(Q)$ to be small over an appreciable range of geometries; this only guarantees that the denominator in Eq. (13) is small. It is also necessary that $E_f(Q) - E_i(Q)$ decrease at a significant rate as the point of closest approach is reached; this is why we say the surfaces must **approach** closely. Viewed another way, if $E_f(Q) - E_i(Q)$ were small yet unvarying over some range of geometries (Q), then the HOMO's electron binding energy (and thus radial extent) would remain unchanged over this range of geometries. In such a case, movement along Q would not modulate the HOMO, and thus $\partial\psi_i/\partial Q$ would vanish. Let us consider a few examples to further illustrate.

1.4 A Few Examples

In Fig. 2 are depicted anion and neutral potential curves that are qualitatively illustrative of (1b,4d) the $X^2\Pi$ NH^- case mentioned earlier. In this anion, the HOMO is a non-bonding $2p_\pi$ orbital localized almost entirely on the N atom. As such, its LCAO-MO coefficients are not strongly affected by motion of the N-H bond (because it is a non-bonding orbital). Moreover, the anion and neutral surfaces have nearly identical R_e and ω_e values, and similar D_e values, as a result of which these two surfaces are nearly parallel to one another and are separated by ca. 0.4 eV or more than 3000 cm^{-1}. It has been seen experimentally that excitation of NH^- to the low rotational states of the v=1 vibrational level, which lies above v=0 NH neutral, results in very slow (e.g., cs. 10^8 sec^{-1}) electron ejection, corresponding to ca. one million vibrational periods before detachment occurs. However, excitation to high rotational levels (e.g., J = 40) of v=1 produces much more rapid electron ejection (ca. 10^9 -10^{10} sec^{-1}). These data have been interpreted as saying that vibrational coupling is weak because of the non-bonding nature of the $2p_\pi$ MO, while rotational coupling becomes significant for high J.

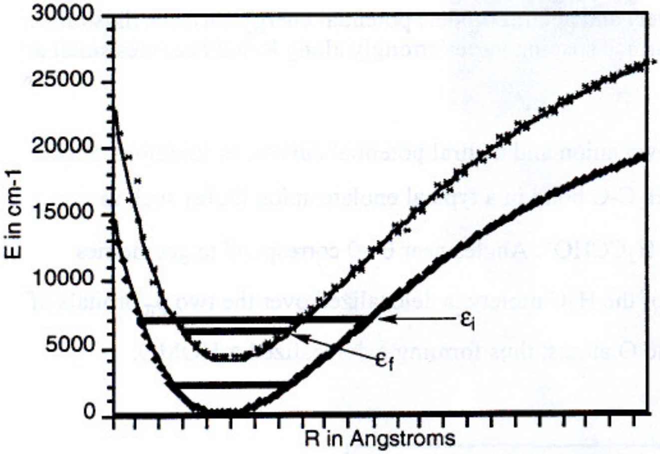


Figure 2. Anion (lower) and neutral (upper) potential energy surfaces illustrative of NH^- where the surface spacing does not vary strongly along R.

Fig. 3 shows a hypothetical case similar to the NH^- situation but for which the anion and neutral curves approach closely at longer bond lengths. In this case, one would expect larger rates of detachment than in NH^- because

1. The state-to-state gap ε_i -ε_f is small for the two states labeled in Fig. 3.
2. The anion and neutral curves approach one another at R values that are accessible to the vibrational wavefunctions of the two states shown in Fig. 3, thus allowing strong modulation of the HOMO.

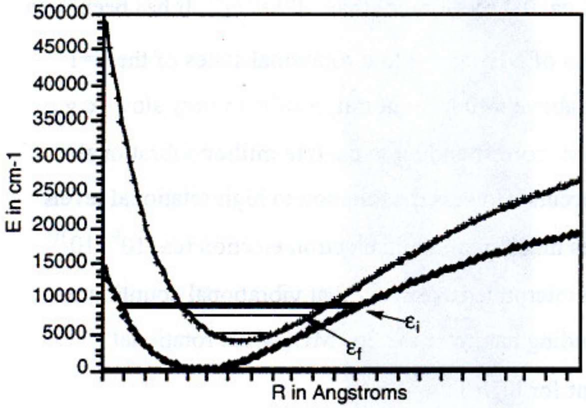


Figure 3. Anion (lower) and neutral (upper) potential energy surfaces illustrative of cases where the surface spacing varies strongly along R and becomes small at some R.

In Fig. 4 are shown anion and neutral potential curves, as functions of the "twist" angle of the H_2C-C bond in a typical enolate anion (2,4e) such as acetaldehyde enolate H_2CCHO^-. Angles near $\theta = 0$ correspond to geometries where the p_π orbital of the H_2C moiety is delocalized over the two p_π orbitals of the neighboring C and O atoms, thus forming a delocalized π HOMO.

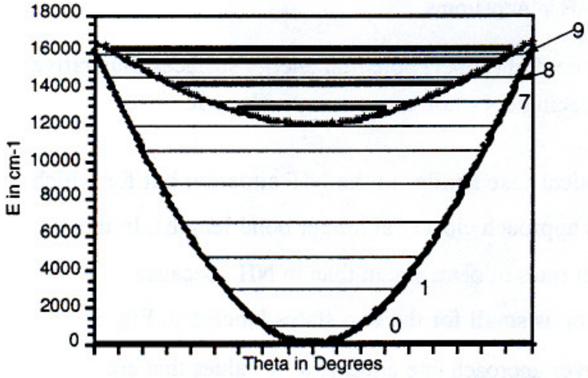


Figure 4. Anion (lower) and neutral (upper) potential energy surfaces illustrative of enolate cases where the surface spacing varies strongly along the H_2C-C torsion angle θ and becomes very small near $\theta = 90°$.

At angles near $\theta = 90°$, the p_π orbital of the H_2C group is no longer stabilized by delocalization; so the HOMO's energy is much higher (as a result of which the anion-neutral surfaces approach closely). In this case, excitation of, for example, v=7 in the H_2C-C torsional mode of the anion might be expected to produce electron ejection because v=7 of the anion lies above v = 0 of the neutral. However, over the range of θ values accessible to both the v=7 vibrational function of the anion and the v=0 function of the neutral, the anion-neutral potential energy gap is quite large (i.e., $E_{ff}(Q) - E_i(Q)$ is large even though $\varepsilon_i - \varepsilon_f$ is small). In contrast, excitation of v=9 of the anion could produce more rapid electron ejection (to v=2 of the neutral, but not to v=0 of the neutral) because for the v=9 → v=2 transition there are angles accessed by both v=9 anion and v=2 neutral vibrational functions for which $E_{ff}(Q) - E_i(Q)$ is small and changing; moreover, the state-to-state gap $\varepsilon_i - \varepsilon_f$ is also small in this case.

The purpose of these examples and of considering the nature of the electronic non BO matrix element was to prepare for critical approximations that are to be introduced. In particular,

1. We will focus on transitions for which $\underline{\varepsilon_i - \varepsilon_f}$ is small.
2. We will focus on molecular deformations that most strongly modulate the anion's HOMO, so
3. we will focus on geometries Q near which the anion-neutral surface spacing is small and changing.

2. TIME CORRELATION FUNCTION EXPRESSION FOR RATES

Before dealing further with the non Born-Oppenheimer case, it is useful to recall how one can cast other rate expressions, such as the rate of photon absorption (7) accompanying an electronic transition in a molecule, in terms of a

Fourier transform of a time dependent function that involves dynamical motions on the initial and final electronic states' potential energy surfaces.

2.1 The Optical Spectroscopy Case

2.1.1 From Wentzel-Fermi Golden Rule to the Time Domain

The expression for the rate R (sec^{-1}) of photon absorption due to coupling V between a molecule's electronic and nuclear charges and an electromagnetic field is given through first order in perturbation theory by the well known Wentzel Fermi "golden rule" formula (7,8):

$$R = (2\pi/\hbar)|\langle\psi_i \chi_i |V| \psi_f \chi_f\rangle|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega). \tag{14}$$

Here, $\psi_{i,f}$ and $\chi_{i,f}$ are the initial and final state electronic and vibration-rotation state wavefunctions, respectively, and $\varepsilon_{i,f}$ are the respective state energies which are connected via a photon of energy $\hbar\omega$. For a particular electronic transition (i.e., a specific choice for ψ_i and ψ_f and for a specific choice of initial vibration-rotation state, it is possible to obtain an expression for the total rate R_T of transitions from this particular initial state into all vibration-rotation states of the final electronic state. This is done by first using the Fourier representation of the Dirac δ function:

$$\delta(\varepsilon_f - \varepsilon_i - \hbar\omega) = (1/2\pi\hbar) \int \exp[it(\varepsilon_f - \varepsilon_i - \hbar\omega)/\hbar]\, dt \tag{15}$$

and then summing over the indices labeling the final vibration-rotation states χ_f:

$$R_T = (2\pi/\hbar)\Sigma_f \ (1/2\pi\hbar) \int \exp[it(\varepsilon_f - \varepsilon_i - \hbar\omega)\ /\hbar] \\ \langle\psi_i \chi_i |V| \psi_f \chi_f\rangle \langle\psi_i \chi_i |V| \psi_f \chi_f\rangle^* \, dt. \tag{16}$$

Next, one introduces the electronic transition matrix element (which may be an electric dipole matrix element, but need not be so restricted for the development presented here)

$$\mu_{i,f} = <\psi_f|V|\psi_i> \tag{17}$$

and uses the facts that the $\psi_{i,f}$ are eigenfunctions of the electronic Hamiltonian h_e and that the $\chi_{i,f}$ are eigenfunctions of the vibration-rotation Hamiltonia $T + V_{i,f}(Q)$ belonging to the two electronic states having potential energies $V_{i,f}(Q)$ and vibration-rotation kinetic energy T (both of which are functions of the molecule's atomic position coordinates collectively denoted Q)

$$h_e \psi_{i,f} = V_{i,f}(Q)\, \psi_{i,f} \tag{18a}$$

$$[T + V_{i,f}(Q)\,]\, \chi_{i,f} = \varepsilon_{i,f}\, \chi_{i,f}\,. \tag{18b}$$

These identities then allow R_T to be rewritten as

$$\begin{aligned} R_T &= (2\pi/\hbar)\Sigma_f \;\; (1/2\pi\hbar) \int \exp[-it\ \omega] \\ &<\chi_i\,|\exp(-ith_i/\hbar)\ \mu_{i,f}{}^*|\ \chi_f> <\chi_f \exp(ith_f/\hbar)|\ \mu_{i,f}\,|\,\chi_i> \mathrm{dt}. \end{aligned} \tag{19}$$

In this form, the completeness of the $\{\chi_f\}$

$$\Sigma_f\, |\chi_f><\chi_f| = 1 \tag{20}$$

can be used to eliminate the sum over the vibration-rotation states belonging to the final electronic state and thus express R_T in the following manner:

$$\begin{aligned} R_T &= \ (2\pi/\hbar)\ (1/2\pi\hbar) \int \exp[-it\ \omega] \\ &< \exp(ith_i/\hbar)\chi_i\ |\ \mu_{i,f}{}^*\ \exp(ith_f/\hbar)\ \mu_{i,f}\,|\ \chi_i > \mathrm{dt}. \end{aligned} \tag{21}$$

The above expression is often visualized (and computed) (9) in terms of the Fourier transform of the overlap of two time-propagated wavefunctions:

(a) One function F_1 is equal to the initial vibration-rotation function $|\chi_i>$ upon which the electronic transition perturbation $\mu_{i,f}$ acts, after which the resultant product function is propagated for a time t on the final-state's potential energy surface by using the propagator $\exp(ith_f/\hbar)$.

(b) The second function F_2 is equal to the initial vibration-rotation function $|\chi_i\rangle$ which is propagated for time t on the initial-state's potential energy surface using the propagator $\exp(ith_i/\hbar)$ (which, of course simply produces $\exp(it\varepsilon_i/\hbar)$ times $|\chi_i\rangle$) , after which the electronic transition perturbation $\mu_{i,f}$ is allowed to act.

The overlap $\langle F_2 |F_1\rangle$ is then Fourier transformed at the energy $\hbar\omega$ of the photon to obtain the rate R_T of absorption of photons of frequency ω.

Before returning to the non-BO rate expression, it is important to note that, in this spectroscopy case, the perturbation (i.e., the photon's vector potential) appears explicitly only in the $\mu_{i,f}$ matrix element because this external field is purely an electronic operator. In contrast, in the non-BO case, the perturbation involves a product of momentum operators, one acting on the electronic wavefunction and the second acting on the vibration/rotation wavefunction because the non-BO perturbation involves an explicit exchange of momentum between the electrons and the nuclei. As a result, one has matrix elements of the form $\langle\chi_i| \langle\psi_i |P| \psi_f\rangle(P/\mu)\chi_f\rangle$ in the non-BO case where one finds $\langle\chi_i| \langle\psi_i |V| \psi_f\rangle|\chi_f\rangle$ in the spectroscopy case. A primary difference is that derivatives of the vibration/rotation functions appear in the former case (in $(P/\mu)\chi$) where only χ appears in the latter.

2.1.2 The Semi-Classical Approximation to R_T

There are various approximations (7) to the above expression for the absorption rate R_T that offer further insight into the photon absorption process and form a basis for comparison to the non Born-Oppenheimer rate expression. The most classical (and hence, least quantum) approximation is to ignore the fact that the kinetic energy operator T does not commute with the potentials $V_{i,f}$ and thus to write

$$\exp(ith_{i,f}/\hbar) \cong \exp(itT/\hbar)\,\exp(itV_{i,f}/\hbar). \tag{22}$$

Inserting this into the above equation for R_T and also assuming that T also commutes with $\mu_{i,f}$ (or that $\mu_{i,f}$ does not depend significantly on geometry Q), gives

$$R_T = (2\pi/\hbar)\,(1/2\pi\hbar) \int \exp[-it\,\omega]$$
$$< \chi_i \exp(itV_i/\hbar)|\, \mu_{i,f}{}^* \exp(itV_f/\hbar)|\, \mu_{i,f} \,|\, \chi_i > dt. \tag{23}$$

Then, carrying out the Fourier integral over time gives,

$$(1/2\pi\hbar) \int \exp[it(V_f - V_i - \hbar\omega)\,/\hbar]\,dt = \delta(V_f - V_i - \hbar\omega). \tag{24}$$

This delta function can be used in the expression for R_T to constrain the multidimensional integral over vibration-rotation coordinates (denoted Q) to those specific values which obey the energy conservation condition

$$\hbar\omega = V_f(Q) - V_i(Q), \tag{25}$$

thereby yielding

$$R_T = (2\pi/\hbar) < \chi_i \,|\, \mu_{i,f}{}^* \,\delta(V_f - V_i - \hbar\omega)\, \mu_{i,f} \,|\, \chi_i > . \tag{26}$$

This semi-classical result can be interpreted as saying that R_T is given as the norm of the function $\mu_{i,f}\chi_i$, consisting of the perturbation $\mu_{i,f}$ acting on the initial vibration-rotation state, constrained to those regions of space which obey the condition $\hbar\omega = V_f(Q) - V_i(Q)$. This condition is equivalent to constraining the integration to those regions within which the change in classical kinetic energy in moving from the initial-state surface V_i to the final-state surface V_f is zero. One can visualize such geometries as those at which the upper potential energy surface $V_f(Q)$ is intersected by the lower surface $V_i(Q)$ once the lower surface is shifted to higher energy by an amount $\hbar\omega$. In Fig. 5 is shown such an intersection between a $V_f(Q)$ surface and a lower-state $V_i(Q)$ surface that has been shifted upward in energy. In this example, transitions between the initial level ε_i and the final level ε_f, whose difference $\varepsilon_f - \varepsilon_i = \hbar\omega$ determines the energy shift, would occur at R values near where the two surfaces cross.

2.1.3 Relation to Landau-Zener Surface Hopping Rates

It is instructive to examine further the approximate semi-classical form for R_T shown above because, when viewed as a rate of transition between two intersecting energy surfaces, one anticipates that connection can be made with the well known Landau-Zener theory (10). For a non-linear molecule with N atoms, the potentials $V_{i,f}(Q)$ depend on 3N-6 internal degrees of freedom (for a linear molecule, $V_{i,f}$ depend on 3N-5 internal coordinates). The subspace S

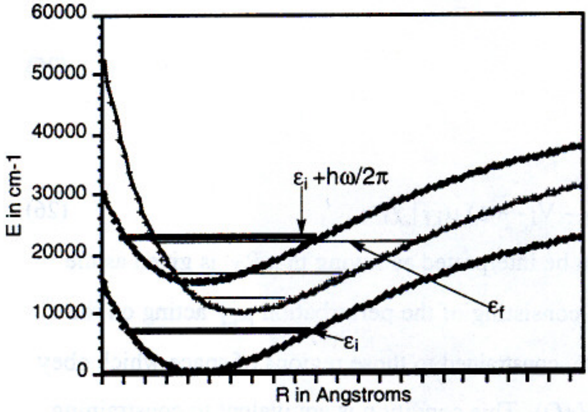


Figure 5. Anion (lowest) and neutral (second lowest at large R) potential energy surfaces arising in the photon absorption case. The curve that is highest in energy at large R is the anion surface that has been shifted upward in energy by the photon's energy $\hbar\omega$ (which has been chosen to make ε_f equal to ε_i plus the photon's energy).

within which $V_f(Q) = V_i(Q) + \hbar\omega$ will be of dimension 3N-7 for the non-linear molecule case. Any geometrical arrangement of the molecule can be described by specifying an orientation Ω (i.e., three orientation or Euler angles for a non-linear molecule), a 3N-7 component vector **s** lying within the subspace S and a distance d along the unit vector **n** that is normal to S at **s**:

$$\mathbf{Q} = \{\Omega , \mathbf{R} \}, \text{ where } \mathbf{R} = \mathbf{s} + \mathrm{d}\ \mathbf{n}. \tag{27}$$

Points lying within S are characterized by d=0.

The integral appearing in R_T can be rewritten (7b) as an integral over orientations, an integral over the 3N-7 dimensional subspace S, and a one-dimensional integral over d:

$$R_T = (2\pi/\hbar)\int d\Omega \int dS \int dd\ |\chi_i(\mathbf{s},d,\Omega)|^2\ |\mu_{i,f}(\mathbf{s},d,\Omega)|^2\ \delta(V_f(\mathbf{s},d) - V_i(\mathbf{s},d) - \hbar\omega). \tag{28}$$

Expanding $V_f(\mathbf{s},d) - V_i(\mathbf{s},d) - \hbar\omega$ in powers of d about the point d=0 and realizing that $V_f(\mathbf{s},0) - V_i(\mathbf{s},0) - \hbar\omega = 0$, allows the delta function to be written as a delta function for the variable d:

$$\delta(V_f(\mathbf{s},d) - V_i(\mathbf{s},d) - \hbar\omega) = \delta(V_f(\mathbf{s},0) - V_i(\mathbf{s},0) - \hbar\omega + [F_f(\mathbf{s}) - F_i(\mathbf{s})]\ d)$$
$$= |F_f(\mathbf{s}) - F_i(\mathbf{s})|^{-1}\ \delta(d). \tag{29}$$

Here, $F_{i,f}(\mathbf{s})$ are the gradients of the respective potentials $V_{i,f}$ along the direction **n** normal to S evaluated at the point **s**,d=0; these gradients, of course, are the negatives of the classical forces normal to S experienced on the $V_{i,f}$ surfaces. With this expression for the delta function, the rate R_T can be expressed as an integral over orientations and over coordinates totally within the space S:

$$R_T = (2\pi/\hbar)\int d\Omega \int dS\ |\chi_i(\mathbf{s},0,\Omega)|^2\ |\mu_{i,f}(\mathbf{s},0,\Omega)|^2\ |F_f(\mathbf{s}) - F_i(\mathbf{s})|^{-1}. \tag{30}$$

The Landau-Zener expression for the probability P of moving from $V_i(Q) + h\omega$ to $V_f(Q)$ under the influence of the perturbation $\mu_{i,f}(\mathbf{s},0,\Omega)$ is

$$P = 2\pi \ |\mu_{i,f}(\mathbf{s},0,\Omega)|^2 \, [\ |\ F_f(\mathbf{s}) - F_i(\mathbf{s})|\ \hbar v_d]^{-1}, \qquad (31)$$

where v_d is the speed at which flux passes through the intersection of the two surfaces (n.b., any velocity components lying within S do not cause flux to move between the surfaces since, within S, the surfaces are degenerate). If this probability is multiplied by the probability of the molecule residing within S (i.e., by $|\chi_i(\mathbf{s},0,\Omega)|^2$), then by the rate at which the molecule moves from d=0 to d=δ (i.e., by v_d/δ), and if one then integrates over all orientations and all S and over the small range d=0 to d=δ, one obtains:

$$\int d\mathbf{S}\, d\Omega \ |\chi_i(\mathbf{s},0,\Omega)|^2 (v_d/\delta)\, P\, \delta$$

$$= (2\pi/\hbar)\int d\Omega \int d\mathbf{S} \ |\chi_i(\mathbf{s},0,\Omega)|^2 \, |\mu_{i,f}(\mathbf{s},0,\Omega)|^2 \, |\ F_f(\mathbf{s}) - F_i(\mathbf{s})|^{-1} = R_T. \qquad (32)$$

That is, the semi-classical approximation to the photon absorption rate is equivalent to a Landau-Zener treatment of the probability of hopping from $V_i + \hbar\omega$ to V_f induced by the electronic coupling perturbation $\mu_{i,f}(\mathbf{s},0,\Omega)$.

2.2 The Non Born-Oppenheimer Case

2.2.1 From Wentzel-Fermi Golden Rule to the Time Domain

Let us now consider how similar the expression for rates of radiationless transitions induced by non Born-Oppenheimer couplings can be made to the expressions given above for photon absorption rates. We begin with the corresponding (6,4g) Wentzel-Fermi "golden rule" expression given in Eq. (10) for the transition rate between electronic states $\psi_{i,f}$ and corresponding vibration-rotation states $\chi_{i,f}$ appropriate to the non BO case:

$$R = (2\pi/\hbar) \int |<\chi_i| <\psi_i\ |P|\ \psi_f >(P/\mu)\chi_f >|^2\ \delta(\varepsilon_f + E - \varepsilon_i)\ \rho(E)\ dE. \tag{10}$$

We recall that $\varepsilon_{i,f}$ are the vibration-rotation energies of the molecule in the anion and neutral molecule states, E denotes the kinetic energy carried away by the ejected electron, and the density of translational energy states of the ejected electron is $\rho(E)$. Also recall that we use the short hand notation to symbolize the multidimensional derivative operators that arise in non BO couplings and that embody the momentum-exchange between the vibration/rotation and electronic degrees of freedom:

$$(P\psi_f\ )(P/\mu\chi_f) = \Sigma_a\ (-i\hbar\partial\psi_f/\partial R_a)\ (-i\hbar\partial\chi_f/\partial R_a)/m_a\ , \tag{11}$$

where R_a is one of the Cartesian coordinates (X_a, Y_a, Z_a) of the a^{th} atom whose mass is m_a. These 3N coordinates span the same space as the three center of mass coordinates plus the Ω , s, and d coordinates used earlier in detailing the semi-classical photon absorption rate expression.

In the event that some subset $\{Q_i\}$ of internal vibration or rotation coordinates have been identified as inducing the radiationless transition, $(P\psi_f\ )(P/\mu\chi_f)$ would represent $\Sigma_j\ (-i\hbar\partial\psi_f/\partial Q_j)\ (-i\hbar\partial\chi_f/\partial Q_j)/(\mu_j)$, where μ_φ is the reduced mass associated with the coordinate Q_j. As indicated in the discussion of Sec. I. C, it is usually straightforward to identify which distortional modes need to be considered by noting which modes most strongly modulate the anion's HOMO. So, for the remainder of this work, we will assume that such active modes have been identified as a result of which the sum $\Sigma_j\ (-i\hbar\partial\psi_f/\partial Q_j)\ (-i\hbar\partial\chi_f/\partial Q_j)/(\mu_j)$ will include only these modes. The integration over all of the other coordinates contained in the matrix element $<\chi_i|\ <\psi_i\ |P|\ \psi_f >(P/\mu)\chi_f>$ in Eq. (10) can then be carried out (assuming the electronic element $<\psi_i\ |P|\ \psi_f >$ to not depend significantly on these coordinates) to produce an effective Franck-Condon like factor (FC):

$$<\chi_i| <\psi_i\ |P|\ \psi_f >(P/\mu)\chi_f >$$

$$= \Pi_{j=\text{inactive}} \int dQ_j <\chi_{i,j}\ |\chi_{f,j}> \Pi_{j=\text{active}} \int dQ_j\ <\chi_{i,j}|\ <\psi_i\ |P|\ \psi_f >(P/\mu)\chi_{f\ ,j}>$$

$$= \text{FC}\ \Pi_{j=\text{active}} \int dQ_j\ <\chi_{i,j}|\ <\psi_i\ |P|\ \psi_f >(P/\mu)\chi_{f\ ,j}>. \qquad (32)$$

Since, by assumption, the anion and neutral molecule do not differ significantly in their geometries (and vibrational frequencies) along the coordinates contributing to the FC factor (otherwise, the anion-neutral energy gap would depend substantially on these modes), the FC factor is probably close to unity in magnitude. Hence, for the remainder of this paper, we will focus only on the active-mode part of this expression, and will do so assuming only one such mode is operative (i.e., we treat one active mode at a time).

Introducing the electronic coupling matrix element

$$m_{i,f} = <\psi_f\ |P|\ \psi_i>, \qquad (33)$$

which plays a role analogous to the $\mu_{i,f}$ of photon absorption theory, and realizing that P is a Hermitian operator, allows the non BO rate R to be rewritten as:

$$R = (2\pi/\hbar) \int <(P/\mu)\chi_i|\ m_{i,f}{}^*|\chi_f> <\chi_f\ |\ m_{i,f}\ (P/\mu)\chi_i>$$
$$\delta(\varepsilon_f\ + E - \varepsilon_i\ )\ \rho(E)\ dE. \qquad (34)$$

If the Fourier integral representation of the delta function is introduced and the sum over all possible final-state vibration-rotation states $\{\chi_f\}$ is carried out, the total rate R_T appropriate to this non BO case can be expressed as:

$$R_T\ = (2\pi/\hbar)\ \Sigma_f \int\ (1/2\pi\hbar) \int \exp[it(\varepsilon_f\ - \varepsilon_i\ +E)/\hbar]$$
$$<(P/\mu)\chi_i|\ m_{i,f}{}^*|\chi_f> <\chi_f\ |\ m_{i,f}\ (P/\mu)\chi_i>\ dt\ \rho(E)\ dE. \qquad (35)$$

The next step is to replace $(\varepsilon_f + E) <\chi_f|$ by $<\chi_f\ |\ (T + V_f\ +E)$ and $(\varepsilon_i\ )|\ \chi_i >$ by $|(T + V_i\ )\ \chi_i>$ which reduces R_T to

$$R_T = (2\pi/\hbar)\, \Sigma_f \int (1/2\pi\hbar) \int \rho(E) <m_{i,f}(P/\mu)\, \exp(it(T + V_i)/\hbar)\, \chi_i| \; |\chi_f> <\chi_f|\exp(it(E+ T + V_f)/\hbar)\, m_{i,f}(P/\mu)\chi_i> dt\, dE. \tag{36}$$

The sum $\Sigma_f |\chi_f><\chi_f| = 1$ can then be carried out to give

$$R_T = (2\pi/\hbar) \int (1/2\pi\hbar) \int \rho(E) \; <m_{i,f}(P/\mu)\, \exp(it(T + V_i)/\hbar)\, \chi_i \,|\, \exp(it(E+ T + V_f)/\hbar)\, m_{i,f}(P/\mu)\chi_i> dt\, dE. \tag{37}$$

In this form, the rate expression looks much like that given for the photon absorption rate in Eq. (21), but with $m_{i,f}(P/\mu)$ replacing the molecule-photon interaction potential V. As in the absorption case, one can view (and even compute) R_T as the Fourier transform of the overlap of two time propagated functions:

(a) The first F_1 is the initial vibration-rotation state χ_i upon which the non BO perturbation $m_{i,f}(P/\mu)$ acts after which propagation on the neutral molecule's potential surface V_f is effected via $\exp(it(T + V_f)/\hbar)$.

(b) The second F_2 is the initial function χ_i which is propagated on the anion's surface V_i via $\exp(it(T + V_i)/\hbar)$ (producing, of course, $\exp(it\varepsilon_i/\hbar)\,\chi_i$) after which the perturbation $m_{i,f}(P/\mu)$ is allowed to act.

The time dependent overlap $<F_2 | F_1>$ is then Fourier transformed at energy $E = \varepsilon_i - \varepsilon_f$, and multiplied by the density of states $\rho(E)$ appropriate to the electron ejected with kinetic energy E.

It should be noted that to use the above time-domain formulas for computing rates, one would need an efficient means of propagating wave packets on the neutral and anion surfaces, and one, specifically, that would be valid for longer times than are needed in the optical spectroscopy case. Why? Because, in the non-BO situation, the $<F_2 | F_1>$ product is multiplied by $\exp(iEt/\hbar)$ and then integrated over time. In the spectroscopy case, $<F_2 | F_1>$ is multiplied by exp(-iωt) and integrated over time. However, in the former case, E corresponds to the (small) energy difference $E = \varepsilon_i - \varepsilon_f$, whereas ħω is equal to the energy of the optical spectroscopic transition. Hence, short time propagators give sufficiently accurate $<F_2 | F_1>$ functions to use in the spectroscopy case, but longer time propagations will be needed in the non-BO case.

2.2.2 The Simplest Semi-Classical Approximation Fails

If one attempts to follow the photon absorption derivation and make the assumption that the kinetic energy operator T commutes with $V_{i,f}$ and with $m_{i,f}$ (n.b., T does commute with P/μ), the following expression is obtained for R_T:

$$R_T = (2\pi/\hbar) \int (1/2\pi\hbar) \int \rho(E)$$
$$<m_{i,f}(P/\mu) \exp(it(V_i)/\hbar)\, \chi_i \,|\, \exp(it(E+ V_f)/\hbar)\, m_{i,f}\, (P/\mu)\chi_i> dt\, dE. \quad (38)$$

The Fourier integral over time can be carried out and one obtains

$$R_T = (2\pi/\hbar) \int \rho(E) <m_{i,f}(P/\mu)\ \ \chi_i \,|\, \delta(V_f + E- V_i)\, m_{i,f}\, (P/\mu)\chi_i> dE. \quad (39)$$

For anions that are electronically bound, the anion's electronic energy V_i (Q) lies <u>below</u> the neutral molecule's electronic energy V_f (Q) as depicted in Figs. 2-5. Hence, because E is a positive quantity, there are no geometries for which the argument of the delta function in the above expression vanishes and, as a result, the non BO rate can not be cast in terms of shifted intersecting energy surfaces as can the photon absorption rate.

Therefore, the simplest classical treatment in which the propagator exp(it (T+V)/ħ) is approximated in the product form exp(it (T)/ħ) exp(it (V)/ħ) and the nuclear kinetic energy T is conserved during the "transition" produces a nonsensical approximation to the non BO rate. This should not be surprising because (a) In the photon absorption case, the photon induces a transition in the electronic degrees of freedom which subsequently cause changes in the vibration-rotation energy, while (b) in the non BO case, the electronic and vibration-rotation degrees of freedom must simultaneously interchange energy and momentum and/or angular momentum, which is impossible to do without the nuclei recoiling.

2.2.3 An Approximation that Works

The matrix element occurring in the non BO rate equation

$$M = \langle m_{i,f}(P/\mu) \exp(it(T + V_i)/\hbar)\, \chi_i \mid \exp(it(E + T + V_f)/\hbar)\, m_{i,f}(P/\mu)\chi_i\rangle \qquad (40)$$

can more fruitfully be handled by

a. replacing $\exp(it(T + V_i)/\hbar)\, \chi_i$ by $\exp(it(\varepsilon_i)/\hbar)\, \chi_i$, which is exact, and

b. approximating $\exp(it(E + T + V_f)/\hbar)$ by $\exp(it(E + T)/\hbar) \exp(it(V_f)/\hbar)$, which is an approximation, thus achieving

$$M = \langle m_{i,f}(P/\mu) \exp(it(\varepsilon_i)/\hbar)\, \chi_i \mid \exp(it(E + T)/\hbar) \exp(it(V_f)\, m_{i,f}(P/\mu)\chi_i\rangle. \qquad (41)$$

Now introducing completeness relations in the forms

$$\int dp\, |p\rangle\langle p| = 1 \qquad (42a)$$

$$\int dQ\, |Q\rangle\langle Q| = 1 \qquad (42b)$$

and using $(T + V_i)\, \chi_i = \varepsilon_i\, \chi_i$, allows M to be written as

$$M = \int dQ' \int dQ \int dp \langle m_{i,f}(P/\mu) \exp(it(\varepsilon_i)/\hbar)\, \chi_i\ |Q'\rangle$$
$$\langle Q'|\, p\rangle \exp(it(E + T_{class})/\hbar) \langle p|Q\rangle\langle Q| \exp(it(V_f(Q)/\hbar)\, m_{i,f}(P/\mu)\chi_i\rangle. \qquad (43)$$

Here T_{class} is the eigenvalue of the Q-coordinate's kinetic energy operator T in the momentum eigenbasis $\{|p\rangle\}$

$$T_{class} = (p^2/2\mu_Q) \qquad (44)$$

and

$$\langle Q'|p\rangle = (2\pi\hbar)^{-1/2} \exp(ipQ'/\hbar) \tag{45}$$

is the coordinate representation of the momentum eigenfunction along the active Q coordinate.

The integration over time can be carried out and gives the following expression fot the total rate:

$$R_T = (2\pi/\hbar) \int \rho(E) \int dQ' \int dQ \int dp \langle m_{i,f} (P/\mu)\, \chi_i \;|Q'\rangle \langle Q'|\, p\rangle$$
$$\delta(T_{class} + E + V_f (Q) - \varepsilon_i) \;\; \langle p|Q\rangle \langle Q|\, m_{i,f} (P/\mu)\chi_i\rangle \, dE. \tag{46}$$

Since the energy E is restricted to match the state-to-state energy differences $E = \varepsilon_i - \varepsilon_f$, the integral over dE in Eq. (46) can be replaced by a sum over accessible final-state ε_f values multiplied by the spacing between neighboring such states $(dE_f = \varepsilon_f - \varepsilon_{f-1})$:

$$R_T = (2\pi/\hbar)\, \Sigma_f\, \rho(\varepsilon_i-\varepsilon_f)dE_f \int dQ' \int dQ \int dp \langle m_{i,f} (P/\mu)\, \chi_i \;|Q'\rangle \langle Q'|\, p\rangle$$
$$\delta(T_{class} + V_f (Q) - \varepsilon_f) \;\; \langle p|Q\rangle \langle Q|\, m_{i,f} (P/\mu)\chi_i\rangle. \tag{47}$$

In this form, which is analogous to Eq. (26) in the photon absorption case, the rate is expressed as a sum over the neutral molecule's vibration-rotation states to which the specific initial state having energy ε_i can decay of (a) a translational state density ρ multiplied by (b) the average value of an integral operator Δ whose coordinate representation is

$$\Delta(Q',Q) = \int dp\, |Q'\rangle m_{i,f} (Q') \langle Q'|\, p\rangle$$
$$\delta(p^2/2\mu_Q + V_f (Q) - \varepsilon_f) \langle p|Q\rangle\, m_{i,f} (Q) \langle Q| \tag{48}$$

with the average value taken for the function

$$\psi = |(P/\mu)\chi_i\rangle \tag{49}$$

equal to the anion's initial vibration-rotation state acted on by P/μ (in the harmonic approximation, $P/\mu\chi_i$ would yield a combination of functions of one higher and one lower quantum of vibration or rotation).

The integral operator Δ can be recast in a different form by carrying out the integration over the p-variable in Eq. (48) identifying

$$f(p) = (2\pi\hbar)^{-1/2} \exp(-ipQ/\hbar)\,(2\pi\hbar)^{-1/2} \exp(ipQ'/\hbar) \qquad (50)$$

and $a = \varepsilon_f - V_f(Q)$. Doing so produces

$$\int_{-\infty}^{\infty} \delta(p^2/2\mu_Q - a) f(p)dp$$

$$= \int_{0}^{\infty} \delta(p^2/2\mu_Q - a) f(p)dp + \int_{-\infty}^{0} \delta(p^2/2\mu_Q - a) f(p)dp$$

$$= \int_{0}^{\infty} \delta(x - a) f(\sqrt{2\mu_Q x}) \frac{\mu_Q dx}{\sqrt{2\mu_Q x}} + \int_{\infty}^{0} \delta(x - a) f(-\sqrt{2\mu_Q x}) \frac{-\mu_Q dx}{\sqrt{2\mu_Q x}}$$

$$= \int_{0}^{\infty} \delta(x - a) \{f(\sqrt{2\mu_Q x}) + f(-\sqrt{2\mu_Q x})\} \frac{\mu_Q dx}{\sqrt{2\mu_Q x}}$$

$$= \{f(\sqrt{2\mu_Q a}) + f(-\sqrt{2\mu_Q a})\} \frac{\mu_Q}{\sqrt{2\mu_Q a}}$$

$$= \frac{1}{2\pi\hbar} 2\mathrm{Cos}\{[Q' - Q]\sqrt{2\mu_Q(\varepsilon_f - V_f(Q))}/\hbar\} \frac{\mu_Q}{\sqrt{2\mu_Q(\varepsilon_f - V_f(Q))}}. \qquad (51)$$

The quantity $\{2\mu_Q(\varepsilon_f - V_f(Q))\}^{1/2}$ is the classical momentum along the Q coordinate with energy ε_f moving on the <u>neutral</u> molecule's surface $V_f(Q)$, so μ_Q divided into this is the speed of movement at Q_0. Substituting this result back into the expression for R_T gives

$$R_T = (2\pi/\hbar)\sum_f \rho(\varepsilon_i - \varepsilon_f)dE_f \int dQ' \int dQ < m_{i,f}(P/\mu)\chi_i \mid Q' > \frac{1}{\pi\hbar}$$

$$\mathrm{Cos}\{[Q' - Q]\sqrt{2\mu_Q(\varepsilon_f - V_f(Q))}/\hbar\}$$

$$\frac{\mu_Q}{\sqrt{2\mu_Q(\varepsilon_f - V_f(Q))}} < Q \mid m_{i,f}(P/\mu)\chi_i > \qquad (52)$$

Bearing in mind the discussion of the nature of the electronic non BO matrix elements $m_{i,f}(Q)$ given in Sec. I. C, the above rate expression can be further approximated by constraining Q' and Q to the region $Q'=Q=Q_0$ where the anion and neutral surfaces approach most closely:

$$d\{V_f(Q) - V_i(Q)\}/dQ = 0 \text{ at } Q = Q_0. \qquad (53a)$$

If, as assumed, $m_{i,f}(Q)$ is significant only near Q_0, then we can approximate $m_{i,f}$ (Q) as

$$m_{i,f}(Q) = \delta(Q - Q_0)m^* \qquad (53b)$$

where the quantity m* is the integral representing the total strength of the $m_{i,f}$ coupling concentrated at the geometry Q_0

$$m^* = \int m_{i,f}(Q)dQ. \qquad (53c)$$

Introducing this approximation into Eq. (52) and using the fact that the argument of the Cos in Eq. (52) vanishes, allows R_T to be written in its simplest form as:

$$R_T = (2\pi/\hbar)\sum_f \rho(\varepsilon_i - \varepsilon_f)dE_f\{(P/\mu)\chi_i(Q_0)\}^2 >\mid m^* \mid^2 \frac{1}{\pi\hbar v_0} \qquad (54)$$

where v_0 is the velocity along the Q-coordinate at the geometry Q_0:

$$v_0 = \frac{\sqrt{2\mu_Q(\varepsilon_f - V_f(Q_0))}}{\mu_Q} \tag{55}$$

and $|m_i^*|^2$ is the square of the integrated electronic non BO matrix element introduced above (n.g., $|m^*|^2$ has units of $(\mathrm{gm\ cm^2/sec})^2$.

3. INTERPRETATION OF RATE EXPRESSION

The semi-classical expression shown in Eq. (54) for the rate of ejection of electrons from a specified initial vibration-rotation state χ_i (Q) induced by non BO coupling to all accessible neutral-molecule-plus-free-electron final states (labeled f) gives this rate as:

1. A sum over all final vibration-rotation states ε_f lying below ε_i for which the geometry Q_0 is within the classically allowed region of the corresponding vibration-rotation wavefunction χ_f (Q) (so that v_0 is real) of
2. the modulus squared of the function $m^*(P/\mu)\chi_i$ evaluated at Q_0
3. multiplied by the state density $\rho(\varepsilon_i - \varepsilon_f)\, dE_f$ for the ejected electron and multiplied by $(2\pi/\hbar)(1/\pi\hbar)$, and finally
4. divided by the speed v_0 of passage through Q_0 .

4. SUMMARY

The rate of ejection of electrons from anions induced by non BO couplings can be expressed rigorously as a Fourier transform of an overlap function between two functions

$$R_T = (2\pi/\hbar) \int (1/2\pi\hbar) \int \rho(E)$$

$$<m_{i,f}(P/\mu) \exp(it(T + V_i)/\hbar)\, \chi_i \,|\, \exp(it(E+ T + V_f)/\hbar)\, m_{i,f}\, (P/\mu)\chi_i>\, dt\, dE \tag{37}$$

one of which is the initial vibration-rotation function χ_i acted on by the non BO perturbation $m_{i,f}(P/\mu)$ and then propagated on the neutral molecule surface, the other being the initial χ_i propagated on the anion surface and then acted on by $m_{i,f}(P/\mu)$. In computer applications, it would be efficient to compute R_T in this manner whenever long-time surface propagation tools are applicable.

By introducing the simplest semi-classical approximation to the propagators, in which the nuclear motion kinetic energy is assumed to commute with the anion and neutral potential energy functions and with the non BO coupling operators, one obtains

$$R_T = (2\pi/\hbar) \int \rho(E) < m_{i,f}(P/\mu)\ \chi_i \,|\, \delta(V_f + E - V_i) \,|\, m_{i,f}(P/\mu)\chi_i > dE. \tag{39}$$

Unlike its success in treating the photon absorption rate expression, this simplest approximation produces a nonsensical expression in the present case because there are no geometries at which $(V_f + E - V_i) = 0$, as a result of which R_T is predicted to vanish. In the photon absorption situation, there are geometries at which the classical momentum is conserved (i.e., where the excited and shifted ground state surfaces intersect). In the non BO transition case, such geometries do not exist because the transition is not one in which the nuclear-motion momentum is conserved. Quite to the contrary, non BO transitions involve the simultaneous interchange of energy (from the nuclei to the electrons) and of momentum and/or angular momentum.

Improving on the semi-classical treatment of the vibration-rotation motion only slightly allows R_T to be recast in a form

$$R_T = (2\pi/\hbar)\sum_f \rho(\varepsilon_i - \varepsilon_f)dE_f \int dQ' \int dQ < m_{i,f}(P/\mu)\chi_i \,|\, Q' > \frac{1}{\pi\hbar}$$

$$\mathrm{Cos}\{[Q' - Q]\sqrt{2\mu_Q(\varepsilon_f - V_f(Q))}\,/\,\hbar\}$$

$$\frac{\mu_Q}{\sqrt{2\mu_Q(\varepsilon_f - V_f(Q))}} < Q \,|\, m_{i,f}(P/\mu)\chi_i > \tag{52}$$

that may prove computationally useful in cases where the geometry (Q)-dependence of the non BO electronic matrix element $m_{i,f}$ is known. In this expression, the rate is given in terms of the functions $m_{i,f}(P/\mu)\chi_i$, the density of state function ρ, the classical momentum on the neutral molecule's surface, and a Cos function whose argument is the classical action connecting the points Q' and Q via the momentum of the neutral molecule having energy ε_f. This Cos function will oscillate rapidly when this action is large, so its dominant contributions to the rate will arise for small momenta and/or small Q'-Q values.

Finally, by using what is known about the geometry dependence of the $m_{i,f}$ functions (i.e., that $m_{i,f}$ is strongly "peaked" near geometries Q_0 where the anion and neutral surfaces approach most closely), it is possible to further simplify the semi-classical equation for R_T

$$R_T = (2\pi/\hbar)\sum_f \rho(\varepsilon_i - \varepsilon_f)dE_f\{(P/\mu)\chi_i(Q_0)\}^2 >|m^* \ |^2 \frac{1}{\pi\hbar v_0} \tag{54}$$

to one that requires knowledge of the derivative of the initial-state vibrational wavefunction $(P/\mu\chi_i)$ evaluated at Q_0, the speed v_0 at which classical motion on the neutral molecule surface passes through Q_0, the density of states ρ, and the magnitude of the integrated strength m* of $m_{i,f}$ at Q_0.

It should be emphasized that it is not the modulus $|\chi_i\ (Q_0)\ |^2$ that enters into the weighting function in Eq. (54), it is the derivative $(P/\mu\chi_i)$ whose modulus squared enters. In contrast, in the photon absorption case, the rate involves, as given either in Eq. (28) or Eq. (30)

$$\begin{aligned} R_T = (2\pi/\hbar)\int d\Omega \int dS \int dd\ |\chi_i(s,d,\Omega)|^2\ |\mu_{i,f}(s,d,\Omega)|^2\ \delta(V_f(s,d) \\ - V_i(s,d) - \hbar\omega). \end{aligned} \tag{28}$$

$$R_T = (2\pi/\hbar)\int d\Omega \int dS \ |\chi_i(\mathbf{s},0,\Omega)|^2 |\mu_{i,f}(\mathbf{s},0,\Omega)|^2 \ | F_f(\mathbf{s}) - F_i(\mathbf{s})|^{-1}. \qquad (30)$$

the modulus squared of χ_i itself. The qualitative difference in the two cases has to do with the inherent requirement that the nuclear-motion momentum and/or angular momentum change in non BO transitions while the same quantities are preserved in photon absorption events (in the semi-classical treatment).

ACKNOWLEDGMENTS

This work has been supported by NSF Grant CHE-9618904 and by proceeds of the Henry Eyring Endowed Chair. The author wishes to acknowledge his friend and colleague, Professor N. Y. Öhrn, for inspiring him to excellence in science, on the slopes, and in the back country.

REFERENCES

(1a) Lykke, K. R.; Neumark, D. M.; Andersen, T.; Trapa, V. J.; Lineberger, W. C. *J. Chem. Phys.* **1987**, *87* , 6842.

(1b) Neumark, D. M.; Lykke,K. R.; Andersen, T.; Lineberger, W. C. *J. Chem. Phys*. **1985**, *83*, 4364.

(1c) Andersen, T.; Lykke, K. R.; Neumark, D. M.; Lineberger, W. C. *J. Chem. Phys*. **1987**, *86*, 1858.

(2a) Marks, J.; Wentzel, D. M.; Comita, P. B.; Brauman, J. I. *J. Chem. Phys*. **1986**, *86*, 5284.

(2b) Meyer, F. K.; Jasinski, J. M.; Rosenfeld, R. N.; Brauman, J. I. *J. Am. Chem. Soc*. **1982**, *104*, 663.

(2c) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys*. **1979**, *71*, 1030. Mead, R. D.; Lykke, K. R.; Lineberger, W. C.; Marks, J.; Brauman, J. I. *J. Chem. Phys*. **1984**, *81*, 4883.

(2d) Jackson, R. L.; Zimmerman, A. H.; Brauman, J. I. *J. Chem. Phys*. **1979**, *71*, 2088.

(2e) Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 7203.

(2f) Zimmerman, A. H.; Brauman, J. I. *J. Chem. Phys*. **1977**, *66*, 5823.

Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc*. **1981**, *103*, 6501.

(4a) Acharya, P.; Kendall, R.; Simons, J. *SASP***1984**, 84.

(4b) Acharya, P. K.; Kendall, R. A.; Simons, J. *J. Am. Chem. Soc*. **1984**, *106*, 3402.

(4c) Acharya, P. K.; Kendall, R.; Simons, J. *J. Chem. Phys*. **1985**, *83*, 3888.

(4d) Chalasinski, G.; Kendall, R. A.; Taylor, H.; Simons, J. *J. Phys. Chem*. **1988**, *92*, 3086.

(4e) O'Neal, D.; Simons, J. *J. Phys. Chem*. **1988**, *93*, 58.

(4f) Simons, J. *J. Chem. Phys*. **1989**, *91*, 6858.

(4g) Simons, J. *J. Am. Chem. Soc*. **1981**, *103*, 3971.

(5) Clary, D. L. *J. Phys. Chem*. **1988**, *92*, 3173.

(6) Berry, R. S. *J. Chem. Phys*. **1966**, *45*, 1228.

(7a) Simons, J. *J. Phys. Chem*. **1982**, *86*, 3615.

(7b) Taylor, H.; Simons, J. *J. Phys. Chem*. **1986**, *90*, 580.

(7c) Lax, M. *J. Chem. Phys*. **1952**, *30*, 1752.

(7d) Noda, C.; Zare, R. N. *J. Mol. Spectros*. **1982,** *95*, 254.

(8a) A good textbook treatment of how time correlation functions relate to photon absorption and other rates is given in D. A. McQuarrie, D. A. "Statistical Mechanics"; Harper and Row: New York, 1976.

(8b) Gordon, R. G. *Adv. Mag. Reson*. **1968**, *3*, 1.

(9a) Bergsma, J. P.; Berens, P. H.; Wilson, K. R.; Fredkin, D. R.; Heller, E. J. *J. Phys. Chem*. **1984**, *88*, 612.

(9b) Heller, E. J.; Brown, R. C. *J. Chem. Phys*. **1983**, *79*, 3336.

(9c) Heller, E. J. *J. Chem. Phys*. **1978**, *68*, 2066.

(9d) Heller, E. J. *J. Chem. Phys.* **1978**, *68*, 3891.

(10a) Landau, L. *Phys. Z. Sowjetunion* **1932**, *1*, 88.

(10b) Zener, C. *Proc. Roy. Soc. London* **1932**, *A137*, 696.