Applications of a Simple Dynamical Model to the Reaction Path Hamiltonian: Tunneling Corrections to Rate Constants, Product State Distributions, Line Widths of Local Mode Overtones, and Mode Specificity in Unimolecular Decomposition

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A simple but often reasonably accurate dynamical model—a synthesis of the semiclassical perturbation (SCP) approximation of Miller and Smith and the infinite order sudden (IOS) approximation—has been shown previously to take an exceptionally simple form when applied to the reaction path Hamiltonian derived by Miller, Handy, and Adams. This paper shows how this combined SCP-IOS reaction path model can be used to provide a simple but comprehensive description of a variety of phenomena in the dynamics of polyatomic molecules.

I. Introduction

The idea of describing a chemical reaction as motion along some reaction coordinate in configuration space is an old one that has been popular at the qualitative level, e.g., in providing a language for describing complex organic reactions, and has also been pursued more quantitatively for describing reaction dynamics at a more precise level. Among these lines one of the present authors and co-workers have recently derived an explicit form of the classical Hamiltonian, the "reaction path Hamiltonian", which characterizes a general polyatomic system as motion along a reaction path (the steepest descent path in mass-weighted Cartesian coordinates) plus harmonic oscillator-like deviations about the reaction path in all the (many) directions orthogonal to it. This particular formulation of the reaction path idea was carried out with the view of using ab initio quantum chemistry calculations to determine all the parameters in the Hamiltonian, and one of its important features is that all such information is in principle obtainable from a relatively small number of calculations of the potential energy surface. Applications of this approach to date have been to the role of tunneling in the unimolecular reactions

- HNC → HCN
- H₂CO → H₂ + CO
- H₂C≡C → HC≡CH

The most recent development involving the reaction path Hamiltonian is that by Miller and Shi in showing how a relatively simple, but reasonably accurate, dynamical model—a synthesis of the semiclassical perturbation (SCP) model of Miller and Smith and the infinite order sudden approximation (IOS)—can be applied to the reaction path Hamiltonian. This leads to explicit closed-form expressions for S-matrix elements (and thus transition probabilities) describing reaction and energy transfer between the reaction coordinate and the transverse vibrational modes of freedom, and thus allows one to deal in a simple way with aspects of the reaction dynamics that involve the interaction between these degrees of freedom. Some other recent work also dealing with the interaction between motion along the reaction coordinate and the transverse vibrational degrees of freedom is that by Kato and Morokuma. The purpose of this paper is to show how the SCP-IOS reaction path model can be applied to a variety of phenomena in polyatomic reaction dynamics and thus provide a unified description of them all within the same dynamical model. The features that make this interesting from a practical point of view are that the dynamical model is relatively simple, and thus applicable to complex systems, and that the quantities which characterize these phenomena quantitatively are all obtainable in a rather straightforward way from ab initio quantum chemistry conditions.

Section II first summarizes the reaction path Hamiltonian and the SCP-IOS approximation to the dynamics. It is also shown here how the model describes tunneling through transition states (i.e., the saddle point region) of potential energy surfaces, and application to the test problem H + H₂ → H₂ + H shows it to be quantitatively useful. Section III considers product state distributions of a reaction, in particular a reduced distribution, e.g., the distribution of final states for only one degree of freedom, say, summed over all the final states for the other degrees of freedom. Also shown is the specific form taken by the final translational energy distribution. Line widths associated with excitation of overtones of local modes (usually CH stretches) are considered in section IV, and it is shown how the SCP-IOS reaction path model provides a description of this phenomenon and also provides a framework for carrying out quantitative calculations. Finally, section V shows how mode specificity in unimolecular rate constants can, in conjunction with a semi-
classical branching model, be described by the SCP-IOS reaction path model, and section VI concludes.

II. The Reaction Path Hamiltonian and SCP-IOS Approximation

For a nonrotating system of $N$ atoms (i.e., with zero total angular momentum) the reaction path Hamiltonian derived by Miller, Handy, and Adams is

$$ H(p_s, s, P, Q) = \sum_{k=1}^{F-1} \left( \frac{1}{2} p_k^2 + \frac{1}{2} \omega_k(s)^2 q_k^2 \right) + V_0(s) + \frac{1}{2} \left[ p_s - \sum_{k=1}^{F-1} Q_k P_k B_k(s) \right]^2 \frac{\omega_k(s)^2}{\left[ 1 + \sum_{k=1}^{F-1} Q_k B_k(s) \right]^2} \quad (2.1) $$

where $F = 3N - 6$ is the number of degrees of freedom, $(s, p_s)$ are the mass-weighted reaction coordinate and its conjugate momentum, $V_0(s)$ the potential energy along the reaction path, $\{Q_k P_k\}$, $k = 1, ..., F - 1$ the mass-weighted normal mode coordinates and momenta for vibration normal to the reaction path, with frequencies $\omega_k(s)$ that are functions of the reaction coordinate.

The coupling elements $B_k(s)$ couple vibrational modes $k$ and $h'$, and $B_k(s)$ couples vibrational mode $k$ to the reaction coordinate (which is designated mode $k = F$). The coupling elements $B_k(s)$ are a measure of how the curvature of the reaction path couples to mode $k$; the total curvature of the reaction path, $\kappa(s)$, is related to these elements by

$$ \kappa(s) = \left[ \sum_{k=1}^{F-1} B_k(s)^2 \right]^{1/2} \quad (2.2) $$

The coupling functions $B_k(s)$ are essentially a Coriolis-like coupling involving the twist of the vibrational modes about the reaction path as a function of $s$. The coupling functions, as well as $V_0(s)$ and $\omega_k(s)$, are obtainable from the ab initio quantum chemistry calculation of the reaction path and the force constant matrix along it. The Hamiltonian for the rotating case, $J \neq 0$, has also been worked out but is more complicated than for $J = 0$ because of various kinds of rotation–vibration coupling.

For most applications it is useful to transform from the vibrational coordinates and momenta $\{Q_k P_k\}$ to their action angle variables

$$ Q_k = \left[ 2n_k + 1 \omega_k(s) \right]^{1/2} \sin q_k \quad (2.3a) $$

$$ P_k = \left[ (2n_k + 1) \omega_k(s) \right]^{1/2} \cos q_k \quad k = 1, ..., F - 1 \quad (2.3b) $$

In terms of these variables the Hamiltonian becomes

$$ H(p_s, s, n, q) = \frac{1}{2} \left[ p_s - \sum_{k=1}^{F-1} B_k(s) \left( 2n_k + 1 \right) \right] \times $$

$$ \left[ \frac{\omega_k(s)}{\omega_k(s)} \right]^{1/2} \left\{ \sin q_k \cos q_k \right\}^2 \left( 2n_k + 1 \right)^{1/2} \left[ \frac{\omega_k(s)}{\omega_k(s)} \right]^{1/2} \left\{ \sin q_k \cos q_k \right\}^2 + $$

$$ \left\{ 1 + \sum_{k=1}^{F-1} B_k(s) \left[ 2n_k + 1 \omega_k(s) \right]^{1/2} \sin q_k \right\}^2 + $$

$$ V_0(s) + \sum_{k=1}^{F-1} \left( n_k + \frac{1}{2} \right) \omega_k(s) \quad (2.4a) $$

where here the diagonal element $B_k(s)$ is defined by

$$ B_k(s) = - \frac{\omega_k(s)}{2 \omega_k(s)} \quad (2.4b) $$

This form is especially useful for semiclassical applications since the action variables $n_k$ are the classical counterpart of vibrational quantum numbers.

The unified semiclassical perturbation (SCP) and infinite order sudden (IOS) approximations discussed by Miller and Shi give the S-matrix elements (i.e., transition amplitudes) from initial state $n$ of the transverse vibrational modes to final state $n'$ as

$$ S_{n,n'}(E) = \frac{\hbar}{(2\pi)^{1/2}} \int_0^\infty dq \exp \left[ -i \Delta n \cdot q + i \Delta \phi(q) \right] \quad (2.5) $$

where

$$ \Delta n = n' - n \quad (2.6) $$

$$ \phi_0 = \phi(n, E) = -i [2(E - V_s(s))]^{1/2} \sin q \left( 2n_k + 1 \right)^{1/2} \quad (2.7a) $$

$$ \Delta \phi(q) = \Delta \phi(q, n, E) = -i \int_{s_1}^{s_2} ds \left[ 2(E - V_s(s)) \right]^{1/2} B_k(s) \left[ 2n_k + 1 \right]^{1/2} \times $$

$$ \sin \left( q_k + \delta_k(q) \right) + \sum_{k=1}^{F-1} \int_{s_1}^{s_2} ds B_k(s) \left( 2n_k + 1 \right)^{1/2} \left[ \frac{\omega_k'(s)}{\omega_k(s)} \right]^{1/2} \sin \left[ q_k + \delta_k(q) \right] \cos \left( q_k + \delta_k(q) \right) \quad (2.7b) $$

with

$$ \delta_k(q) = \int_{0}^{q} dq' \frac{\omega_k'(s)}{[2(E - V_s(s))]^{1/2}} \quad (2.7c) $$

$V_s(s)$ in eq 2.7 is the vibrationally adiabatic potential

$$ V_s(s) = V_0(s) + \sum_{k=1}^{F-1} \left( n_k + \frac{1}{2} \right) \omega_k(s) \quad (2.8) $$

and $[q_k]$ are the integration variables $q$ of eq 2.5. To ensure a symmetric S matrix, the quantum number $[n_k] = n$ in eq 2.7–2.8 are actually taken to be the averages of the initial and final quantum numbers, i.e., $n \rightarrow 1/2$ (and $n'$).

The phase $\phi_0$ is the WKB phase shift from the vibrationally adiabatic potential, and the phase $\Delta \phi(q)$ is the contribution from the transverse vibrational modes and is therefore what causes inelastic transitions between the various modes and the reaction coordinate. In most scattering applications one is interested in the limits $s_1 \rightarrow -\infty$, $s_2 \rightarrow +\infty$, but we leave open the possibility of other cases. For example, one may wish to choose $s_1 = 0$ and $s_2 = +\infty$, so that the initial state $n$ corresponds to the transition state and the final state $n'$ to products. The transition probability of the $n \rightarrow n'$ transition is, of course, given by

$$ |P_{n,n'}(E)|^2 = |S_{n,n'}(E)|^2 \quad (2.9) $$

As discussed before, eq 2.5 incorporates the infinite order sudden approximation (which would result if the vibrational phase shifts $\delta_k(q)$ of eq 2.7 were set to zero), which is correct in the limit that the transverse vibrational motion is much slower than motion along the reaction coordinate, and also the limit of adiabatic perturbation theory, which is correct when the transverse vibrational motion, is much faster than motion along the reaction coordinate. There is thus a reasonable basis for expecting that the model will be at least semiquantitative in fairly general circumstances.

Miller and Shi have applied this SCP–IOS reaction path model to one of the standard benchmarks for inelastic
Figure 1. Transition probability for the $0 \rightarrow 1$ vibrational excitation of H$_2$ by collision with He, as a function of total energy. H$_2$ is modeled as a Morse oscillator. QM, SCP, and HAR denote the essentially exact quantum mechanical results computed for this collinear system (ref 11), the present results of the SCP-10s reaction path model, and the exact quantum results if H$_2$ is treated as a harmonic oscillator, respectively.

The SCP-10s reaction path model can also be used to describe tunneling through transition state (i.e., saddle point) regions of a potential energy surface. Consider, for example, the standard test problem, collinear H + H$_2 \rightarrow$ H$_2 +$ H. For the total reaction probabilities

$$P_R(E) = \sum |S_{n,0}(E)|^2$$

eq 2.5 and 2.7 give (with $F = 2$)

$$P_R(E) = (2\pi)^{-1} \int_0^{2\pi} dq \exp[i\phi_0 + i\Delta \phi(q)]$$

(2.10)

where the closure relation

$$\sum_{\Delta n} e^{i\Delta n(q-q')} = 2\pi \delta(q-q')$$

has been used. The action integrals $\phi_0$ and $\Delta \phi(q)$ are complex inside the barrier region, i.e., where $E < V_a(s)$, so that eq 2.10 becomes

$$P_s(E) = e^{-2\kappa (2\pi)^{-1} \int_0^{2\pi} dq e^{-2\Delta \phi(q)}}$$

(2.11)

where $\theta_1$ is the vibrationally adiabatic barrier penetration integral

$$\theta_0 = \int_{s_>} ds [2[V_a(s) - E]^{1/2}]$$

(2.12a)

and if only the first term in eq 2.7b for $\Delta \phi$ is retained (i.e.,

scattering, the Secrest–Johnson$^{10}$ version of collinear He + H$_2$ collisions, and it was seen to give quite reasonable results for a wide range of energies and also for multiple quantum transitions. We have also considered the version of this problem in which the H$_2$ oscillator is described by a Morse rather than harmonic potential,$^{11}$ and Figure 1 shows the results given by this model for the 0 – 1 transition probability as a function of energy, compared to the exact quantum mechanical values. The model is seen to do surprisingly well.

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The curvature term) and symmetry of the barrier taken into account, then

$$\Delta \phi(q) = \theta_1 \sin q$$

with

$$\theta_1 = \int_{s_>} ds [2[V_a(s) - E]^{1/2}]$$

(2.12b)

where $\kappa(s) = B_{1r}(s)$ is the reaction path curvature and

$$\delta(s) = \int_0^s ds' \omega(s')/[2[V_a(s') - E]^{1/2}]$$

(2.12c)

$s_<$ and $s_>$ above are the left and right classical turning points at the barrier, and the quantum number $n$ has been set to 0. With eq 2.12b for $\Delta \phi(q)$ the integral in eq 2.11 is easily performed to give

$$P_s(E) = e^{-2\kappa I_0(2\theta_1)}$$

(2.13)

where $\theta_1$ is given by eq 2.12b and $I_0$ is a modified Bessel function of the first kind. One notes that $e^{-2\kappa I_0}$ is the "vibrationally adiabatic zero-curvature" (VAZC) approximation to the tunneling probability which is regained if the curvature $\kappa$ is set to zero.

Figures 2 and 3 show the tunneling probability given by eq 2.13 for both the Porter–Karplus$^{12}$ and the Truhlar–Kuppermann$^{13}$ potential energy surfaces, compared to the zeroth order VAZC approximation and to the exact
quantum mechanical values\textsuperscript{13,14} for these collinear reactions. One sees that this simple model does a reasonable job of incorporating the effects of reaction path curvature.

### III. Reduced Distributions

When dealing with truly polyatomic systems it is unlikely that one will be interested in the distribution of final quantum states for all the degrees of freedom. We thus consider here the simplifications that result when one desires the probability distribution of final quantum states for, say, only one of the degrees of freedom orthogonal to the reaction path. This treatment, and especially eq 3.2, is essentially an example of the general “partial averaging” methodology\textsuperscript{15} of classical S-matrix theory, applied here within the SCP-IOS approximation.

The reduced transition probability for the single degree of freedom $k = 1$, say, is defined as the complete transition probability of eq 2.9 summed over all final states for the other degrees of freedom $k = 2, ..., F - 1$:

$$ P_{n'_1;n_1} = \sum_{n_2, ..., n_{F-1}} P_{n'_1,n_2 \ldots n_{F-1}} $$

(3.1)

with eq 2.5 and the closure relations

$$ \sum_{n_k} e^{-i\Delta n_k(q_k - q_{k'})} = 2\pi \delta(q_k - q_{k'}) $$

it is not hard to obtain the following expression for the reduced transition probability

$$ P_{n'_1;n_1} = \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \frac{2\pi}{2\pi} \exp[-i\Delta n_1(q_1 - q_{1'}) + i\Delta n_2(q_2 + q_{2'}) - i\Delta n_{F-1}(q_{F-1} + q_{F-1'})] $$

(3.2)

where $\Delta \phi(q)$ is the phase function of eq 2.7b. From eq 3.2 one sees that terms in $\Delta \phi(q)$ that are independent of $q_1$ do not contribute to the reduced transition probability; in eq 2.7b for $\Delta \phi(q)$ one thus needs to include only the terms associated with coupling elements $B_{1,F}, B_{1,1}, B_{1,2}, B_{2,1}, k = 2, ..., F - 1$. Thus

$$ \Delta \phi(q_1, q_2, ..., q_{F-1}) = \Delta \phi(q_1, q_2, ..., q_{F-1}) $$

$$ \phi_1(q_1) - \phi_{1'}(q_{1'}) + \sum_{k=2}^{F-1} \int_{s_1}^{s_2} ds B_{k,1}(s)(2n_k + 1)(2n_k + 1)^{1/2} \left[ \frac{\omega_k}{\omega_1} \right]^{1/2} \sin(q_k + \delta_k)[\cos(q_1 + \delta_1) - \cos(q_{1'} + \delta_{1'})] $$

+ $\sum_{k=2}^{F-1} \int_{s_1}^{s_2} ds B_{k,1}(s)(2n_k + 1)(2n_k + 1)^{1/2} \left[ \frac{\omega_k}{\omega_1} \right]^{1/2} \cos(q_k + \delta_k) \times$ 

$$ \sin(q_1 + \delta_1) - \sin(q_{1'} + \delta_{1'}) $$

(3.3)

where

$$ \phi_1(q_1) = \int_{s_1}^{s_2} ds [2[E - V_1(s)]^{1/2} B_{1,1'}(s) \left[ 2n_1 + 1 \right]^{1/2} \left[ \frac{\omega_1}{\omega_k} \right]^{1/2} \sin(q_1 + \delta_1(s)) - \int_{s_1}^{s_2} ds \frac{\omega_k'(s)}{4\omega_k(s)}(2n_1 + 1) \times$$

$$ \sin(q_1 + \delta_1(s)) \left[ \frac{\omega_k'(s)}{4\omega_k(s)}(2n_1 + 1) \times $$

(3.4)

The fact that the phase difference in eq 3.3 is a first harmonic in the angles $[q_k], k = 2, ..., F - 1$, allows one to perform the integration over these variables using an identity for the Bessel function $J_0$

$$ (2\pi)^{-1} \int_0^{2\pi} dq_k \exp[i\alpha \sin(q_k) + i\beta \cos(q_k)] = J_0((\alpha^2 + \beta^2)^{1/2}) $$

so that eq 3.2 becomes

$$ P_{n'_1;n_1} = \int_0^{2\pi} \int_0^{2\pi} \exp[-i\Delta n_1(q_1 - q_{1'}) + i\Delta n_2(q_2 + q_{2'})] $$

(3.2a)

where the correlation function $C$ is

$$ C(q_1, q_{1'}) = \prod_{k=2}^{F} \{ [\gamma_k(q_1, q_{1'})] \} $$

(3.6a)

with $\gamma_k$ given by

$$ \gamma_k(q_1, q_{1'}) = [(2n_1 + 1)(2n_k + 1)]^{1/2} $$

$$ \times \sin(\delta_k(\cos(q_1 + \delta_1) - \cos(q_{1'} + \delta_{1'}))) $$

+ $\prod_{k=2}^{F} \{ [\gamma_k(q_1, q_{1'})] \} $
one expects $b_k$ of eq 3.7b to be such that

$$|b_k| << |b|$$

and if one neglects $|b_k|$ eq 3.7a becomes

$$\gamma_k(q_1; q_1') = \gamma_k(q_1 - q_1') = a_k \left[ \frac{\sin \left( \frac{q_1' - q_1}{2} \right)}{2} \right]$$

where

$$a_k = \frac{(2n_k + 1)^{1/2}}{(2n_k + 1)} \times \left[ \int_{-\infty}^{\infty} \frac{d\Delta q}{2\pi} e^{-i\Delta q} B_k \left( \frac{\omega_1}{\omega_k} \right)^{1/2} \right]$$

With this approximation $\gamma_k$ and thus the correlation function $C$ is a function only of $q_1 - q_1'$, so that eq 3.5 can be written as

$$P_{n_1; n_1} = \frac{1}{\pi} \int d\Delta q e^{-i\Delta q} C(\Delta q) \times$$

$$\frac{1}{\pi} \int d\Delta q e^{-i\Delta q} C(\Delta q) \times$$

$$\int_0^{2\pi} dq \exp \left[ i\phi_k \left( q + \frac{\Delta q}{2} \right) - i\phi_k \left( q - \frac{\Delta q}{2} \right) \right]$$

$$J_0[2a_1 \sin (q/2)]$$

where

$$a_1 = \left( \int_0^\infty \frac{ds}{2\pi} [E - V_1(s)]^{1/2} B_1(b) \left( \frac{2n_1 + 1}{\omega_1} \right)^{1/2} e^{i\theta_i(s)} \right)$$

Combining eq 3.11 and 3.10, one can write the final expression as

$$P_{n_1; n_1} = \frac{1}{\pi} \int d\Delta q e^{-i\Delta q} C(\Delta q) \times$$

$$\int_0^{2\pi} dq \exp \left[ i\phi_k \left( q + \frac{\Delta q}{2} \right) - i\phi_k \left( q - \frac{\Delta q}{2} \right) \right]$$

$$J_0[2a_1 \sin (q/2)]$$

with

$$C(\Delta q) = \frac{1}{\pi} \sum_{k=1}^{\infty} J_0[2a_k \sin (q/2)]$$

where $a_k$ is defined by eq 3.11b and $|a_k|$, $k = 2, ..., F - 1$ by eq 3.9b.

Equation 3.12 has a pleasing simple structure; each degree of freedom, $k = 1, ..., F - 1$, contributes to the function $C$ multiplicatively. The primary mode $k = 1$ contributes a factor that, by itself, would give the $n_1 \to n_1$ transition probability if no other modes were present; i.e., one has the identity

$$\int_0^{2\pi} dq \frac{e^{-i\Delta q} J_0[2a_1 \sin (q/2)]}{2\pi} = |J_{\Delta q}(a)|^2$$

the right-hand side of which is eq 3.8 if $\phi_0$ is approximated by only its first term. The bath modes, $k = 2, ..., F - 1$, contribute factors to $C$ that result from the coupling of mode 1 to mode $k$ (through the coupling elements $B_{1k}$).

In concluding this section we consider a different type of reduced distribution, namely, the translational energy distribution

$$P(\Delta E) = \sum_{\Delta n} P_{\Delta n} \delta[\Delta E + \epsilon_n - \epsilon_{\Delta n}]$$

where $\Delta E_{\Delta n} = \epsilon_n - \epsilon_{\Delta n}$. Often in molecular beam experiments this is the most detailed quantity observed. By expressing the energy-conserving $\delta$ function in terms of a Fourier integral

$$\delta(\Delta E + \epsilon_n - \epsilon_{\Delta n}) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp[i(\Delta E + \epsilon_n - \epsilon_{\Delta n})t]$$

using the SCP–IOS approximation for $P_{\Delta n}$, and invoking closure in the sum over $\Delta n$, one can easily show that

$$P(\Delta E) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp[i(\Delta E + \epsilon_n - \epsilon_{\Delta n})t]$$

where the correlation function $T(t)$ is

$$T(t) = \prod_{k=1}^{\infty} J_0[2a_k \sin (\omega_k t/2)]$$

with

$$a_k = \left( \int_0^\infty ds [E - V_{nk}(s)]^{1/2} B_{nk}(s) \left( \frac{2n_k + 1}{\omega_k} \right)^{1/2} e^{i\theta_k(s)} \right)$$

Equation 3.17 is a simple, closed-form expression for the time correlation $T$, the Fourier transform of which (cf. eq 3.5) gives the translational energy distribution.

IV. Line Widths of Local Mode Overtones

Another aspect of polyatomic dynamics that has attracted considerable attention recently is the broad line shape of high overtones in the absorption spectrum of local modes, usually a CH stretch of a relatively large (≥10 atoms) molecule.18 The width of the absorption line is taken as indicative of relaxation of the CH stretch mode due to coupling with other modes in the molecule. Here we show how the reaction path Hamiltonian plus the SCP–IOS approximation can be used to characterize this phenomenon quantitatively.

For this application the local mode coordinate itself, e.g., roughly a CH bond coordinate, is chosen as the reaction coordinate $s$ so that the Hamiltonian consists of this one special degree of freedom plus harmonic modes normal to it. The potential function $V_0(s)$ is thus a Morse-like potential, the eigenvalues of which $\omega_k$ give the positions of the overtones of the local mode excitation. In this paper we sketch the simplest version of the model, and thus in most places neglect the $s$ dependence of the frequencies $\omega_k$, $k = 1, ..., F - 1$. Also, the reaction path Hamiltonian of eq 2.3 is approximated as

$$H(\eta_{a,b} s, s, n) = H_0(\eta_{a,b} s, n) + H_1(\eta_{a,b} s, n)$$

where the reaction coordinate and momenta $(s, p_s)$ have

been replaced by their action angle variables \((n, q_s)\) (defined with respect to \(V_0(s)\)), and
\[
H_0(n, n) = \epsilon(n_j) + \sum_{k=1}^{F-1} (n_k + \frac{1}{2}) \omega_k
\] (4.2a)
and
\[
H_1(n, q_s, n, q) = -p_s^2 \sum_{k=1}^{F-1} B_{k,k}(s) \left[ \frac{2n_k + 1}{\omega_k} \right] \sin q_k - p_s \times
\]
\[
\sum_{k,k'=1}^{F-1} B_{k,k'}(s) [(2n_k + 1)(2n_{k'} + 1)]^{1/2} \frac{\omega_{k'}}{\omega_k} \sin \frac{q_{k'}}{2} \cos q_k
\] (4.2b)

(s.p.) above are algebraic functions of \((n, q_s)\). If \((n_j=0, n)\) is the initial state of the molecule—and the state \(n\) of the transverse modes will usually also be taken to be the ground state 0—then the absorption spectrum \(I(\omega)\) is given by \(17\)
\[
I(\omega) = \sum_{0}^{\infty} dt \ e^{iE_\omega + \mu \omega t/\hbar} (0, n) |e^{-i\omega t}|(0, n)\] (4.3)
where \(E_\omega = (\epsilon(n_j) + \hbar \omega (n + \frac{1}{2})\), and \(\mu\) is the dipole moment function of the molecule. As is usual, one assumes that \(\mu\) is a function only of the reaction coordinate \(s\) (i.e., the local model coordinate), so that insertion of complete sets of states before and after the propagator in eq 4.3 gives
\[
(0, n)|e^{-i\omega t}|(0, n) = \sum_{n,\mu} (0|\mu|n_s) (n|\mu|n_{s'}) (n_s|\mu|0)
\] (4.4)
In one neglects mode mixing—i.e., the terms \(n_s' \neq n_s\) in eq 4.4—then the absorption spectrum associated with the \(0 \rightarrow n_s\) overtone of the \(s\) mode takes the standard form
\[
I_{n,0}(\omega) = \left|\langle n_s|\mu|0\rangle\right|^2 \int_{-\infty}^{\infty} dt \ e^{i\omega t} C(t)
\] (4.4a)
\[
\Delta \omega = \omega - \omega_{n,0}
\] (4.4b)
where \(\omega_{n,0}\) is the nominal position of the \(0 \rightarrow n_s\) overtone absorption line
\[
\omega_{n,0} = \epsilon(n_s) - \epsilon(0)
\] (4.4c)
and the correlation function \(C(t)\) is
\[
C(t) = e^{iE_{n,s}} (n, n)|e^{-i\omega t}|(n, n)
\] (4.5)
with
\[
E_{n,s} = \epsilon(n_s) + \hbar \omega (n + \frac{1}{2})
\]

With the SCP approximation to the propagator the correlation function of eq 4.5 is given by
\[
C(t) = \int_{0}^{\infty} \frac{2\pi dq_s}{2\pi} \int_{0}^{2\pi} \frac{dq}{(2\pi)^{F-1}} \exp \left[ -i \int_{0}^{t} dt' H_1(t') \right]
\] (6.6)
with
\[
H_1(t') = H_1(n, q_s + \omega t', n, q + \omega t')
\] (4.7)
\[
\omega_s = \epsilon'(n_s)
\]
As with previous applications, the fact that the coupling term in the Hamiltonian, \(H_1\), of eq 4.2b, depends on the angles \(\{|q|, k = 1, \ldots, F-1\}\) in such a simple way allows the integrals over them in eq 4.7 to be performed. As discussed below, for example, there is reason to believe that the couplings \(B_{k,k}(s)\) are the most important ones in \(H_1\), so for the present analysis we consider only these terms in \(H_1\)
\[
H_1 = -p_s \sum_{k=1}^{F-1} B_{k,k}(s) (n_k + \frac{1}{2}) \sin (2q_k)
\] (4.8a)
in which case it is not hard to show that eq 4.6 for the correlation function gives
\[
C(t) = \int_{0}^{\infty} \frac{2\pi dq_s}{2\pi} \int_{0}^{\infty} \frac{dJ_{0}(\gamma_{k}(q_s,t))}{2\pi \omega_k}
\] (4.8b)
with
\[
\gamma_{k}(q_s,t) = (n_k + \frac{1}{2}) \int_{0}^{t} dt' p_{s} B_{k,k}(s) e^{i2 \omega t'}
\] (4.8c)
In the integrand of the last equation \(\rho_s\) and \(q_s\) are algebraic functions of \(n_s\) and \(q_s\) with \(q_s = q + \omega t'\), and \(n_s = n + \omega t'\). The formulae are more cumbersome if all the terms in \(H_1\) are retained, but in practice it is not much more difficult to do so.

It is interesting to show how eq 4.8 can be further digested to produce one of the current qualitative pictures of local mode line widths. The idea is that the excited state \((n_s, n)\) is broadened primarily by interaction with nearly resonant states of the type \((n_j - 1, n + \Delta n)\), where \(\Delta n > 0\) for one or more of the bath modes \(k = 1, \ldots, F - 1\). Since the local mode is of such high frequency, \(\hbar \omega_s \approx 2000-3000\) \(cm^{-1}\), and most bath modes of lower frequency, \(\hbar \omega_k \approx 1000-1500\) \(cm^{-1}\), it is felt \(18\) that one must have \(\Delta n_k = 2\) or larger in order to have near resonance and thus strong interaction. This is the reason for suspecting that the terms in eq 4.8 are the most important ones in \(H_1\); the first term in eq 4.2b gives rise to the couplings of the type \(\Delta n_k = 0, \pm 2, \ldots\) and \(\Delta n_k = \pm 1, \ldots\), and thus cannot cause the transitions though to be the most important.

Proceeding further in the present qualitative analysis, we take \(B_{kk}\) in eq 4.8 to be time independent and make a harmonic approximation for \(\rho_s(n_s, q_s + \omega t')\)
\[
\rho_s(n_s, q_s + \omega t') \approx \left|\langle n_s + 1|\omega_s\rangle\right|^2 \cos (q_s + \omega t')
\] so that eq 4.8c for \(\gamma_{k}\) then gives
\[
\gamma_{k}(q_s,t) = (n_k + \frac{1}{2}) B_{k,k}(2n_k + 1)(\omega_s + 1)\right|^2 \times
\]
\[
\left|\exp \left[ \frac{e^{i(2\omega_k + \omega_s)} - 1}{2i(2\omega_k + \omega_s)} \right] + e^{i\omega_s} \frac{e^{i(2\omega_k - \omega_s)} - 1}{2i(2\omega_k - \omega_s)} \right|
\] (4.9)

Furthermore, only the resonant term in eq 4.9 is retained, so that \(\gamma_{k}\) becomes independent of \(q_s\)
\[
\gamma_{k}(q_s,t) = \gamma_{k}(t) = (n_k + \frac{1}{2}) B_{k,k}(2n_k + 1)(\omega_s + 1)\right|^2 \times
\]
\[
\sin \left[ (2\omega_k - \omega_s) t/2 \right] / (2\omega_k - \omega_s)^2
\] (4.10)
If one also makes a weak coupling (i.e., small \(\gamma_{k}\)) approximation, then eq 4.8b becomes
\[
C(t) \approx \int_{0}^{\infty} \frac{2\pi dq_s}{2\pi} \exp \left[ -\frac{1}{4} \sum_{k=1}^{F-1} \gamma_{k}(q_s,t)^2 \right]
\]
with eq 4.10 this becomes
\[
C(t) = \exp \left[ -\frac{1}{4} \sum_{k=1}^{F-1} (n_k + \frac{1}{2}) B_{k,k}(2n_k + 1)(\omega_k + 1) \right] \times
\]
\[
\sin^2 \left[ (2\omega_k - \omega_s) t/2 \right] / (2\omega_k - \omega_s)^2
\] (4.11)

The final approximation in this treatment is a continuum approximation to the frequency distribution in the molecule; i.e., one makes the replacement


where \( \rho(\omega) \) is the number of vibrational modes per unit frequency. Equation 4.11 then reads (setting \( n_h = 0 \))

\[
C(t) = \exp \left[ -\frac{(2n_s + 1)\omega_s}{16} \int \rho(\omega) B(\omega)^2 \times \sin^2 \left( \frac{(2\omega - \omega_s)t/2}{2\omega + \omega_s} \right) d\omega \right]
\]

For long times the contribution to the integral over \( \omega \) is peaked strongly at the resonance value \( \omega = \omega_s/2 \), so that

\[
C(t) \approx \exp \left[ -\frac{(2n_s + 1)\omega_s}{16} \rho \left( \frac{\omega_s}{2} \right) B \left( \frac{\omega_s}{2} \right)^2 \times \int \rho(\omega) \sin^2 \left( \frac{(2\omega - \omega_s)t/2}{2\omega + \omega_s} \right) d\omega \right]
\]

The integral over \( \omega \) gives \( \pi t/2 \), so that finally

\[
C(t) = e^{-\pi t/4} \rho(\omega) B(\omega)^2 (2\omega + \omega_s)^2/16
\]

with

\[
\omega_h = \exp(\omega_s/2)(2n_s + 1)\omega_s B(\omega_s/2)^2/16
\]

Since \( C(t) \) decays exponentially, the line shape \( I(\omega) \) is Lorentzian with a width at half-height of \( \omega_h \). The narrowing of the overtone line as \( n_h \) increases beyond \( 5-6 \) is thought in this picture to result because the density of modes in the molecule at frequency \( \omega_s/2 \), i.e., \( \rho(\omega_s/2) \), decreases (since \( \omega_s \) decreases with increasing \( n_h \)).

Because of the many approximations introduced from eq 4.8 onwards, the above analysis is presented only for qualitative purposes. It is important, however, to see that the model being proposed, i.e., eq 4.1-4.7, is capable of producing the resonance “golden rule”-like result when the relevant approximate solutions are introduced. One of the exciting possibilities for future work, of course, is to generate all the coupling elements \( [B_{k\ell}] \) and \( [B_{\ell k}] \) from ab initio quantum chemical calculations and then to use the more complete version of the present model to generate the line shape without making any a priori assumptions about which couplings are most important and without resorting to some of the relatively crude arithmetic approximations used above.

V. Semiclassical Branching Model for Mode Specificity

Earlier work by Waite and Miller has been concerned with mode-specific effects in the unimolecular decay of isolated polyatomic molecules, i.e., the question of whether the unimolecular decay rate is a function only of the total energy of excitation in the molecule or also dependent on the particular modes of the molecule that are excited. The model problems that have been treated to date are two-oscillator systems, and the calculations carried out were completely quantum mechanical computation of the complex (i.e., Siegert) eigenvalues of the system. The real part of such an eigenvalue is the energy of the metastable state, and the imaginary part gives its unimolecular decay rate (inverse lifetime).

Quantum calculations such as these, however, are not practical for molecules with significantly more than two degrees of freedom, so we present here a simpler semi-classical model for determining the complex eigenvalues. The approximation is a multichannel version of a semiclassical branching model that has been shown to yield the complex eigenvalues for one-dimensional systems that are metastable with respect to tunneling.

Suppose the potential along the reaction coordinate for the system of \( F \) degrees of freedom is as in Figure 4, and consider inelastic scattering from it; i.e., the system approaches from \( s = +\infty \) and eventually returns to \( s = -\infty \). The \( S \) matrix for the inelastic scattering at total energy \( E, S(E) \), is approximated in this branching model as the sum of amplitudes associated with the different possible “trajectories” that can contribute. Referring to Figure 4, the first of these is reflected from the barrier; the second tunnels through the barrier, makes one oscillation in the well, and then tunnels back out; the third tunnels through the barrier, makes two oscillations in the well, and then tunnels back out; and so on. The multichannel aspect of the model is to allow for inelastic transitions between the transverse vibrational modes and the reaction coordinate during the oscillations within the well. Thus if \( S_{out}(E) \) is the \( S \) matrix associated with inelastic transitions from \( s = -\infty \) to the outer turning point of the barrier, \( P(E) \) the matrix of tunneling probabilities through the barrier (which will be assumed to be diagonal), and \( S_{in}(E) \) the \( S \) matrix for inelastic transitions per oscillation in the well, then the various terms contributing to the net \( S \)-matrix \( S \) are

\[
S = S_{out}^{1/2}(1 - P)^{1/2}S_{out}^{1/2} + S_{out}^{1/2}P^{1/2}S_{in}^{1/2}P^{1/2}S_{in}^{1/2} + (-1)S_{out}^{1/2}P^{1/2}S_{in}^{1/2}(1 - P)^{1/2}S_{in}^{1/2}P^{1/2}.
\]

\[
S_{out}^{1/2} + \sum_{k=0}^{\infty} S_{out}^{1/2}(1 - P)^{1/2}S_{out}^{1/2} + \sum_{k=0}^{\infty} S_{out}^{1/2}P^{1/2}S_{in}^{1/2}(1 - P)^{1/2}S_{in}^{1/2}P^{1/2}.
\]

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\]

\[
S_{out}^{1/2} + \sum_{k=0}^{\infty} S_{out}^{1/2}(1 - P)^{1/2}S_{out}^{1/2} + \sum_{k=0}^{\infty} S_{out}^{1/2}P^{1/2}S_{in}^{1/2}(1 - P)^{1/2}S_{in}^{1/2}P^{1/2}.
\]

Figure 4b illustrates the “trajectory” associated with the term \( k = 1 \) in eq 5.1. The phase factor \((-1)^k\) is due to the additional reflections experienced by the \( k \)th “trajectory.”

Equation 5.1 is a geometric series which is easily summed to give

\[
\]

Dynamic Model of Reaction Path Hamiltonian

\[ S = S_{\text{out}}^{1/2} (1 - P)^{1/2} S_{\text{out}}^{1/2} + S_{\text{out}}^{1/2} P^{1/2} S_{\text{in}}^{1/2} \]

or

\[ S(E) = S_{\text{out}}^{1/2} (1 - P)^{1/2} S_{\text{out}}^{1/2} + S_{\text{out}}^{1/2} P^{1/2} , \]

\[ [S_{\text{in}}^{-1} + (1 - P)^{1/2}]^{-1} P^{1/2} S_{\text{out}}^{1/2} \] (5.2)

This is the general result of the multichannel branching model.

The complex eigenvalues of the composite system are defined as the poles of the S-matrix \( S(E) \), and from eq 5.2 it is clear that these occur at values of the energy \( E \) for which the inverse matrix is singular, i.e., the values of \( E \) for which

\[ \det [S_{\text{in}}^{-1}(E) + (1 - P(E))^{1/2}] = 0 \] (5.3)

The SCP-IOS approximation is now used to determine \( S_{\text{in}}(E) \) as in section II, i.e.

\[ S_{\text{in}}(E) = e^{i\phi(E)} \int_0^{2\pi} dq \frac{1}{2\pi} \exp[-i\Delta m q + i\Delta \phi(q, n, E)] \] (5.4)

and because of the symmetry of the trajectory back and forth across the well, one has (with \( s_c = 0 \))

\[ \phi_0(n, E) = 2 \int_0^{2\pi} ds [2(E - V(s))]^{1/2} \] (5.5a)

\[ \Delta \phi(q, n, E) = \sum_{k=1}^{F-1} 2 \sin q_k \int_0^{2\pi} ds [2(E - V(s))]^{1/2} \]

\[ B_{k,F}(\sigma) \left[ \frac{2n_k + 1}{\omega_k(\sigma)} \right]^{1/2} \cos [\delta_k(\sigma)] + \]

\[ \sum_{k+1}^{F-1} \left[ \cos (q_k - q_k') \int_0^{2\pi} ds B_{k,F}(s)(2n_k + 1) \times \right. \]

\[ (2n_{k'} + 1)^{1/2} \left[ \frac{\omega_k'}{\omega_k} \right] \sin (\delta_k - \delta_k') + \]

\[ \left. \cos (q_k + q_k') \int_0^{2\pi} ds B_{k,F}(s)(2n_k + 1) \times \right. \]

\[ (2n_{k'} + 1)^{1/2} \left[ \frac{\omega_k'}{\omega_k} \right] \sin (\delta_k + \delta_k') \] (5.5b)

Similarly, the tunneling probabilities \( P \) can be determined as in section II.

Equations 5.3–5.5 are the complete model for determining the complex eigenvalues of the polyatomic system. Though we have formulated the problem as though there were a barrier along the reaction coordinate (cf. Figure 4), it can also be applied to the case that there is no barrier. This is the standard situation of "Feshbach resonances", and one can indeed show that in this limit the branching model is capable of reproducing the standard Feshbach expressions for resonance energies and widths.

It is easy to see that eq 5.3–5.5 reduce to the previously obtained semiclassical result\(^{(20)}\) for the one-channel case, i.e., potential scattering. Equation 5.3 becomes

\[ e^{-2i\phi(E)} + (1 - P)^{1/2} = 0 \] (5.6a)

where

\[ \phi(E) = \int_0^{2\pi} ds [2(E - V(s))]^{1/2} \] (5.6b)

and for small \( P \) this becomes

\[ \phi(E) = (n + \frac{1}{2})\pi - \frac{i}{4} P(E) \] (5.6c)

The complex eigenvalue \( E_n - i\Gamma/2 \) then has its real part \( E_n \) determined by the WKB eigenvalue equation

\[ \phi(E_n) = (n + \frac{1}{2})\pi \] (5.7a)

and its width \( \Gamma \) given by

\[ \Gamma = \left( \frac{dE}{dn} / 2\pi \right) P \] (5.7b)

the unimolecular decay rate is \( \Gamma / h \).

Applications using eq 5.3–5.5 have been made to the two-oscillator problems treated earlier, and they quantitatively reproduce these earlier exact quantum mechanical calculations.\(^{(19)}\) An appropriate modification of this branching model can also be applied to determine the eigenvalues in a two-dimensional double-well potential. These results and other aspects of the branching model will be presented elsewhere.\(^{(21)}\)

VI. Concluding Remarks

This paper has shown how the combined SCP-IOS reaction path model of Miller and Shi can be applied to a variety of different dynamical phenomena in polyatomic systems. Another such process, which we have not discussed, is multiple photon absorption (with possible subsequent dissociation) of infrared radiation; in this case the principal infrared active mode of the molecule (e.g., the \( v_3 \) mode of SF\(_6\)) would be chosen as the reaction coordinate and this mode thus treated beyond the harmonic approximation, while all other transverse modes would be treated harmonically.

The two features that make this approach interesting are that it is extremely simple, and thus readily applicable to complex chemical systems, and that the parameters which characterize these phenomena quantitatively are obtainable in a relatively straightforward way from ab initio quantum chemistry calculations. We thus look forward to such ab initio calculations of polyatomic dynamical phenomena in the next few years.

Finally, one should note that the simple SCP-IOS approximation to the dynamics may not be accurate enough in some situations, and there is always the possibility—still within the reaction path Hamiltonian model—of going to a more rigorous dynamical description.

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