Nonadiabatic interactions in the photodissociation of ICN

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Photodissociation of ICN in the $\tilde{A}$ continuum has been modeled using classical trajectories assuming that all absorption from the linear ground state is to a single linear diabatic excited state which dissociates to form $\text{I}^* (^2P_{1/2})$ and $\text{CN}(^2\Sigma^+, \nu = 0)$. It is also assumed that, in nonlinear excited state configurations, nonadiabatic transitions occur to a bent surface which correlates diabatically to ground state $\text{I}^2(\tilde{P}_{3/2})$ and $\text{CN}(^2\Sigma^+, \nu = 0)$. Empirical potential surfaces with frozen CN bond lengths are employed, while transitions between the surfaces are treated using either the Miller–Meyer classical electron model or a simple diabatic version of the Tully–Preston surface-hopping model. With the above assumptions, the Miller–Meyer method is found to give much better agreement with the experimental results. Theoretical results obtained with the Miller–Meyer method are compared with recent experimental data on the $\text{I}^*/\text{I}$ branching ratio, the average CN rotational energies, and the product CN rotational distributions as a function of photolysis wavelength for $\lambda = 248$, 266, 280, 290, and 308 nm. Except for the branching ratio at 248 nm, we obtain satisfactory agreement with the experimental results.

I. INTRODUCTION

The photodissociation of ICN in the $\tilde{A}$ continuum has long been a subject of experimental and theoretical investigation as well as a considerable amount of controversy.\textsuperscript{1–12} It is now established experimentally that there are two different electronic pathways involved in the reaction:\textsuperscript{3,5,10,11}

\[
\text{ICN} + h\nu \rightarrow \text{I}^* (^2P_{3/2}) + \text{CN}(^2\Sigma^+) \quad (1)
\]

\[
\rightarrow \text{I}^* (^2P_{1/2}) + \text{CN}(^2\Sigma^+). \quad (2)
\]

Pitts and Baranovski have measured the $\text{I}^*/\text{I}$ branching ratio as a function of photolysis wavelength.\textsuperscript{11} At 266 nm, the excited spin-orbit state of iodine, $\text{I}^*$, accounts for approximately 60% of the iodine product yield; the ratio falls off markedly at both higher and lower wavelengths. Ling and Wilson, in time-of-flight measurements of the recoil velocity of the ICN fragments, determined that both product channels result from primarily parallel transitions.\textsuperscript{3} Recent experimental determinations of recoil velocity anisotropies\textsuperscript{17} and product rotational alignments\textsuperscript{20} corroborate these results. The nascent CN fragments exhibit very little vibrational excitation in the photolysis region 235–290 nm.\textsuperscript{4,12,16} The rotational distributions, however, are much more interesting; they appear to be "multimodal" and depend markedly on the photodissociation energy. At 266 nm, the distribution is peaked at very low $N''$ with a broad lower intensity tail out to at least $N'' = 60$.\textsuperscript{12,16,17} ($N''$ is the rotational quantum number of the CN fragment.)

There has also been much theoretical work on the photolysis of the ICN molecule, which has been taken as a model to test various theories of photodissociation, both quantum mechanical and classical. The early theoretical work concentrated on calculating the nascent CN vibrational distributions, often treating the system collinearly.\textsuperscript{1,6} While these calculations were quite successful in predicting that little energy would go into vibrational excitation, they did not anticipate the importance of rotation as a channel for the released energy. After the experimental study of the rotational distributions at 266 nm, theorists have attempted to interpret or compute the nascent CN rotational distributions.\textsuperscript{8,9,16,18,19} Using a Franck–Condon model, Morse, Band and Freed,\textsuperscript{8} and also Beswick and Gelbart,\textsuperscript{9} attempted to explain these distributions as a function of parent-molecule bending and overall rotation. The calculations used excited state potential surfaces which were independent of bending angle. Pattengill, employing a 3D classical trajectory method, has continued this study using the potential surfaces developed by Morse, Band, and Freed.\textsuperscript{18} His calculations result in the prediction that the CN which comes from the $\text{I}^*$ surface is rotationally hotter than the CN which comes from the surface which correlates to ground state I. This conclusion is at odds with the experimental results.\textsuperscript{17} Models based on excited state potentials which are independent of the bending angle have not been able to reproduce either the extremely cold portion of the distribution or the broad shape of the tail. Experiments using a supersonic beam reveal that the CN rotational distributions resulting from ICN cooled to a few degrees Kelvin differ little from ICN at room temperature.\textsuperscript{15,16} Therefore, the dynamics of the photodissociation process must play a key role in determining the nascent CN rotational distributions. Furthermore, the excited state surfaces involved must be anisotropic; they must in fact be strong functions of the bending angle. Using classical trajectory methods, Waite et al. have investigated the dynamics on the various bent excited state surfaces to see if the experimental rotational distributions at 266 nm could be reproduced.\textsuperscript{19} However, these authors include initial conditions which result from photolysis at a wide range of photolysis energies (∼7500 cm⁻¹); hence their computed rotational distributions are superpositions of distributions representing a wide range of photodissociation wavelengths rather than distributions which result from photodissociation at a single wavelength. Marinelli et al.\textsuperscript{16} have also used a classical trajectory model to compute the rotational distributions. Based upon the deconvolution of the absorption spectrum given by Pitts and Baranovski,\textsuperscript{11} they postulate that
three excited state surfaces are involved in the photodissociation process: a linear surface that correlates to $I^* + CN$ and is responsible for the cold portion of the rotational distributions and two bent surfaces that correlate to ground state I and CN and contribute to the high temperature portion of the distribution. They obtain excellent agreement with the average rotational energies but their distributions are too narrow. Neither the deconvolution of the ICN spectrum of Pitts and Baranovski nor the work of Marinelli et al. allow for nonadiabatic transitions between the excited state surfaces. Marinelli et al., in fact, suggest that nonadiabatic interactions may account for the discrepancies between their theoretical and their experimental results.

There are other reasons to consider that nonadiabatic interactions may play an important role in the photodissociation dynamics. A simple correlation diagram proposed by Morse et al. based on Hund's case c coupling ($\Omega_\pi, \omega$) indicates that there is only one linear excited state which can be reached through a parallel transition in the absence of vibronic interactions$^8$ (see Fig. 1). This state, which correlates to $I^*$ and ground state CN, has $0^+$ symmetry. Furthermore, the only possible bent state which can be accessed through a predominantly parallel transition from the linear $0^+$ ground state is one which arises from a $0^+$ state.$^{17}$ However, in the linear configuration the $0^+$ surfaces will cross other surfaces which correlate dialibatically to ground state I and CN. These latter surfaces, which are partners in a doubly degenerate state in the collinear configuration, give rise in nonlinear configurations to two surfaces, one of $A'$ and $A^*$ symmetry. The surfaces of $A'$ symmetry will interact with the $0^+(A^*)$ state which carries most of the oscillator strength.

Therefore, if the potential coupling between these states is sizeable, there may be a large probability that the reaction will produce ground state products, even if all of the absorption is to the surface which correlates to $I^*$ in the collinear geometry.

In order to examine the possible effects of these crossings and avoided crossings, we have assumed that all of the absorption is to one linear diabatic ($0^+$) state which correlates to $I^* + CN$. There is recent experimental evidence$^{20}$ that perhaps 15% of the absorption is due to perpendicular transitions, and we will discuss this matter further below. Although there are in all likelihood more than two states involved in the photodissociation process, for the sake of simplicity we will consider only two: a bent diabatic surface which correlates to $I^*(2P_{3/2})$ and $CN(^2\Sigma^+)$, and the $0^+$ state in the collinear configuration which it crosses.

In this paper we will explore the nonadiabatic dissociation dynamics using classical trajectory methods. There is as yet no rigorously correct procedure for using classical dynamics in multisurface problems and we will have to adopt an approximate method. We will discuss the applicability of both classical-analog$^{21}$ and surface-hopping$^{22}$ methods to problems of this type. We will calculate nascent CN rotational distributions and product branching ratios at four photodissociation energies and compare our results with recent experimental ones.

II. THEORY
A. Photodissociation

The photodissociation process may be thought of as consisting of two steps: the first, a molecular excitation which involves a Franck–Condon transition between the ground state and the excited state or states and the second, a “half-collision” in which the fragments dissociate on the excited state potential surface(s). Exact quantum treatments of photodissociation neither require nor imply this separation$^{23}$ but many approximate quantum mechanical treatments do.$^{8,24,25}$ For a purely classical calculation this separation is, however, essential, since the initial conditions for the classical trajectories are determined by a vertical transition from the ground state.

In our model, we ignore the CN vibration. We assume that motion takes place in a plane; this assumption is appropriate in the case of zero overall angular momentum, which is the case we will deal with. The Hamiltonian is given by

$$H = P_R^2 / 2M + (J - P_\theta)^2 / 2MR^2 + P_\theta^2 / 2mR^2_{CN} + V(R, \theta),$$

(3)

where $R$ is the distance from I to the CN center-of-mass, $\theta$ is the angle between the vector $\vec{R}$ and the CN axis, $J$ is the total angular momentum (in this paper, $J = 0$), $P_R$ is the radial linear momentum, $P_\theta$ is equal to the angular momentum of the CN with respect to its center-of-mass, $M$ and $m$ are the reduced masses of I–CN and CN, respectively, and $V(R, \theta)$ is the potential energy. In motion confined to the plane, $(J - P_\theta)$ is $l$, the orbital angular momentum. In the case of $J = 0, l = - P_\theta$.

The potential of the ground state of ICN is taken to be

$$V_{gr} = 0.5k_R (R - R_0)^2 + 0.5k_\theta (\theta - \theta_0)^2,$$

(4)
where \( k_R \) and \( k_\theta \) are force constants calculated from the harmonic frequencies of the I-CN stretch and bend, respectively. We are assuming rotationless ICN in its ground vibrational state. The initial conditions are selected according to a modified Wigner distribution method developed by Patten-gill.\(^{18}\) The Wigner distribution allows us to sample classically forbidden regions of phase space necessary for the examination of photodissociation in the low energy wings of the absorption spectrum. Moreover, overall total energy must also be conserved in order to run trajectories which correspond to particular photolysis wavelengths. For rotationless ICN in its ground vibrational state, we can write the ground state Hamiltonian (for small displacements from equilibrium) as
\[
H_g = H_R + H_\theta,
\]
where
\[
H_R = P_R^2/2M + 0.5k_R (R - R_e)^2
\]
and
\[
H_\theta = \mu P_\theta^2 + 0.5k_\theta (\theta - \theta_e)^2,
\]
where \( R_e \) is the equilibrium position of the distance of I from the CN center-of-mass, \( \theta_e = 0.0 \), and
\[
\mu = 1/(2MR_e^2) + 1/(2mR_{CN}^2).
\]
The unnormalized Wigner distribution for the ground vibrational state can be written as
\[
W(R,\theta,P_R,P_\theta) = \exp\left\{ -2H_R/\hbar\omega_1 + ( -2H_\theta/\hbar\omega_2) \right\},
\]
where \( \omega_1 \) and \( \omega_2 \) refer to the I-CN stretch and bend frequencies, respectively. The total energy after absorption of a photon is
\[
E_{tot} = \hbar \nu + \epsilon_1 + \epsilon_2,
\]
where \( \hbar \nu \) is the energy of the absorbed photon and \( \epsilon_1 \) and \( \epsilon_2 \) are the zero-point energies of the two normal modes. We can consider \( E_{tot} \) to be an independent variable and can use the Jacobian of the transformation
\[
\{E_{tot},R,\theta,P_\theta\} \rightarrow \{R,\theta,P_R,P_\theta\},
\]
to write
\[
W(E_{tot},R,\theta,P_\theta) = |P_R^{-1}| W(R,\theta,P_R,P_\theta).
\]
This distribution allows us to select initial conditions which represent Franck-Condon transitions and which conserve total energy.

At a given photolysis energy, \( R, \theta, \) and \( P_\theta \) are picked randomly and \( P_R \) is computed from Eq. (3) using the excited state potentials. If \( P_R \) is real, then we use Eq. (9) to assign a statistical weight to the trajectory. This method is not, however without its computational difficulties. The distribution is inherently unnormalized so that the statistical weights vary widely in magnitude. If all trajectories are kept, then very low-probability trajectories make it difficult to get good statistics using a reasonable number of trajectories. Therefore we introduce a cutoff; exploratory work determined that results are not sensitive to moderate variations in this cutoff. The cutoffs are varied with wavelength to reflect the relative intensity of the absorption spectrum at the various wavelengths. The other potential problem is the possibility of extremely high-probability trajectories which swamp out all other contributions. To avoid this problem we set a probability maximum; the few trajectories which exceeded this maximum were given the maximum statistical weight. 500 trajectories were usually enough to determine average energies and branching ratios; however more trajectories are needed to obtain CN rotational distributions.

B. Excited state potential surfaces

Nothing is really known about the excited state potential surfaces of ICN; the potentials used in previous work are empirically based and were chosen to reproduce available experimental results \textit{within a given dynamical model}. Our potential surfaces are no different; the \( 0^+ \) surface, which carries the oscillator strength, is chosen to give good agreement with the absorption spectrum as calculated using the Wigner distribution. It has the form
\[
V_1 = A_1 \exp(-\alpha_1 R) - C/R^6 + B_1 \exp(-\beta_1 R)\theta^2 + E_{\text{dis}} + E_{\text{so}},
\]
where \( E_{\text{dis}} \) is the dissociation energy of I-CN bond in the ground state and \( E_{\text{so}} \) is the spin-orbit splitting of the iodine atom. The absorption spectrum could not be fit properly using a purely repulsive potential surface dissociating to \( 1^+ \) and CN since the potential must decrease to nearly the dissociation limit at low photon energies in order that the predicted absorption match the observed spectrum. The attractive term in the energy expression allows the correct absorption at wavelengths greater than 280 nm. Roughly speaking \( A_1 \) controls the position of the absorption maximum while \( \alpha_1 \) and \( C \) determine the width of the absorption. The \( R \) dependent bending force constant, \( B_1 \exp(-\beta_1 R) \), plays little part in reproducing the absorption spectrum but is important in determining the final CN rotational energy for fragments dissociating on this surface. The experimental and theoretical absorption spectrum are shown in Fig. 2.

The purely repulsive bent excited state surface is given by

![FIG. 2. Absorption spectrum of ICN calculated using classical-analog Hamiltonian as described in the text. The open circles denote absorption to the diabatic linear state. The solid line is the experimental absorption spectrum as measured by Pitts and Baranovski.](image)
\[ V_2 = A_2 \exp(- \alpha_2 R) \exp(- \gamma_2 \theta^2) + \exp(- \beta_2 R \theta^2) + E_{\text{diss}}, \] (11)

and the coupling potential is
\[ V_{12} = A_{12} \exp(- \alpha_{12} R) \{1 - \exp(- \gamma_{12} \sin^2 \theta)\}. \] (12)

The potential parameters were chosen to give the best fit to the experimental data at 266, 280, and 290 nm, i.e., the average energies, branching ratios, and rotational distributions, with slightly more emphasis placed on getting a good fit at 266 nm, using the classical-analog model.

Since we assume that the bent state does not have 0° symmetry in collinear configurations, we constrain the coupling potential to be zero when \( \theta = 0 \). Depending upon the collinear symmetry of this excited state, the coupling potential will behave linearly at small \( \theta \) (\( \Omega = 1 \)), or quadratically (\( \Omega = 2 \)).\(^{30}\) We explored both linear (sin \( \theta \)) and various quadratic couplings. We were unable to reproduce the experimental data using the sin \( \theta \) form of the coupling potential; one problem was that the rotational energy of the CN resulting from the 1* surface was much too high. Since we have used a quadratic coupling potential, we have in effect assumed the predissociation of the linear state by a “dark” state (\( \Omega = 2 \)) to which absorption is forbidden.

\( A_{12} \) determines the absolute magnitude of the coupling potential while \( \gamma_{12} \) controls how fast the coupling turns on with the bending angle. It turns out that both the branching ratios and the rotational distributions are very sensitive to \( \gamma_{12} \), but unfortunately in opposite ways. Generally speaking, large values of this parameter result in better agreement with the experimental 1*/1 branching ratios but also give rise to rotational distributions which are narrower than the experimental ones. The value finally chosen represents a compromise. The various molecular parameters used in these calculations are collected in Table I.

Various sections of the diabatic and adiabatic potential surfaces are shown in Figs. 3 and 4. As can be see, the surfaces are strongly coupled in the Franck–Condon region. Such strong coupling in this region is necessary to obtain the sensitivity to photolysis wavelength of both the branching ratios and CN rotational distributions. It is also needed to

\begin{table}[h]
\centering
\caption{Molecular parameters used in calculations.}
\begin{tabular}{lccc}
\hline
 & Linear surface & Bent surface & Coupling \\
\hline
\( A \) (cm\(^{-1}\)) & \( 1.725 \times 10^{14} \) & \( 1.49 \times 10^{10} \) & \( 1.88 \times 10^{9} \) \\
\( B \) (cm\(^{-1}\)) & \( 3.40 \times 10^{10} \) & ... & ... \\
\( \alpha \) (Å\(^{-1}\)) & 8.5 & 5.0 & 2.25 \\
\( \beta \) (Å\(^{-1}\)) & 12.32 & 5.1 & ... \\
\( \gamma \) & ... & 14.0 & 25.0 \\
\( C_p \) (cm\(^{-1}\) Å\(^4\)) & \( 1.92 \times 10^6 \) & ... & ... \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Cuts through the potential surfaces at fixed values of \( \theta \). The dashed lines denote diabatic curves; the solid lines denote adiabatic curves. The dotted line indicates the equilibrium position of \( R \) for the ground state surface. (a) \( \theta = 0 \), (b) \( \theta = 0.075 \) rad, (c) \( \theta = 0.125 \) rad.}
\end{figure}
achieve the large transfer of energy into CN rotation which occurs on the bent diabatic surface.

C. Dynamics—Classical-analog method

There is no straightforward way to apply classical mechanics to nonadiabatic processes.\textsuperscript{30a} We have used two different methods to treat the fragmentation dynamics: the classical-electron method developed by Meyer and Miller\textsuperscript{21} and a simple diabatic version of the Tully–Preston surface-hopping method.\textsuperscript{22} The classical-analog method turns out to be the most appropriate for this type of problem for reasons to be discussed below.

The classical-analog method, as well as the related self-consistent eikonal method,\textsuperscript{26} attempts to treat relevant electronic degrees of freedom on an equal footing with the nuclear degrees of freedom. This method has been applied with reasonable success to molecular scattering problems\textsuperscript{27,28} and some bound-state problems.\textsuperscript{29,30} It is an appropriate method for treating surfaces which are strongly coupled over a wide range of nuclear separations since it does not depend on the definition of a localized "crossing seam," as do the simpler versions of the surface-hopping method that use Landau–Zener type expressions for hopping probabilities. However, one advantage of surface-hopping is that different electronic channels are clearly associated with different trajectories; the assignment of electronic channels to particular trajectories is not so simple in any of the classical-path methods.

In the classical-electron method, a self-consistent averaged path is computed. In a two state system, we can define diabatic wave functions \(||\rangle\) and \(|2\rangle\) corresponding asymptotically to the two different electronic channels. The general time-dependent electronic wave function in this diabatic basis is given by

\[
|\Psi\rangle = a_1(t)|1\rangle + a_2(t)|2\rangle.
\]

In the classical-analog method the complex time-dependent coefficients are replaced by real conjugate action-angle-like variables \((n, q)\), such that

\[
a_i(t) = \left(\frac{n_i(t)}{\sqrt{2}}\right)^{1/2} \exp\{-i\,q_i(t)\}.
\]

The quantum mechanical electronic Hamiltonian is replaced by its expectation value,

\[
H_{el} = n_1H_{11} + n_2H_{22} + 2(n_1n_2)^{1/2}H_{12}\cos(q_1 - q_2).
\]

In this case, \(H_{11}\), \(H_{22}\) and \(H_{12}\) correspond to the diabatic potentials \(V_1\), \(V_2\) and \(V_{12}\) respectively. The total Hamiltonian \(\hat{H}\) is given by adding the appropriate classical kinetic energy expression to this classical analog electronic Hamiltonian.

The time evolution of both electronic and nuclear degrees of freedom is given by Hamilton’s equations (if \(\hbar\) is set equal to 1)\textsuperscript{31}:

\[
dn_i/\,dt = -\partial H/\partial q_i, \quad dq_i/\,dt = \partial H/\partial n_i, \quad \text{etc.}
\]

Two changes are made to this Hamiltonian in the actual calculation. Since total electronic probability is conserved, i.e., \(n_1 + n_2 = 1\), we can employ a canonical transformation to eliminate one of them and rewrite the Hamiltonian in terms of just one pair of action-angle variables, \(n\) and \(q\).\textsuperscript{21} An additional modification is the use of the Langer correction to the actions, which increments the actions by 1/2, i.e., \(n\rightarrow n + 1/2\). The final form of the electronic Hamiltonian is then

\[
H_{el} = nH_{11} + (1 - n)H_{22} + 2\left(n + 1/2\right)\left(3/2 - n\right)^{1/2}H_{12}\cos q.
\]

One reason for the use of the Langer modification is the avoidance of singularities in the equations of motion. However, these singularities could have been avoided simply by integrating the equations of motion in Cartesian coordinates,

\[
x = (2n)^{1/2}\cos(q), \quad y = (2n)^{1/2}\sin(q).
\]

A more compelling reason for the Langer correction arises when the classical-analog model is used in conjunction with the classical \(S\) matrix approach, where it is necessary to determine the final value of the action, \(n_f\), as a function of initial phase, \(q_0\).\textsuperscript{21} If the Langer modification is not made and
if the initial action is chosen to correspond to a particular
electronic state, i.e., \( n_f = 0 \) or 1 for the two state case, then
the final action will be independent of initial phase.\(^{21}\) Her-
man and Currier discuss further implications of this matter in
a recent publication.\(^{32}\)

In this paper, which describes the first application of the
classical-analog method to model nonadiabatic interactions
in a photodissociation process, the Langer modification has
an influence on both the Franck–Condon absorption step and
the subsequent fragmentation dynamics. Although \( n = 1 \) represents the purely linear diabatic state, \( n \) ranges from
\(-\frac{1}{2}\) to \( \frac{3}{2} \). In the initial conditions, \( n \) is set to 1 and
\( q \) is picked randomly from 0 to \( 2\pi \). Under these conditions, the electronic Hamiltonian is

\[
H_{el} = H_{11} + (3)^{1/2}H_{12} \cos q.
\]

(19)

We use this \( H_{el} \) in place of \( V \) in Eq. (3) and therefore the
coupling potential and electronic phase enter into the deter-
mination of initial conditions. The absorption spectrum in
Fig. 2 was calculated using Eq. (19).

Trajectories are run until \( R \) reaches a value where \( n \) and
\( P_o \) are stable. The final values of \( P_o \), which is the CN angular
momentum, are binned in the usual manner to give discrete
values of \( N^* \). The final electronic state is determined using a
simple quasiclassical quantization method. The final results are
binned; if \(-\frac{1}{2} < n < \frac{1}{2} \), then the system is defined to be
in the ground state \( I \) channel. Otherwise, excited \( I \) is pro-
duced. This method averages the primitive value of the tran-
sition probability over an integer width about the final quan-
tum number.\(^{21}\) Clearly, such an averaging procedure is
possible only when the Langer correction is used.

The method of quantization is the main difference
between the classical-analog method and other classical-
path methods.\(^{21}\) For example, an equally simple method of
determining the transition probability would be not to use
the Langer modification, to integrate in Cartesian coor-
dinates, and to interpret the final value of \( n \) as the probability
of remaining on the linear surface.\(^{21}\) In this method, each
averaged path corresponds to more than one final electronic
state. In our method, any given trajectory is associated with
only one final electronic state. We also compute, for each
batch of trajectories, a more global value of the electronic
transition probability, \( P_{1-o} \), by equating the average change
in quantum number, \( \langle n_f - n_i \rangle \), to its quantum mechanical
equivalent \( (\hat{n}_f - \hat{n}_i) \) \( P_{1-o} \).\(^{27}\) where \( n_f \) and \( n_i \) are the final
and initial values of \( n \). In our case, \( \hat{n}_i = 0 \) and \( \hat{n}_i = 1 \), so that,

\[
P_{1-o} = -\langle n_f - n_i \rangle.
\]

Except for the fact that we have used the Langer correction,
this number is equivalent to the value that would be obtained
using the classical-path method outlined above. The values
for the electronic transition probability which we compute
using the two methods typically agree to within 6\% al-
though occasionally they differ by as much as 20\%. Compar-
isons of several of these methods (and more elaborate
methods of determining transition probabilities) with exact
quantum mechanical results have been made, but it is not yet
clear that any one of them works best in all instances.\(^{21,27,28}\)

It is clearly desirable, for our purposes, to be able to assign a
given trajectory emerging in a specific rotational state \( N^* \) to
a particular electronic state.

One final comment is in order concerning coordinate
systems. Singularities exist in the equations of motion at the
extremal values of \( n \), -\( \frac{1}{2} \) and \( \frac{3}{2} \). Numerical instabilities
develop when \( n \) approaches these values as happens quite
frequently. In each of these regions it is necessary to perform
canonical transformations to Cartesian coordinates, where
the time-evolution equations have no singularities in that
region of phase space. Currier and Herman have described
this procedure in detail and we refer those interested to their
recent paper.\(^{28}\) We will only add that we find for our pur-
poses that, once the transformation to Cartesian coordinates
has been made, it saves a great deal of computer time to
continue computing in those coordinates, transforming to
the other set of Cartesian coordinates when necessary but
not back to action-angle variables. Because, unlike Currier
and Herman, we use a quasiclassical rather than a semiclassi-
cal quantization scheme, we do not have to worry about
transforming to the proper branch of \( q \).

D. Dynamics—Surface hopping

Simple diabatic surface-hopping calculations were car-
ried out on the above surfaces. The trajectories were begun
on the linear diabatic surface and propagated until they
reached the crossing seam, where the two surfaces are equal
in energy. At that point a two dimensional Landau–Zener
transition probability is computed\(^{33}\); the probability of
"hopping" to the bent diabatic surface is

\[
P_{1-o} = 1 - \exp(-2\pi Y/\hbar),
\]

(20a)

\[
Y = H^2_{12}/(\nabla V \cdot \nabla),
\]

(20b)

where \( v \) is the nuclear velocity on the diabatic surface and

\[
F = V_i(R, \theta) - V_j(R, \theta).
\]

(20c)

All quantities are evaluated at the position of the crossing.
Statistical weights are assigned to each branch of the trajec-
tory and each branch is continued until it reaches either an-
other crossing or its asymptotic value. Since typically a tra-
jectory reaches the crossing point only one or two times it
is easy enough to use all of the branches emerging from a
given set of initial conditions, i.e., we use the "ants" method
described by Tully and Preston.\(^{22}\) Each branch then emerges in
a definite electronic state with a statistical weight (Wigner
times Landau–Zener).

III. RESULTS AND DISCUSSION

A. Nascent CN rotational distributions

Our main goal in performing these calculations was to
 reproduce the nascent CN rotational distributions, the aver-
age rotational energy in each channel, and the I/I* branch-
ing ratio, all as a function of the photolysis wavelength. We
report here the results of our classical-analog calculations,
and compare our results with experimental results from a
number of sources.\(^{1,14,16,17}\) Figures 5 and 6 display our theo-
retical CN rotational distributions resulting from photolysis
at 248 and 266 nm. The distributions from each electronic
channel as well as the total distribution are shown. Figure 7

\[
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\]
shows a similar plot from Nadler et al. of experimentally determined nascent CN rotational distributions following 266 nm photolysis of 300 K ICN.\textsuperscript{17} By using sub-Doppler resolution laser-induced fluorescence and polarized photolysis and probe lasers these workers were able to resolve the contribution from each asymptotic channel for most values of \( N^* \). There is good overall agreement between theory and experiment, although we have less intensity in the intermediate \( N^* \) range and our cold part is "colder." Part of the discrepancy may be due to the fact that the experimental results are for 300 K ICN while our calculations should more properly be compared to experiments using nozzle-cooled ICN. The major effect of the higher temperatures is to shift the distributions to higher \( N^* \).\textsuperscript{16} Indeed, Table II indicates that our average CN rotational energy for the \( I^* \) channel at 266 nm is in much better agreement with the experiments of Marinelli et al. using nozzle-cooled ICN.\textsuperscript{16}

The nascent CN rotational distribution has been described as trimodal by various workers.\textsuperscript{12,16} Marinelli et al. assign temperatures of 57, 379, and 5622 K to their distributions.\textsuperscript{16} Baranovski has obtained similar results.\textsuperscript{12} The two lowest temperatures are thought to come from the \( I^* \) channel. It is possible that nonadiabatic interactions are responsible for the trimodal character of these distributions. A study of our trajectories indicates that they come in roughly three types: the extremely cold portion of the distribution results from trajectories which behave \textit{diabatically}, i.e., they never reach angles in which coupling is large and they remain on the linear surface throughout. The hot portion of the distribution results from trajectories which manage to reach larger angles where the coupling is greater and essentially follow the bent surface. However, it is not necessary that these trajectories ever actually encounter the crossing seam; in fact, the diabats cross for a very small range of intermolecular separations. The intermediate portion of the distribution results from trajectories which traverse a more complicated electronic path; they spend some time on the bent surface picking up rotational energy before they return to the linear surface to stay.

In Table II, we compare theoretically determined aver-

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Channel</th>
<th>Experimental\textsuperscript{a} ( (E_{rot}) )</th>
<th>Theoretical\textsuperscript{b} ( (E_{rot}) )</th>
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<tbody>
<tr>
<td>248</td>
<td>I</td>
<td>3039</td>
<td>3057</td>
</tr>
<tr>
<td></td>
<td>I\textsuperscript{*}</td>
<td>276</td>
<td>236</td>
</tr>
<tr>
<td>266</td>
<td>I</td>
<td>3274</td>
<td>3205</td>
</tr>
<tr>
<td></td>
<td>I\textsuperscript{*}</td>
<td>172</td>
<td>187</td>
</tr>
<tr>
<td></td>
<td>I\textsuperscript{*}</td>
<td>3300\textsuperscript{a}</td>
<td></td>
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<tr>
<td></td>
<td>I\textsuperscript{*}</td>
<td>355\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>I</td>
<td>2466</td>
<td>2910</td>
</tr>
<tr>
<td></td>
<td>I\textsuperscript{*}</td>
<td>51</td>
<td>229</td>
</tr>
<tr>
<td>290</td>
<td>I</td>
<td>1788</td>
<td>2522</td>
</tr>
<tr>
<td></td>
<td>I\textsuperscript{*}</td>
<td>96</td>
<td>219</td>
</tr>
<tr>
<td>308</td>
<td>I</td>
<td>1252\textsuperscript{a}</td>
<td>1585</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From Ref. 16 beam data unless otherwise noted.
\textsuperscript{b}2250 trajectories were run at each wavelength except 308 nm where 250 were run.
\textsuperscript{c}From Ref. 17, 300 K data.
\textsuperscript{d}From Ref. 14(b), 300 K data.
age rotational energies to those of Marinelli et al. and others. Marinelli et al. determine the rotational energies for the two channels from a Boltzmann analysis assuming that the low and intermediate rotational temperatures result from CN coming from the I* surface while the high temperatures are the result of the CN which comes from the I surface. The general agreement is satisfactory although our average energies at 280 and 290 nm are too high. The distributions at these wavelengths are also too narrow especially at 290. We also compare our results with those of Marinelli et al. in Boltzmann plots in Figs. 8 and 9. The bump in our plot at 290 nm at higher N* reflects the narrowness of our distributions which is more pronounced at lower photodissociation energies. As suggested above, the distributions could be broadened by adjusting various potential parameters, particularly the steepness of the coupling potential as a function of \( \theta \), but at the expense of the branching ratios. Because of the potential coupling term in Eq. (18), we can model the photodissociation process at energies below the threshold for I* production. We include the results of one such calculation at 308 nm and compare with an experimental result in Table II.\(^{14}\)

### B. Branching ratios

In Table III, we compare the computed percentage of I* to the experimental results of Pitts and Baranovski.\(^{11}\) We are able to get the correct trend at wavelengths greater than 266 nm. The results reported here represent compromise values, since by increasing \( \gamma_{12} \) we can obtain excellent agreement with experiment at 280 and 290 nm but at the expense of the rotational distributions. The effect of the coupling on the branching ratio is due largely to the absorption process rather than to the dynamics. Due to the coupling term in Eq. (19), the energy of the 0* excited state will be raised or lowered depending on the value of the electronic phase \( q \). If the coupling potential is sufficiently large at relatively small values of \( \theta \), certain values of \( q \) will result in a significant lowering of the excited state potential. Therefore, initial conditions which were previously unavailable to photolysis at low energies become accessible. These new initial conditions tend to have higher statistical weights because they involve values of \( R \) which are closer to \( R_c \). Those trajectories at 280 and 290 nm which begin at smaller \( R \) and larger \( \theta \) almost always end up on the surface which correlates to ground state I.

The discrepancy at 248 nm is another matter. There is no set of potential parameters which will give both the results at 266 and 248 nm. We are not able to describe 235 nm.

![FIG. 8. Semilog plot of theoretical total relative CN rotational populations divided by \( (2N^* + 1) \) vs rotational energy at the wavelengths indicated. The populations were computed using the classical-analog method.](image)

![FIG. 9. Semilog plot of \( I/(S_{N^*} \cdot \cdot \cdot) \) vs rotational energy for CN \((v = 0)\) from nozzle-cooled beam experiments of Marinelli et al. at the wavelengths indicated. Figure is taken from Ref. 16.](image)

### Table III. Fraction of I* in final product.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Theoretical</th>
<th>Experimental*</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>0.339</td>
<td>&lt;0.30</td>
</tr>
<tr>
<td>280</td>
<td>0.50</td>
<td>0.30</td>
</tr>
<tr>
<td>266</td>
<td>0.625</td>
<td>0.62</td>
</tr>
<tr>
<td>248</td>
<td>0.69</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*From Ref. 11.
photolysis at all with these two potential surfaces. At this wavelength over 90% of the product is in the ground state I channel and the average rotational energy of that channel is > 6000 cm⁻¹. Clearly another bent state is involved; the potential coupling with the linear state must be quite large. Preliminary investigations indicate that a bent state of I₁ = 1 symmetry in collinear configurations which is very strongly coupled to the 0+ state in the absorption region may reproduce the results at 235 nm. Some direct absorption to this state is also possible. The participation of this state in the photodissociation process would affect the results at 248 nm and perhaps the other wavelengths but presumably to a much smaller extent.

Although our CN rotational distribution at 248 nm is very broad, it is not as broad as the experimental distribution of Marinelli et al. As at most wavelengths, the intensity is too low in the intermediate N⁺ region. The distribution at 248 nm has been analyzed by these workers as trimodal and the low and intermediate temperatures assigned to the I* channel. This would mean, however, that 31% of the product I should be in the excited state, whereas Pitts and Baranovski measure only 14% I* at that wavelength. Therefore, the intermediate N⁺ region should largely correlate with the ground state I product channel. In this interpretation, the experimental average energies at 248 nm given in Table II would change somewhat; the energies for each channel would be reduced. More interestingly, the distribution from the ground state I channel would have to be very broad.

Even with the inclusion of nonadiabatic effects, at least three surfaces seem to be required to account fully for the photodissociation dynamics. The discrepancies between our results and experiment may result from the limitations of the two-surface model. Superposition of distributions from two bent surfaces may succeed in broadening the CN rotational distributions. Also, a surface strongly coupled to the linear surface at small values of R is needed to explain the I*/I branching ratios at 235 and 248 nm. Fitting three coupled surfaces to the experimental data using the classical-analog method could prove, however, to be a difficult task.

**C. Surface-hopping results**

The classical-analog method is well suited to the type of potentials used in this problem because it does not depend on the existence of a well-defined localized crossing seam. Insofar as the dynamics are the same whether an adiabatic or diabatic basis is used, the choice of basis reflects the choice of initial conditions. The simplest surface-hopping methods use a Landau-Zener type transition probability; such methods are not accurate near classical turning points. If the crossing seam is in or near the Franck-Condon region, then one is bound to have "hops" near classical turning points.

It is not surprising that our simple diabatic surface-hopping model gave very different results from the classical-analog method. Table IV summarizes the results on the potential surfaces described above. For these surfaces, the diabats actually cross only for a small range of nuclear separations and many trajectories never reach the seam. Also, the crossings are confined to the region of small θ where the coupling is small. Therefore, most of the trajectories remain on the linear surface. We attempted to adjust the surface parameters to fit the data using this method but we were unable to find surfaces that would reproduce the experimental results as long as one of the surfaces was linear. While we could find potential parameters which resulted in large numbers of trajectories "hopping" to the bent surface, generally the average energies were too low. Confined to diabatic surfaces, a trajectory is required to travel on the linear surface until it hops to the bent one. This results in lower product rotational energies. By the time a trajectory begins on the bent surface, it has either lost some of its initial bending momentum or it is traveling in the wrong θ direction and must turn around. The potential is so steep in the R direction that rotational energy must be picked up immediately upon absorption if rotation is to successfully compete with translation for the required share of the released energy. Perhaps a surface-hopping method using adiabatic surfaces would do a better job; however, a localized crossing seam is still required.

**D. Conclusion**

We have used the classical-analog method to explore the role of nonadiabatic transitions in the photodissociation of ICN assuming that all absorption is to one linear diabatic surface and have obtained good agreement with the experimental results of Nadler et al., at 266 nm. We have also achieved some successes in reproducing branching ratios, nascent rotational distributions, and average rotational energies at other wavelengths, although our results show the need to include at least three surfaces in a calculation which would hope to reproduce all of the experimental results. However, our results do indicate that it is possible to explain the experimental data assuming that most of the oscillator strength is carried by a linear surface as long as that surface is appropriately coupled to bent surfaces.

There are further two-surface calculations which are worthwhile to undertake. The next step would be to assume that absorption is to the lower adiabatic surface, integrating the trajectories using the adiabatic classical-analog Hamiltonian. Using simple eikonal methods it would be possible to explore the effects of the Langer modification on both the trajectory dynamics and our modeling of the photon-absorption process.

The most important theoretical advance in the understanding of the photodissociation of ICN, however, would be the development of good ab initio potential surfaces for the ground and first few excited states of ICN, as well as the calculation of the transition dipole moments and nonadiabatic coupling terms. Since good relativistic effective core po-

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>〈E₉⁺〉 (cm⁻¹)</th>
<th>〈E₁⁺〉 (cm⁻¹)</th>
<th>%1⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>266</td>
<td>2772</td>
<td>47</td>
<td>86</td>
</tr>
<tr>
<td>280</td>
<td>2410</td>
<td>38</td>
<td>90</td>
</tr>
</tbody>
</table>

*1000 trajectories at each photodissociation wavelength.
tentials for iodine are becoming available as well as increasingly sophisticated molecular structure computer codes, such a calculation is perhaps within the reach of current quantum chemistry.

ACKNOWLEDGMENTS

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31If $\pi$ is not equal to 1, then one must replace $n$ with $n_{\pi}/\pi$, where $n_{\pi}$, not $n$ itself, is the classical electronic action variable conjugate to $q$ (Ref. 35).

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