

An Eikonal Treatment of Electronically Diabatic Photodissociation: Branching Ratios of $\text{CH}_3\text{I}^\dagger$

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Collision-induced and photoinduced electronically diabatic transitions in polyatomic systems are described, starting with an eikonal representation of the molecular wave function and developing a self-consistent eikonal approximation for short deBroglie wavelengths. The approach provides state-to-state transition amplitudes for electronic excitation without requiring any preliminary knowledge of the nature of transitions between potential energy surfaces. The formalism has some similarities to recent semiclassical treatments using the initial value representation. It has been applied to the electronically diabatic dissociation $\text{CH}_3\text{I} + \phi \rightarrow \text{CH}_3 + \text{I}$ induced by absorption of UV light using previously introduced potential energy surfaces and couplings to compare with accurate quantal results. Results for the model are given for branching ratios in the formation of I and I^* , and for the final distribution of vibrational states of CH_3 for two light wavelengths.

1. Introduction

Semiclassical methods provide a computationally practical approach for molecular systems with many atomic degrees of freedom and can be readily implemented for phenomena involving only one electronic state (usually the ground state), frequently giving quite accurate results.^{1,2} The semiclassical method is less obviously implemented for several coupled electronic potential energy surfaces, because in this case it is necessary to consistently treat the coupling of electronic probability amplitudes and nuclear motions, and several approaches have been developed for this purpose.^{3–17} This has also been our motivation for the early development of a self-consistent eikonal (SCE) approximation,¹⁸ which we have applied to collision-induced and photoinduced phenomena. The approach has some features in common with cellular methods¹⁹ and the initial value representation for electronically nonadiabatic dynamics²⁰ in that it involves sums over initial conditions. In our work, trajectories and mechanical actions have been used to construct eikonal wave functions and to calculate transition amplitudes, as they appear in models of electron transfer in ion-diatom collisions,²¹ inelastic atom–atom collisions,^{22,23} and atom–diatomic energy transfer²⁴ and more recently in a first-principles treatment of quantum dynamics of diabatic collisions combining the eikonal treatment with time-dependent many-electron theory.^{25–27} The approach provides state-to-state transition amplitudes for electronic excitation without requiring any preliminary knowledge of the nature of transitions between potential energy surfaces. It was also applied to the photoinduced break-up of the C–I bond in CH_3I ^{28,29} to describe the dissociative dynamics on a single excited potential energy surface. The results for partial and total cross sections from that model calculation compared well, at all light wavelengths, with exact wave packet calculations.³⁰ The formalism has been extended to treat several excited electronic states and will be summarized before it is applied to the electronically diabatic dissociation of

CH_3I . It has some similarities to a recent semiclassical treatment of nonadiabatic photodissociation.³¹

A purpose of this contribution is to focus on our intermediate semiclassical approach, between the straightforward use of classical trajectories with surface hopping and sampling of initial and final values,^{6,32} and the initial value representations with propagation of trajectories and Jacobians,³³ and integration over initial conditions.^{20,31,34} Our calculations have given branching ratios accurate to within about 10% and required only 10^3 to 10^4 trajectories, instead of the much larger numbers in more accurate IVR studies. It appears to be a useful compromise when high accuracy is not needed for state-to-state probabilities, as can also be found in recent comparisons of methods.^{35–37}

The photodissociation of polyatomic molecules has been studied with fully quantum mechanical and semiclassical methods. Whereas quantal methods are in principle the most accurate,^{38,39} in practice they are limited to models with only a few degrees of freedom for the atomic motions. In addition to CH_3I , the triatomic ICN has also been studied in detail^{34,40} and would be a good subject for comparisons. Larger molecules have been the subject of theoretical and experimental comparisons and could serve as additional subjects of study with the semiclassical method we are considering.^{41,42} The CH_3I molecule has continued to serve as an excellent test case for various computational treatments. This is in part because it can be modeled as a pseudotriatomic. Early theoretical treatments were limited to two degrees of freedom for nuclear motions and one excited dissociative state. More recent work has included two coupled dissociative potentials^{43–45} and more than two degrees of freedom.⁴⁵ In the present study the formalism is applied in a model with semiempirical potential energy surfaces, including the same two excited dissociative electronic states, to investigate the suitability of the self-consistent eikonal treatment to accurately calculate state-to-state cross sections and branching ratios.

In the next section, molecular wave functions are expressed in the formally exact eikonal representation and are then obtained in an eikonal approximation for short deBroglie wavelengths. The treatment expands our previous formulation

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in two ways: internal states are expressed as exponentials in a way consistent with the eikonal representation; and transition integrals are obtained from biased sampling of initial conditions. Section 3 derives expressions for photodissociation cross sections of polyatomics in terms of matrix elements of an electric dipole operator between an initially bound state and a final scattering state, and section 4 gives results for a model of the photodissociation $\text{CH}_3\text{I} + \phi \rightarrow \text{CH}_3 + \text{I}$ induced by absorption of photons ϕ of UV light.

2. The Self-Consistent Eikonal Treatment

A. The Self-Consistent Eikonal Representation. A molecule M is described here in terms of its electronic variables \mathbf{X} and nuclear position coordinates \mathbf{Q} . The molecular Hamiltonian, \hat{H}_M , contains the kinetic energy operator \hat{K} of the nuclei, the electronic Hamiltonian, \hat{H}_Q , for fixed nuclear positions, and spin-orbit coupling, \hat{H}_{SO} , for electrons in the molecule, so that, using mass scaled nuclear positions with mass parameter M ,

$$\begin{aligned}\hat{H}_M &= \hat{K} + \hat{H}_Q \\ \hat{K} &= -\hbar^2(\partial/\partial\mathbf{Q})^2/(2M) \\ \hat{H}_Q &= \hat{H}_Q^0 + \hat{H}_{SO}\end{aligned}\quad (1)$$

with the Hamiltonian operators applying to functions of the electronic variables. We want to solve the time independent Schroedinger equation $(\hat{H}_M - E)|\Psi\rangle = 0$ for the molecular states $\Psi(\mathbf{X}, \mathbf{Q}) = \langle\mathbf{X}|\Psi(\mathbf{Q})\rangle$ with total energy E , where we make explicit the nuclear coordinates and use a bracket notation for state functions of electronic variables. We introduce a basis of N_B electronic states $\Phi_\Gamma(\mathbf{X}; \mathbf{Q}) = \langle\mathbf{X}|\Gamma; \mathbf{Q}\rangle$ with electronic quantum numbers, Γ , that are parametrically dependent on nuclear positions. Molecular states are expanded in this basis as

$$|\Psi(\mathbf{Q})\rangle = \sum_\Gamma |\Gamma; \mathbf{Q}\rangle \psi_\Gamma(\mathbf{Q}) \quad (2)$$

where the expansion coefficients are amplitudes of nuclear motion. This transforms the Schroedinger equation

$$\left[-\frac{\hbar^2}{2M}\left(\frac{\partial}{\partial\mathbf{Q}}\right)^2 + \hat{H}_Q - E\right]|\Psi(\mathbf{Q})\rangle = 0 \quad (3)$$

into the matrix differential equation

$$\begin{aligned}\left\{\frac{1}{2M}\left[\mathbf{I}\frac{\hbar}{i}\frac{\partial}{\partial\mathbf{Q}} + \mathbf{G}(\mathbf{Q})\right]^2 + \mathbf{H}_Q - E\right\}|\psi(\mathbf{Q})\rangle &= 0 \\ \mathbf{G}(\mathbf{Q}) &= \left[\left\langle\Gamma; \mathbf{Q}\left|\frac{\hbar}{i}\frac{\partial}{\partial\mathbf{Q}}\right|\Gamma'; \mathbf{Q}\right\rangle\right]\end{aligned}\quad (4)$$

where \mathbf{H}_Q and ψ are square $N_B \times N_B$ and column $N_B \times 1$ matrices representing a Hamiltonian and nuclear state, \mathbf{I} is the identity matrix, and $\mathbf{G}(\mathbf{Q})$ is the momentum coupling matrix that describes the effect of electron drag by the nuclear motions. The momentum couplings can be removed by a transformation of the original electronic basis set to a strictly diabatic (d) or "P-representation"^{46,47} to simplify the treatment of the dynamics, in which case we can set $\mathbf{G}^{(d)}(\mathbf{Q}) = \mathbf{0}$. We assume in what follows that this has been done, and omit the (d) index.

We proceed by defining an eikonal representation of the total molecular wave functions, and developing an eikonal approximation valid for short deBroglie wavelengths, generated in such a way that it is possible to deal with transitions between

electronic states as they occur when a molecule M is excited by visible or UV light and breaks up into fragments $A + X$. We concentrate on the scattering molecular states, because bound states can be readily generated for low vibrational quantum numbers. The initial molecular scattering states $\psi_{\Gamma\alpha}^{(\pm)}(\mathbf{Q}; \mathbf{p}_1)$ where \mathbf{p}_1 is an initial relative momentum, $\alpha = (\Gamma_\alpha, \nu_\alpha)$, and Γ is a final electronic state, can always be written as

$$\psi_{\Gamma\alpha}^{(\pm)}(\mathbf{Q}; \mathbf{p}_1) = \chi_{\Gamma\alpha}^{(\pm)}(\mathbf{Q}; \mathbf{p}_1) \exp[\pm iS_\alpha(\mathbf{Q}; \mathbf{p}_1)/\hbar] \quad (5)$$

where $\chi_{\Gamma\alpha}^{(\pm)}(\mathbf{Q}; \mathbf{p}_1)$ is in general complex and $S_\alpha(\mathbf{Q}; \mathbf{p}_1)$ is a common eikonal function independent of Γ , to be defined. Dropping the labels \pm , α , and \mathbf{p} temporarily, we shall use a matrix notation with row and column indices Γ , and wave functions arranged in columns so that eq 5 becomes

$$\psi(\mathbf{Q}; \mathbf{p}_1) = \chi(\mathbf{Q}) \exp[iS(\mathbf{Q})/\hbar] \quad (6)$$

where χ is a column matrix with elements $\chi_{\Gamma\alpha}(\mathbf{Q}; \mathbf{p}_1)$. Replacing eq 6 in eq 4 with $\mathbf{G} = 0$, we find

$$\left[\frac{1}{2M}\left(\frac{\hbar}{i}\frac{\partial}{\partial\mathbf{Q}} + \frac{\partial S}{\partial\mathbf{Q}}\right)^2 + \mathbf{H}_Q - E\right]\chi(\mathbf{Q}) = 0 \quad (7)$$

Writing this as $\mathcal{F}\chi = 0$, where \mathcal{F} is an operator, multiplying on the left by the row χ^\dagger , and adding the adjoint of the result, we have that

$$(2M)^{-1}(\partial S/\partial\mathbf{Q})^2 + V_{\text{qu}}(\partial S/\partial\mathbf{Q}, \mathbf{Q}) = E \quad (8)$$

$$V_{\text{qu}}(\mathbf{P}, \mathbf{Q}) = (\chi^\dagger\chi)^{-1} \left\{ \chi^\dagger\mathbf{H}_Q\chi + \frac{i\hbar}{2M}\mathbf{P} \cdot \left[\left(\frac{\partial\chi}{\partial\mathbf{Q}}\right)^\dagger\chi - \chi^\dagger\frac{\partial\chi}{\partial\mathbf{Q}} \right] - \frac{\hbar^2}{2M} \frac{1}{2} \left[\left(\frac{\partial^2\chi}{\partial\mathbf{Q}^2}\right)^\dagger\chi + \chi^\dagger\frac{\partial^2\chi}{\partial\mathbf{Q}^2} \right] \right\} \quad (9)$$

where we have defined the multidimensional momentum $\mathbf{P} = \partial S/\partial\mathbf{Q}$. Equation 8 has the form of the time-independent Hamilton-Jacobi equation for the action S . It can be solved by the method of characteristics introducing a time parameter t and the functions $\mathbf{P}(t)$ and $\mathbf{Q}(t)$, which are solutions of

$$\begin{aligned}H_{\text{qu}} &= \mathbf{P}\cdot\mathbf{P}/(2M) + V_{\text{qu}}(\mathbf{P}, \mathbf{Q}) \\ d\mathbf{Q}/dt &= \partial H_{\text{qu}}/\partial\mathbf{P} \\ d\mathbf{P}/dt &= -\partial H_{\text{qu}}/\partial\mathbf{Q}\end{aligned}\quad (10)$$

Here V_{qu} can be interpreted as an effective quantal potential and H_{qu} as the corresponding effective Hamiltonian, dependent on the variables \mathbf{P} and \mathbf{Q} and the functions $\partial^r\chi_\Gamma/\partial\mathbf{Q}^r$, $r = 0, 1, 2$, which leads to coupled equations for trajectories and electronic amplitudes that must be solved self-consistently. The action functions $S(\mathbf{Q})$ can be obtained from the momenta. They are given by the line integrals

$$S(\mathbf{Q}) = S(\mathbf{Q}_1) + \int_{\mathbf{Q}_1}^{\mathbf{Q}} d\mathbf{Q} \cdot \mathbf{P} \quad (11)$$

where $\mathbf{Q}_1 = \mathbf{Q}(t_1)$ and $\mathbf{P}_1 = \mathbf{P}(t_1)$ are chosen at the initial time t_1 .

B. The Self-Consistent Eikonal Approximation. We must yet obtain the equations for $\chi(\mathbf{Q})$. This is greatly simplified when a short wavelength approximation is valid so that gradients of the preexponential functions can be neglected compared to deBroglie wavenumbers $2\pi/\lambda$. In this case we have that

$$\left| \frac{\partial^2 \chi_\Gamma}{\partial \mathbf{Q}^2} \right| \left| \frac{\partial \chi_\Gamma}{\partial \mathbf{Q}} \right| \ll \frac{2\pi}{\lambda} \text{ and } \left| \frac{\partial \chi_\Gamma}{\partial \mathbf{Q}} \right| |\chi_\Gamma| \ll \frac{2\pi}{\lambda} \quad (12)$$

Using these inequalities, eqs 7 and 8 are approximated by the convenient nonlinear differential equation

$$\begin{aligned} \left[\frac{\mathbf{P}}{M} \cdot \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{Q}} + \mathbf{H}_\mathbf{Q} - \mathbf{I}W(\mathbf{Q}) \right] \chi(\mathbf{Q}) &= 0 \\ W(\mathbf{Q}) &= V(\mathbf{Q}) + iU(\mathbf{Q}) \\ V(\mathbf{Q}) &= (\chi^\dagger \chi)^{-1} \chi^\dagger \mathbf{H}_\mathbf{Q} \chi \\ U(\mathbf{Q}) &= \frac{\hbar}{2M} \frac{\partial}{\partial \mathbf{Q}} \cdot \mathbf{P} \end{aligned} \quad (13)$$

with the functions $\mathbf{P}(t)$ and $\mathbf{Q}(t)$ given by

$$\begin{aligned} d\mathbf{P}/dt &= -\partial V/\partial \mathbf{Q} \\ d\mathbf{Q}/dt &= \mathbf{P}/M \end{aligned} \quad (14)$$

To specify boundary conditions, we reintroduce indices and recall that in photodissociation we need scattering wave functions $\psi_{\Gamma\alpha}^{(-)}$ with incoming wave asymptotic forms that develop from the free state ψ_α^0 . In the center-of-mass frame we have

$$\begin{aligned} \psi_\alpha^0(\mathbf{Q}; \mathbf{p}_1) &= (2\pi\hbar)^{3/2} \exp(i\mathbf{p}_1 \cdot \mathbf{r}/\hbar) u_\alpha(\mathbf{Q}') \\ u_\alpha(\mathbf{Q}') &= \sum_\zeta \chi'_{\alpha\zeta}(\mathbf{Q}') \exp[iS'_{\alpha\zeta}(\mathbf{Q}')/\hbar] \end{aligned} \quad (15)$$

where we have separated the coordinates into the relative vector position \mathbf{r} and the remaining internal coordinates \mathbf{Q}' and have written the bound state u_α of the fragments as a sum of eikonal-like exponentials. We then find

$$\begin{aligned} \psi_\alpha^0(\mathbf{Q}; \mathbf{p}_1) &= \sum_\zeta \chi_{\alpha\zeta}^0(\mathbf{Q}) \exp[iS_{\alpha\zeta}^0(\mathbf{Q}')/\hbar] \\ S_{\alpha\zeta}^0(\mathbf{Q})/\hbar &= \mathbf{p}_1 \cdot \mathbf{r} + S'_{\alpha\zeta}(\mathbf{Q}') \\ \chi_{\alpha\zeta}^0(\mathbf{Q}) &= (2\pi\hbar)^{-3/2} \chi'_{\alpha\zeta}(\mathbf{Q}') \end{aligned} \quad (16)$$

with $p_1^2 + |\mathbf{P}'|^2 = (\mathbf{P}^0)^2 = 2M[E - V^0(\mathbf{Q})]$, where \mathbf{r} and \mathbf{Q}' are in regions with vanishing couplings, and \mathbf{P}^0 is the total momentum in those regions.

To account for these free-motion conditions, we define new amplitudes within a column matrix \mathbf{F}_α of functions by means of

$$\begin{aligned} \psi_\alpha(\mathbf{Q}) &= \sum_\zeta \chi_{\alpha\zeta}(\mathbf{Q}) \exp[iS_{\alpha\zeta}(\mathbf{Q})/\hbar] \\ \chi_{\alpha\zeta}(\mathbf{Q}) &= \chi_{\alpha\zeta}^0(\mathbf{Q}_1) \mathbf{F}_{\alpha\zeta}(\mathbf{Q}) \end{aligned} \quad (17)$$

so that at $t = t_1$ we find

$$\mathbf{F}_{\alpha\zeta}(\mathbf{Q}_1) = [\delta_{\Gamma\alpha}] = \mathbf{I}_\alpha \quad (18)$$

where Γ_α signifies (Γ_A, Γ_X) ; $\mathbf{F}_{\alpha\zeta}$ at \mathbf{r}_1 contains a 1 in the Γ_α position and zeroes elsewhere.

Equation 13 and the initial condition at t_1 take simple forms when use is made of the dependence of \mathbf{Q} on time. Dropping temporarily the index ζ , eq 14 gives $(\mathbf{P}/M) \cdot (\partial/\partial \mathbf{Q}) = (d/dt)$. Further defining

$$\begin{aligned} \mathbf{F}_\alpha(\mathbf{Q}) &= \exp\{i \int_{t_1}^t dt' W[\mathbf{Q}(t')]/\hbar\} \mathbf{A}_\alpha(t) \\ &= \exp\{i \int_{t_1}^t dt' V[\mathbf{Q}(t')]/\hbar\} \\ &\quad \times \exp\{-\int_{t_1}^t dt' U[\mathbf{Q}(t')]/\hbar\} \mathbf{A}_\alpha(t) \end{aligned} \quad (19)$$

and $\mathbf{H}_t = \mathbf{H}_\mathbf{Q}(t)$, we find that the magnitude of \mathbf{F} changes with the divergence of streamlines, as it contains the real integrand U/\hbar in the second exponent. This exponential factor can be expressed as $(J/J_1)^{-1/2}$,²³ where J is the Jacobian of a transformation from space \mathbf{Q} to trajectory variables $(t, \bar{\mathbf{Q}}_1)$, with $\bar{\mathbf{Q}}_1$ a collection of coordinate values at t_1 . Equation 13 gives the set of coupled ordinary differential equations

$$\left(\frac{\hbar}{i} \frac{d}{dt} + \mathbf{H}_t \right) \mathbf{A}_\alpha(t) = 0 \quad (20)$$

for the column matrix $\mathbf{A}(t)$, which satisfies the simple initial conditions $\mathbf{A}_\alpha(t) = \mathbf{I}_\alpha$. From the hermitian property of \mathbf{H} , one finds $\mathbf{A}_\alpha^\dagger(t) \mathbf{A}_\alpha(t) = \mathbf{I}$, and as a result,

$$V(\mathbf{Q}) = \mathbf{A}_\alpha^\dagger \mathbf{H} \mathbf{A}_\alpha = V_t \quad (21)$$

with $V_{t_1} = E_{\Gamma_f}(\mathbf{Q}_1)$. Equation 20 is the standard one for the time-dependent Schrödinger equation with a hermitian Hamiltonian in a basis of electronic states.

The procedure required to obtain $\psi_\alpha^{(-)}(\mathbf{Q}; \mathbf{p}_1)$ is now clear. One must solve eqs 14 and 20 simultaneously, to obtain solutions in which the nuclear motions and electronic transitions are self-consistently coupled. The wave function $\psi_\alpha^{(-)}$ can be reconstructed from eqs 5, 17, and

$$\begin{aligned} S_\alpha(\mathbf{Q}) &= S_\alpha(\mathbf{Q}_1) + \int_{\mathbf{Q}_1}^{\mathbf{Q}} (d\mathbf{r} \cdot \mathbf{p} + d\mathbf{Q}' \cdot \mathbf{P}') \\ &= \mathbf{p}_1 \cdot \mathbf{r} + S'_\alpha(\mathbf{Q}'_1) + \Delta S_\alpha^{(r)}(\mathbf{r}) + \Delta S'_\alpha(\mathbf{Q}') \\ \Delta S_\alpha^{(r)}(\mathbf{r}) &= \int_{r_1}^r d\mathbf{r} \cdot (\mathbf{p} - \mathbf{p}_1) \\ \Delta S'_\alpha(\mathbf{Q}') &= \int_{\mathbf{Q}'_1}^{\mathbf{Q}'} d\mathbf{Q}' \cdot \mathbf{P}' \end{aligned} \quad (22)$$

Here the third line gives the shift of the action for relative motion, which goes to zero for $r > r_1 \rightarrow \infty$, and the last line gives the shift of the action for internal motion.

From eqs 6 and 17, the full eikonal wave function takes the form, in a column notation,

$$\psi_\alpha^{(-)}(\mathbf{Q}) = \sum_\zeta \chi_{\alpha\zeta}^0(\mathbf{Q}_1) \mathbf{F}_{\alpha\zeta}(\mathbf{Q}) \exp\{iS_{\alpha\zeta}(\mathbf{Q})/\hbar\} \quad (23)$$

where we have restored the ζ index.

It is of interest that if one decomposes the elements of \mathbf{A}_α into their real and imaginary parts by means of

$$A_{\Gamma\alpha} = (2\hbar)^{-1/2} (X_{\Gamma\alpha} + iY_{\Gamma\alpha}) \quad (24)$$

one finds that the $X_{\Gamma\alpha}$ and $Y_{\Gamma\alpha}$ components behave like coordinate and momentum variables whose time-derivatives follow from the Hamiltonian equations, with the Hamiltonian $H(\mathbf{P}, \mathbf{Q}, X, Y)$ of eq 10 considered now a function of all the indicated arguments. This provides an alternative, purely Hamiltonian treatment of the dynamics of coupled electronic

and nuclear motions,^{3,21} which we have used in calculations of ion-diatom collisions.²¹

3. Photodissociation Cross Sections

Photodissociation cross sections can be obtained from the matrix elements of the dipole vector component \hat{D}_σ , which is an operator on electronic and nuclear variables. The matrix elements for the initial electronic state $\Gamma = 1$ with vibrational quantum numbers \mathbf{v}_1 take the form¹⁰

$$D_{\text{fi}} = \sum_{\Gamma} \langle \psi_{\Gamma\alpha}^{(-)}(\mathbf{p}_f) | (D_\sigma)_{\Gamma 1} | \psi_{1\mathbf{v}_1} \rangle$$

$$(D_\sigma)_{\Gamma 1} = \langle \Gamma; \mathbf{Q} | \hat{D}_\sigma | 1; \mathbf{Q} \rangle \quad (25)$$

where the initial molecular state i is given by $|1; \mathbf{Q}\rangle \psi_{1\mathbf{v}_1}(\mathbf{Q})$ insofar as the initial electronic state is $\Gamma = 1$, and $\psi^{(-)}$ is a scattering state for final relative momentum \mathbf{p}_f and with incoming wave boundary conditions. Hence, the second eq 25 gives the transition dipole between the electronic states 1 and Γ , which is an operator on the nuclear variables. The explicit form of D_{fi} in terms of a multiple integral is

$$D_{\text{fi}} = \sum_{\Gamma} \int d\mathbf{Q} \psi_{\Gamma\alpha}^{(-)}(\mathbf{Q}; \mathbf{p}_f)^* [D_\sigma(\mathbf{Q})]_{\Gamma 1} \psi_{1\mathbf{v}_1}(\mathbf{Q}) \quad (26)$$

with $\psi_{1\mathbf{v}_1}$ the nuclear bound state in the center-of-mass frame, and $\psi_{\Gamma\alpha}^{(-)}$ given by the eikonal approximation of the previous section. This integral may be rewritten in a way convenient for calculations, in terms of new variables.

At the time t_1 , with r_1 outside the interaction region, we can write (in Cartesian coordinates with the z -axis parallel to \mathbf{p}_f), $\mathbf{r}_1 = (b\cos\phi_1, b\sin\phi_1, z_1)$ and $\mathbf{p}_1 = (0, 0, p_f)$, where b is the impact parameter for the final scattering state and ϕ_1 is the azimuthal angle of relative motion at t_1 . Next, instead of the internal momenta and positions $(\mathbf{P}'_1, \mathbf{Q}'_1)$, we introduce internal action and angle variables $(\mathbf{I}_1, \mathbf{w}_1)$ with the actions \mathbf{I}_1 determined by the initial internal energies. Then $\mathbf{Q} = \mathbf{Q}(t; b, \phi_1, z_1, \mathbf{I}_1, \mathbf{w}_1)$, and one can choose the arguments of \mathbf{Q} , for fixed z_1 , as new variables. The multiple integral in eq 26 may be rewritten in terms of these new variables with a Jacobian transformation to obtain

$$D_{\text{fi}} = \sum_{\Gamma} \int dt db d\phi_1 d\mathbf{w}_1 J(r, \theta, \phi, \mathbf{Q}'; t, b, \phi_1, \mathbf{w}_1) \times$$

$$\psi_{\Gamma\alpha}^{(-)}(\mathbf{Q}; \mathbf{p}_f)^* [D_\sigma(\mathbf{Q})]_{\Gamma 1} \psi_{1\mathbf{v}_1}(\mathbf{Q}) \quad (27)$$

where J is the Jacobian determinant and we have used spherical coordinates for \mathbf{r} . This equation is very convenient for computational work. The integral can be calculated starting with chosen values of b, ϕ_1, z_1 and \mathbf{w}_1 and adding over t as one integrates the equations of motion. For a fixed z_1 , this must be repeated and the results added for several sets of initial variables $(b, \phi_1, \mathbf{w}_1)$ as needed to obtain a converged result. To carry out the integration over \mathbf{w}_1 , it is sometimes advantageous to incorporate the factor $\chi^0(\mathbf{Q}_1)$ of eq 17 in a biased sampling of initial internal coordinates. For example, from eq 16 for one internal variable this is accomplished changing w_1 to a new variable

$$y_{\alpha\zeta}(w_1) = \int_0^{w_1} dw' |\chi'_{\alpha\zeta}[Q'(w')]| \quad (28)$$

with a maximum $y_{\alpha,\text{max}}$ for $w_1 = 2\pi$. In this way, when one samples y at equal intervals one is choosing more w_1 values in the regions where $|\chi'_{\alpha\zeta}(Q'_1)|$ is largest.

Equation 27 gives a function of z_1 that must be averaged over values between z_a and z_b . Comparing the eikonal wave function constructed from trajectories starting at the two arguments $\mathbf{Q}_a = (z_a, \mathbf{Q}'_a)$ and $\mathbf{Q}_b = (z_b, \mathbf{Q}'_b)$ in the asymptotic region, one finds that their phases differ by

$$\Delta = [\mathbf{p}_1 \cdot (\mathbf{r}_b - \mathbf{r}_a) + \int_{\mathbf{Q}_b}^{\mathbf{Q}_a} d\mathbf{Q}' \cdot \mathbf{P}'] / \hbar \quad (29)$$

The first term is common to all trajectories irrespective of the choice of \mathbf{Q}'_0 , whereas the second term is the internal action accumulated between z_a and z_b . The latter can be set equal to $\hbar(N + \delta)$, with N an integer and $\delta = 0$ or $1/2$, by proper choice of z_a and z_b and, again irrespective of the value of \mathbf{Q}'_0 . Then D_{fi} oscillates asymptotically with a period of length $|z_a - z_b|$ or $2|z_a - z_b|$.

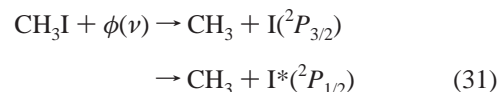
The photodissociation cross sections can be obtained averaging over these periods by means of

$$\frac{d\sigma_{\text{fi}}}{d\Omega} = \frac{2\pi}{\hbar c} p_{\text{fi}} m g(\omega)^2 \frac{1}{|z_b - z_a|} \int_{z_a}^{z_b} dz_1 |D_{\text{fi}}(z_1)|^2 \quad (30)$$

where $g(\omega) = i[\hbar\omega/(2\epsilon_0)]^{1/2}$, and $p_{\text{fi}} = [2m(E_{1\mathbf{v}_1} + \hbar\omega - E_\alpha)]^{1/2}$ is the final relative momentum for the transition.

4. Model and Results for CH₃I

A. The Model. The process of interest starts with the CH₃I molecule in its ground electronic and vibrational state absorbing light (a photon) of frequency ν to get excited to states 1Q_1 and 3Q_0 from which it dissociates as



where CH₃ is a planar radical. The CH₃I molecule is modeled as a collinear three-body system made up of C, I, and the three H atoms constrained to a plane perpendicular to the C–I bond. In this model there are only two coordinates describing the vibrational motions and dissociation: R , the distance from I to the center of mass of CH₃; and r , the distance between the carbon and the plane of the three hydrogen atoms. The initial ground vibrational state is designated as $(v_1, v_2) = (0, 0)$, with one of the quantum numbers referring to the umbrella mode where the three H atoms remain on a plane and this vibrates with respect to the C atom, and corresponding to the final vibrational quantum number v , for the two-body model of CH₃.

The potential energy surfaces corresponding to the three electronic states $\Gamma = 0, 1, 2$ of CH₃I are designated by V_{00} for the bound ground state, V_{11} for the $^3Q_{0+}$ state going asymptotically to CH₃ + I*, and V_{22} for the 1Q_1 state going asymptotically to CH₃ + I after a crossing. These and their diabatic coupling V_{01} have been constructed semiempirically in previous similar model studies.^{43,44} The transition dipole functions $D_{\Gamma, \Gamma'}(R) = D_{01}, D_{02}$ were also constructed from experimental information.⁴³ Here we use the same functions, to compare our results, only with regard to the dynamics of photodissociation. The initial vibrational state of CH₃I was written as a product of harmonic oscillator functions, as commonly done,³⁰ and the final vibrational state of CH₃ was also treated as harmonic.

The eikonal treatment with the two variables $\mathbf{Q} = (R, r)$ has been described in detail in reference 28, and will only be summarized. Integration of the trajectory equations gives the functions $R(t), r(t), P(t), p(t)$, and $S[R(t), r(t)]$, which depend parametrically on the values R_1, r_1, P_1, p_1 at t_1 . These are chosen

to satisfy energy conservation, with $P_f = P_i$ the final relative momentum, p_1 and r_1 related by the phase space trajectory of the C–H₃ harmonic oscillator, R_1 chosen to be large, and $r_1 = a \sin(w_1)$ with w_1 an angle variable to be chosen between 0 and 2π . Introducing the Jacobian $J(t, w_1) = \partial(R, r) / \partial(t, w_1)$ for the $(R, r) \rightarrow (t, w_1)$ transformation, the preexponential function in the eikonal wave function is

$$\chi(t, r) = \chi_1 |J_1 / J(t, w_1)|^{1/2} \exp[-\mu(t, w_1)/2] \mathbf{A}(t, w_1) \quad (32)$$

where the subindex 1 refers to values at t_1 , χ_1 contains the vibrational state $u_v(r_1)$, and $\mu = \arg(J) - \arg(J_1)$ is a trajectory index. The matrix \mathbf{A} has two components corresponding to the states $\Gamma = 1, 2$ and satisfies a 2×2 matrix differential equation in t . Finally, transition integrals are obtained integrating over time along trajectories, using the transformation

$$\int dR dr |u(r_1) F(R, r) = \int dt dw_1 J(t, w_1) |u(r_1) F[R(t, w_1), r(t, w_1)] \quad (33)$$

which is constructed as a sum over discrete values of w_1 . Calculations were done by numerical integration with a predictor-corrector sequence with variable step size. In all cases, only a very small number of trajectories (of the order of 1000) were needed to obtain the transition integrals to the desired accuracy.

The quantities related to experiments are the relative values of integral photodissociation cross sections for the various products in their electronic and vibrational states, which can be obtained from our theory as state-to-state cross sections. Adding over final vibrational states of CH₃, it is also possible to obtain total integral cross sections σ_s into the two final electronic states $s = g, e$ of I and I*, from which branching ratios $R_s = \sigma_s / (\sigma_g + \sigma_e)$ are found so that $R_e + R_g = 1$.

B. Branching Ratios and Partial Cross Sections. Results for the dominant branching ratio, R_e , for production of I*, were found in our calculations to equal 0.63 and 0.71 for the two dissociation wavelengths $\lambda = 266$ and 248 nm, respectively, to be compared to the full quantum theoretical results of 0.61 and 0.81. We therefore find that at 266 nm there is excellent agreement with the quantal result, while the SCE approximation is 12% lower at 248 nm.

The other comparison of interest is the distribution of final vibrational states of the CH₃ fragment. Our previous work using only one excited potential surface compared very well with exact quantum results,³⁰ but the addition of a second excited potential surface to the model has led to different vibrational distributions in the full quantum results.⁴⁴ In Figures 1 and 2, the partial cross sections from our treatment (SCE) and that of ref 44 (G. & S.) are compared for the two dissociation products, with our results normalized to give the same area under the curves so that the values of R_e are the same for both sets of numbers. Panels (a) and (b) of Figure 1 show that when the final product is I*, the present results are nearly identical to the full quantal results. For the I final product, for which cross sections are small at $v = 0$ as shown in panels (a) and (b) of Figure 2, the trends with increasing quantum numbers and magnitudes are generally well reproduced, except for small v . It is not surprising that the largest discrepancy occurs for I and small v . This is because the wave function amplitude starting on the potential V_{11} and leading to I must evolve from an initial excitation through the potentials crossing along a seam, which is sensitive to semiclassical approximations; also, the eikonal approximation for low vibrational states $v = 0, 1$ is less accurate than for the higher v values. The fact that the more significant deviation occurs at

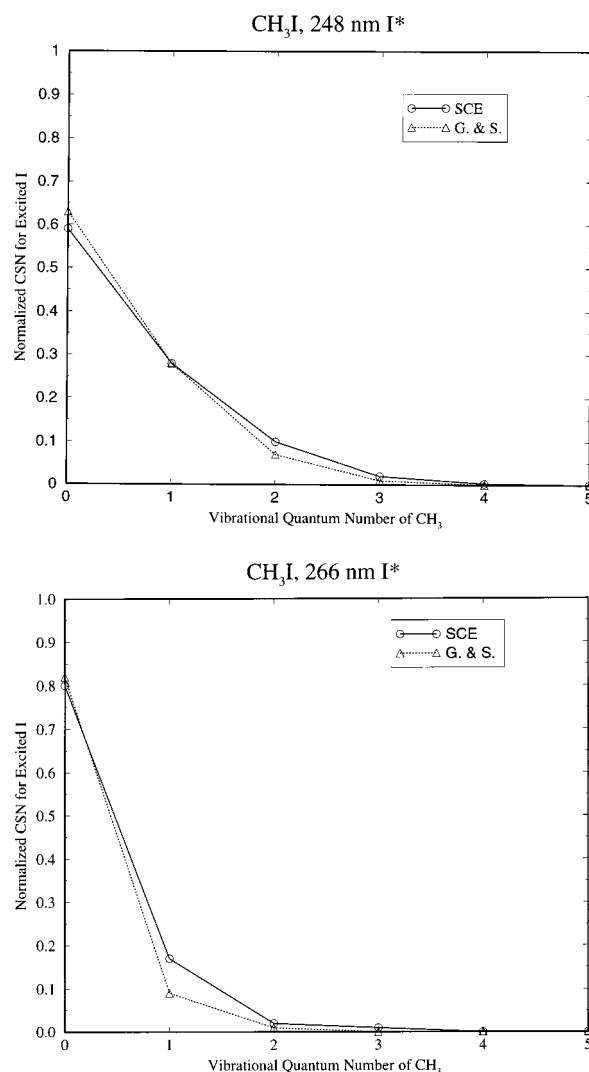


Figure 1. Partial photodissociation cross section for production of excited iodine vs final vibrational quantum number of the CH₃ state for the umbrella mode: (a) for a photon wavelength of 248 nm; (b) for a photon wavelength of 266 nm.

the lower photon energy (266 nm) is also to be expected, because this gives a lower kinetic energy at the crossing and a short wavelength approximation is then less accurate. Overall, however, the SCE results have given quite accurate branching ratios for both I and I*, and good distributions of final vibrational states for the predominant product species, I*.

5. Conclusion

In this contribution, incoming wave scattering states needed in photodissociation have been obtained in an eikonal approximation that neglects terms slowly varying over the deBroglie wavelengths of nuclear motions. Doing this consistently and starting with an eikonal representation of the wave function, we obtained coupled differential equations for the nuclear motions and the time-dependence of the electronic amplitudes, which must be solved simultaneously. Their boundary conditions result from energy conservation and from the asymptotic form of the wave functions when the internal ones are also given in eikonal, or semiclassical, form. This leads to self-consistent eikonal wave functions for each of the electronic states of the polyatomic system. With this information, one can calculate the needed dipole transition integrals. A change of variables allows calculation of state-to-state cross sections from

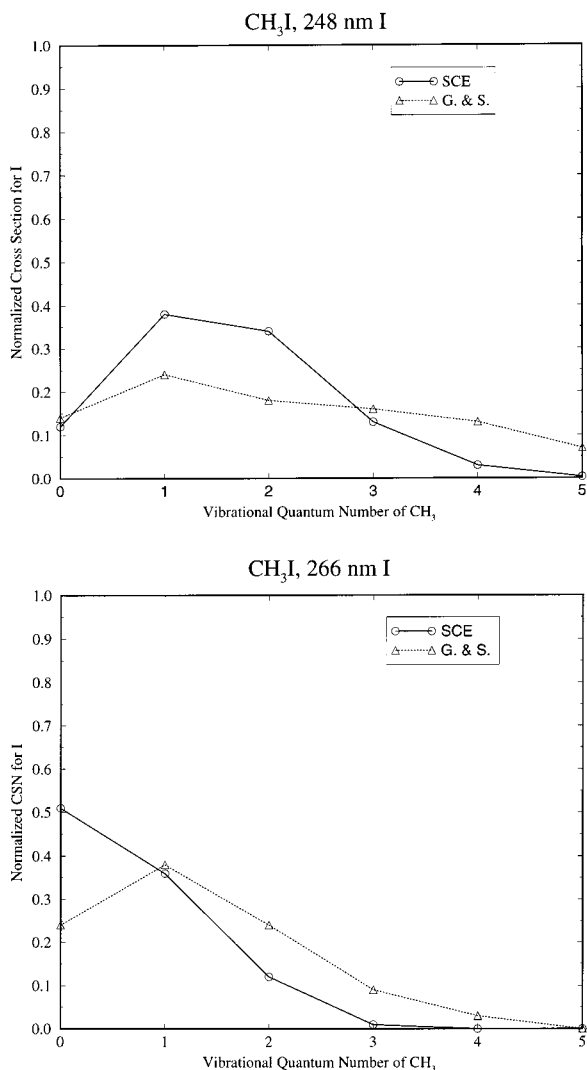


Figure 2. Partial photodissociation cross section for production of ground-state iodine vs final vibrational quantum number of the CH₃ state for the umbrella mode: (a) for a photon wavelength of 248 nm; (b) for a photon wavelength of 266 nm.

information on nuclear classical trajectories. The procedure allows for phase interference, because it incorporates the mechanical actions in the phase of integrands as one adds over the time variable. The integration of differential equations requires only knowledge of the initial conditions, so that there is no need to search for those trajectories that would reconstruct a given final state. Instead, one projects on the desired final state.

The application to a model of CH₃I photodissociation was done for two purposes: illustration of the method, which is quite simple in its numerical implementation, and a type of initial variable representation insofar as it requires only choices of initial conditions; and second for comparison with accurate quantal calculations with the same potential surfaces. This gave, overall, quite accurate branching ratios and good distributions of final vibrational states for the predominant product species; in effect, the figures for the partial cross sections, normalized to a scale of 0.0–1.0, show deviations from accurate quantal calculations of the order of 10% for most final vibrational states. The largest deviation is for formation of I and CH₃($v = 0$) at 266 nm, the most unfavorable case for a semiclassical treatment insofar as the relative kinetic energy of the fragments is smaller and the vibrational state is the lowest. The most likely way to improve on this should be to start with a more accurate

semiclassical representation of the $v = 0$ final state and to add more initial values of the vibrational coordinate r_1 . Applications to similar polyatomic systems, such as ICN, could be done with the same approach. It is encouraging that only a very small number of trajectories (of the order of 1000) were needed to obtain the transition integrals to the desired accuracy. Even if a factor of 20 more trajectories might be needed to include rotational motions, our approach provides an alternative to the 10^5 to 10^6 trajectories and Jacobians needed for the more accurate calculations with initial value representations.

Perhaps the biggest advantage of the present SCE approach is that it appears applicable to the dissociation of large polyatomic with no modifications in the computational procedure. It can deal with several vibrational degrees of freedom as well as rotational ones, and it can also describe changes in the conformation of the excited polyatomic. On the other hand, the eikonal approximation can describe only processes that occur in classically allowed regions of the effective potential $V(\mathbf{Q})$, i.e., in regions accessible to trajectory bundles. It also restricts the initial conditions to those allowed by the form of the asymptotic wave functions, so that the initial positions must fall within the classical turning points of the initial internal motions. Physical quantities of interest are, however, sums over many initial conditions, and errors due to exclusion of classical forbidden regions are frequently small because only small fractions of the trajectories are likely to originate in these regions for most applications to photodesorption and collisional energy transfer.

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