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Authors
Ali, D.P.
Miller, W.H.

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Domenic P. Ali and William H. Miller

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Effect of Electronic Transition Dynamics on

Iodine Atom Recombination in Liquids

Domenic P. Ali and William H. Miller

Department of Chemistry, and Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720

Abstract

The Langevin stochastic trajectory model used by Hynes, Kapral, and
Torrie [J. Chem. Phys. 72, 177 (1980)] to describe secondary recombina-
tion of iodine atoms in solution has been generalized to allow for
electronically inelastic transitions between the ten I-I potential
curves that dissociate to ground state iodine atoms. The electronic
transitions are treated via the Miller-George version of the Tully-
Preston surface hopping model. The main qualitative result is that
electronically inelastic processes substantially slow down the rate
(and ultimate probability) of recombination. It is also seen that
the electronic inelasticity changes from being strong at large r,
where an essentially Boltzmann distribution over the various
electronic states is maintained, to being weak at small r, where the
distribution is far from Boltzmann.

I. Introduction.

Since the earliest experiments by Noyes and co-workers[1] on iodine recombination in liquids, an extensive interest has developed in the study of recombination reactions. Iodine recombination has been studied in a variety of solvents,[2-6,14] and there have also been a number of experimental[7-8] and theoretical[9-11] studies of the process in the gas phase. Of particular importance are the picosecond experiments[2-6,14] which allow one to study the short time scale inherent in these reactions.

Since recombination is perhaps the simplest "chemical reaction" that one can study in liquids, it has attracted considerable theoretical attention. Studies have included molecular dynamics simulations[12-14] and stochastic trajectory,[15-16] or Langevin approaches. While molecular dynamics is relatively common nowadays, the computational effort involved is considerable in following the specific dynamics of each individual particle in the system. The Langevin approach is much easier to employ and can describe longer time behavior, but it incorporates many more approximations whose validity is difficult to ascertain. There are thus many fundamental theoretical questions about the dynamics of recombination in liquids that merit further investigation.

The present work follows closely the Langevin stochastic trajectory model of Hynes, Kapral, and Torrie,[15] where the focus is on secondary recombination[17] of the iodine atoms; i.e., one considers the iodine atoms that, after photo-excitation of I_2, have separated to a distance of $\sim$ 4-6 Å, from which they either recombine (on a time scale of $\sim$ 10-30 picoseconds) or dissociate permanently.

(Primary recombination of the atoms immediately after the excitation takes place within a picosecond and is typically obscured by the exciting laser pulse.) In their Langevin simulation Hynes, et al., considered motion of iodine atoms only on the ground electronic potential curve of I_2, although they noted that the other electronic states which dissociate to ground state iodine atoms should also be taken into account. Figure 1 shows the ten diatomic potential curves of I_2 that arise from two $^2P_{3/2}$ iodine atoms,[18] and one sees that at $\sim$ 4-6 Å they are all within kT of each other, suggesting that electronic transition between them should be facile in this region.

Previous work dealing with the question of electronic transitions in iodine recombination includes that of Bunker,[9] who discussed it only on statistical grounds, and that of Martire and Gilbert,[16] who used a Folker-Planck equation which included rate constants for transitions between the various electronic states of I_2. In their actual calculations Martire and Gilbert assumed only one electronically excited state, and the rate of transitions between it and the ground state was varied in order to obtain agreement with experiment. While this was a good start of dealing with the effects of electronic transitions, one would like to have a less phenomenological approach that is also tractible enough to allow practical calculations.

In the present paper we follow the Langevin stochastic trajectory approach of Hynes, et al., but generalize it to incorporate the effects of electronic transitions between the various potential curves (i.e., electronic states) of I_2. Specifically, we utilize the Tully-Preston surface-hopping model[19] to allow for localized "hops" from one potential curve to another, with the electronic transition probability determined by the generalized Stückelberg model of Miller

and George.[20] Since the surface-hopping model is typically formulated
in a probabilistic framework--i.e., a "hop" from the current electronic
state is made or not by comparing the electronic transition probability
to a random number--it is relatively easy to include it in the stochastic
trajectory simulation.

Section II describes the surface-hopping Langevin trajectory
model as we employ it, and the results of our calculations are
discussed in Section III. If electronic transitions between all the
states were extremely facile, one would expect the relative population
on each potential curve to be a Boltzmann distribution; since this is
an important limiting case, results based on assuming a Boltzmann
distribution over the electronic states are also presented in Section
III and compared to those of the surface-hopping Langevin model. Very
interesting differences are seen. Section IV summarizes our
conclusions.

II. The Surface-Hopping Langevin Trajectory Model.

Following Hynes et al.,[15] we describe the relative motion of

two iodine atoms by a Langevin equation,

$$\frac{d}{dt} \vec{r}(t) = \vec{p}/\mu \tag{2.1a}$$

$$\frac{d}{dt} \vec{p}(t) = - \vec{\nabla} V(r) - \xi \vec{p} + \vec{R}(t) \tag{2.1b}$$

where $\vec{r}$ is the relative coordinate vector, $\vec{p}$ the conjugate momentum,

$V(r)$ the potential function for the I-I interaction, ξ the friction

constant, and $\vec{R}(t)$ the random force exerted by the surrounding

solvent molecules. (The approximations inherent in describing a

dynamical system via a Langevin equation have been discussed by

Deutch and Oppenheim;[21] basically, it is necessary that correlations

between solvent molecules decay much faster than the rate of solute

velocity relaxation, and Hynes et al., have argued that these conditions

are reasonable for iodine recombination if the solvent molecules

are light.)

All the aspects of the Langevin model are the same as in the work

of Hynes, et al.:   e.g., $\vec{R}(t)$ is assumed to be gaussian random, its

correlation function is related to the friction coefficient through

the fluctuation-dissipation theorem,[22]

$$2 \xi \delta(t) = \langle \vec{R}(t) \cdot \vec{R}(o) \rangle \quad , \tag{2.2}$$

and the friction constant is related to the self-diffusion constant

D_0 by

$$\xi = \frac{kT}{2\xi D_0} \qquad . \qquad (2.3)$$

According to Enskog theory[23] the temperature dependence of D_0 is $T^{1/2}$,

so one has

$$D_0(T) = D_0(300)(T/300)^{1/2} \qquad , \qquad (2.4)$$

and $D_0(300)$ is taken as

$$D_0(300) = 10^{-5} \ cm^2/sec \qquad .$$

For other specifics of the Langevin model we refer the reader to

Hynes, et al.. Also, a good general discussion of Langevin equations

is that by Chandrasekar.[24]

As noted in the Introduction, the new aspect of the present

work is that we allow the potential function V(r) (i.e., the electronic

state) for the two iodine atoms to change during the Langevin trajectory

according to the surface-hopping model. (Hynes, et al., also include

in V(r) a "caging potential" which includes the average effect of

the solvent on the I-I interaction; since its effect is rather small

and since our interest here is in investigating the effect of electronic

transitions between the different I-I potential curves, we ignore

this term in the present work.) Within the Miller-George[20] version

of the surface-hopping model,[19] an electronic transition from state

i to state j is localized to the time (or times) at which $\Delta V_{ij}(t) =$

$\Delta V_{ij}(r(t)) \equiv |V_i(t) - V_j(t)|$ passes through a local minimum as a

function of t; if t_0 is such a time, then the probability of the

$i \rightarrow j$ transition is given approximately by

$$P_{j \leftarrow i} \simeq \exp[- \frac{4}{3} (\Delta V_{ij}/\hbar)(2\Delta V_{ij}/\Delta \ddot{V}_{ij})^{1/2}] \quad , \tag{2.5}$$

where

$$\Delta V_{ij} = \Delta V_{ij}(t_0)$$

$$\Delta V_{ij} = \Delta V_{ij}''(t_0) \quad .$$

For the present application the potential curves $\{V_i(r)\}$ for the various electronic states (see below for their specific form) are such that

$$|V_i(r) - V_j(r)|$$

is a monotonically decreasing function of r for all i and j; thus $\Delta V_{ij}(t) \equiv \Delta V_j(r(t))$ passes through a local minimum only when $r(t)$ experiences an *outer* *turning* *point*, i.e., when

$$\dot{r}(t_0) = 0 \tag{2.6a}$$

and

$$\ddot{r}(t_0) < 0 \quad . \tag{2.6b}$$

This happens whenever the trajectory experiences a sufficient "kick" from the random force that the separating I atoms are turned around and headed back towards each other. Furthermore, this means that a local minimum occurs in $\Delta V_{ij}(t)$ <u>simultaneously</u> for all possible final electronic states j.

The way the surface-hopping model works, therefore, is that one begins in electronic state i, say, and thus integrates the stochastic trajectory, Eq. (2.1), with $V(r) = V_i(r)$; when r(t) experiences an outer turning point, i.e., Eq. (2.6) occurs, one calculates the probability (via Eq. (2.5), and see below) of "hopping" to other electronic states j, and makes a "hop" by comparing these probabilities to random numbers; if a hop is made to electronic state j, then one continues integrating the stochastic trajectory with $V(r) = V_j(r)$, until r(t) experiences another outer turning point, at which point another "hop" is allowed, etc.

There is one significant modification we need to make in the above discussion: the transition probability given by Eq. (2.5) applies to an isolated I-I collision and thus satisfies the relation

$$P_{j \leftarrow i} = P_{i \leftarrow j} \quad . \tag{2.7}$$

The Langevin model, however, describes the I-I system in interaction with a thermal bath; we thus use Eq. (2.5) to calculate the probability of <u>de</u>-excitation transitions i→j, and then invoke <u>detailed</u> <u>balance</u> to obtain the probabilities of excitation transitions:

$$P_{j \leftarrow i} = (g_j/g_i) P_{i \leftarrow j} \, e^{-\beta(V_j - V_i)} \quad , \tag{2.8}$$

where $V_i < V_j$ are the electronic energies at the time of transition, and g_i and g_j are the degeneracies of states i and j. Detailed balance has the effect that after many transitions a Boltzmann distribution over the states would result if the energies $\{V_i\}$ were constant. Also, the "primitive" semiclassical transition probabilities given by Eqs. (2.5) and (2.8) are not normalized as they stand, i.e., do not satisfy conservation of probability, so they are modified as follows,

$$(P_{j \leftarrow i})_{normalized} = P_{j \leftarrow i} / \sum_k P_{k \leftarrow i} \quad , \quad (2.9)$$

in order to do so.

One particularly interesting limit of this model to consider is that in which transitions between electronic states are much faster than the relative I-I motion, for all values of r. If this were true, then the electronic states would maintain themselves in a Boltzmann distribution for all values of r, and the effective I-I potential V(r) in the Langevin equation, Eq. (2.11), would be simply the Boltzmann average of the potential functions $V_i(r)$,

$$\bar{V}(r) = \sum_i g_i V_i(r) e^{-\beta V_i(r)} / \sum_i g_i e^{-\beta V_i(r)} \quad . \quad (2.10)$$

We have thus carried out the Langevin stochastic trajectory calculation using this average I-I potential function in order to compare it to the results of the surface-hopping model. It is clear that it is much simpler in practice to use one average potential function rather

than to deal with the dynamics of transitions between several different potentials, so it is important to see how the results of using this thermally averaged potential compare with those of the more dynamically correct surface-hopping model.

For the potential functions we have been used a standard Morse potential,

$$V_1(r) = De[e^{-2\alpha(r-r_e)} - 2 e^{-\alpha(r-r_e)}] \quad , \quad (2.11)$$

with

$$D_e = 5.7144 \times 10^{-2} \text{ hartrees}$$
$$\alpha = 0.98819 \ a_0^{-1}$$
$$r_e = 5.03962 \ a_0$$

for the ground electronic state, and all the others are described as quadrupole-quadrupole interactions,[18]

$$V_i(r) = C_i/r^5 \quad , \quad (2.12)$$

$i=2,\ldots,10$; the constants C_i are given in Table I, along with their symmetry labels and degeneracies. Since we only heed to follow the I-I dynamics for $r \geq 4$ Å (see next section), this description of the excited state potential functions should be a reasonable approximation. Of the ten states, five are repulsive and five attractive.

Finally, we note one simplifying modification we made in carrying out the surface hopping calculations. It was assumed above that $\Delta V_{ij}(r) \equiv |V_i(r) - V_j(r)|$ is a monotonically decreasing function of

r for all states i and j, so that $\Delta V_{ij}(t)$ has a local minimum--and thus electronic transitions occur--only at an outer turning point of the r(t) motion. One sees in Figure 1, however, that this is not true if state i or j is the ground electronic state and $r > 6$ Å. Thus for $r > 6$ Å there is the possibility of electronic transitions other than at an outer turning point, but we have ignored them in our calculations. While it would certainly have been possible to include them in the surface-hopping description, the results are essentially unchanged by their neglect. This is because electronic transitions are already very facile for $r > 6$ Å, generating a Boltzmann-like distribution over the electronic states (see next section), so that including even more electronic transitions in this region of r would not change the situation.

III. Results and Discussion.

The stochastic trajectories are begun at I-I internuclear distance r_0, in electronic state i, with the momentum $\vec{p}$ selected at random from a Boltzmann distribution. We have used two different initial distances r_0 = 5.5 Å and 6.67 Å, to assess this effect on the results, and in addition to T = 300°K have also carried out the calculations for T = 500° and 700°. There is only on a small effect (a few %) on the results of choosing different initial electronic states.

Similar to Hynes et al., we choose inner and outer cut-off points for the trajectory to determine when the iodine atoms have either recombined or permanently separated respectively; these values are 4 Å and 12 Å, respectively. Recombination is said to have occurred, therefore, if r(t) reaches the value 4 Å and the electronic state is the ground state; at this point the iodine atoms are drawn essentially monotonically inward, and the electronic energy gap to other states is sufficiently large that no further transitions occur. Trajectories are followed until r(t) reaches one of these cut-off points, up to a total time of 150 psec; 99% of the trajectories have reached one of the cut-offs by this time limit. Specifics of the numerical integration procedure are discussed by Turq, Lantelme, and Friedman.[25]

Before discussing the major results, it is useful to note that within the present model there is a qualitative correspondence between the collision frequency of I_2 in the liquid and the number of outer turning points that the relative I-I motion experiences (which is also the number of opportunities the I-I system has to make an electronic transition). Thus the collision frequency can be estimated by[26]

$$Z \simeq Z_g \, g(r) \qquad ,$$

where Z_g is the gas phase collision frequency and g(r) the radial

distribution function at contact. Typical values give a collision

frequency that varies from ∿ 20 to 30 collisions per picosecond as T

varies from 300°K to 700°K, while the average number of outer classical

turning points in our stochastic trajectory surface-hopping calculations

varies from ∿ 20 to 25 over this temperature range.

Figure 2 shows the principal results of the paper, the probability

P(t) that the iodine atoms have not recombined by time t. All three

curves result from a Langevin stochastic trajectory calculation, the

one labeled G being the result of Hynes et al., that used the ground

state I-I potential curve, that labeled T the result of using the

thermally average potential curve, Eq. (2.10), and that labeled S the

result of allowing V(r) to change to the various potentials $\{V_i(r)\}$

according to the semiclassical surface-hopping model. The first

qualitative observation is that both curves T and S, which include the

effects of electronically excited states, give less recombination, and

this is easy to understand: recombination can only take place on

the ground state potential, so any transitions out of the ground

electronic state will lead to less recombination, i.e., more dissociation.

One sees, however, that the surface-hopping model (curve S) produces

a larger correction to the ground state results (curve G) than does use

of the thermally averaged potential (curve T); i.e., the surface-hopping

model yields even less recombination than does the thermally averaged

potential. This also has a simple explanation: at relatively large

values of r, where the potential curves are close together, electronic

transitions between the states are facile and do essentially produce

a relative Boltzmann distribution among the states, but when r decreases

the separation of the ground state potential from the others makes

transitions into or out of the ground electronic state improbable;
thus the approximate Boltzmann distribution over electronic states
at large r is "frozen in" as r decreases, and this means that the
surface hopping model produces less population in the ground electronic
state at small r than that given by assuming a Boltzmann distribution
at small r. With less population in the ground state at
small r, the surface hopping model thus gives less recombination
than the thermally averaged potential model.

To see more clearly that this interpretation is correct, we show
in Figure 3 the average relative population of the different electronic
states that results from the surface-hopping calculation (points
connected by solid line), compared to a Boltzmann distribution (broken
line). Figure 3A is for a region of large r (7-8 $\overset{\circ}{A}$), and one sees that
here the surface-hopping model does indeed produce an essentially
Boltzmann distribution over the electronic states; for small r (4-5 $\overset{\circ}{A}$),
however, Figure 3B shows that the surface-hopping model produces much
less population in the ground electronic state (state #1) than that
given by the Boltzmann distribution at small r. This lack of complete
electronic relaxation during the relative I-I motion thus appears to
be an important feature in the dynamics of recombination.

The results shown in Figure 2 are for initial separation $r_0 = 5.5 \overset{\circ}{A}$
and temperature T = 300°K. Changing either of these does not change
the qualitative natures of these curves nor their positions relative
to each other, so that the above discussion concerning the effect
of electronic transitions is unchanged. The asymptotic value of
P(t), i.e., P(∞), the dissociation probability, does of course depend
on r_0 and T. The temperature dependence of P(∞) is shown in Figure 4,

and one sees that it is qualitatively the same for the three different cases.

The dependence of $P(\infty)$ on r_0 is quite sensitive: increasing r_0 from 5.5 Å to 6.67 Å increases $P(\infty)$ by about a factor of 2. This is understandable--i.e., starting the trajectories at larger r leads to larger dissociation probability--but it suggests that if the overall model is to be self-contained, one needs to extend it so that the appropriate initial value of r is determined by the dynamics itself and is not an ad hoc parameter. One way to do this would be to begin the trajectory calculation at small r on one of the excited electronic potential curves, the one that is initially excited from the ground electronic state by the laser. The iodine atoms would initially separate on this repulsive electronic state, but as the frictional effects of the bath slow them down and as electronic transitions become probable at larger r values, some trajectories would be "turned around" and lead to recombination. This type of calculation obviously asks a great deal more of the Langevin model, but it also has the potential of providing a more comprehensive description of the process.

Finally, although comparison of the results of these model calculations with experimental recombination rates is clearly tenuous, it is nevertheless interesting. Hynes, et al., estimate a rate constant of $\sim 4 \times 10^{13}$ cm^3/mole-sec from their calculations using only the ground state I-I potential curve,[15,27] compared to the experimental value of $\sim 1-2 \times 10^{13}$ cm^3/mole-sec of Troe and co-workers.[28] Hynes, et al., attribute this difference to curve-crossing effects in the I_2 electronic levels. If we crudely relate the rate to the time it takes P(t) to fall to half its asymptotic value, then Figure 2 indicates that the rate given by our surface-hopping model (curve S)

would be $\sim$ 4-5 times slower than that of Hynes, et al. (curve G) and thus roughly the same rate as the experimental value. This is interesting and encouraging, but one should of course not make too much of the actual numerical values.

IV. Concluding Remarks.

While there are undoubtedly many limitations of the present model for describing recombination dynamics in liquids, we believe it is realistic enough that the qualitative results of our calculations are meaningful. The most significant of these are that electronically inelastic transitions substantially reduce the rate (and final probability) of recombination and that the character of the electronic dynamics changes during the recombination process. Thus at large r electronic transitions are strong and produce a Boltzmann-like distribution over the various electronic states, but as r decreases electronic relaxation ceases to be complete. There is thus an interesting inter- play between the electronically inelastic dynamics and the relative motion of the iodine atoms in interaction with the solvent.

One of the most unsatisfying features of the present model is the dependence of the results on the initial starting position r_0. As discussed at the end of the preceeding section, one would like to extend the model to eliminate this ad hoc initial condition, and one way to do this would be to begin the stochastic trajectory at small r on the excited I_2 potential curve that results from the initial laser excitation. This would also have the possibility of describing primary recombination events along with secondary recombination in one unified model.

Another aspect of the model that could be improved involves the inner cut-off at $r = 4 \overset{\circ}{A}$, i.e., the assumption that all trajectories which reach this point will recombine. It is possible that the iodine atoms might rebound from the repulsive wall of the

ground state potential curve and separate again to distances greater than 4 Å. This would be particularly likely if one generalizes the frictional force in the Langevin equation to realize that there are no solvent molecules between the iodine atoms at small values of r.

There are thus many aspects of the model one can imagine improving in order to make the approach a more realistic description of chemical reactions in solution, and the results obtained in the present paper are sufficiently encouraging that we think it is worthwhile to pursue these extensions.

Acknowledgments

Figure Captions

1. Potential curves for the ten electronic states arising from two ground state ($^2P_{3/2}$) iodine atoms.

2. Probability that at time t the two iodine atoms have not recombined; $T = 300^{\circ}K$, $r_o = 5.5$ Å. All results are from the stochastic trajectory model; curve G (the results of reference 15) utilizes the ground state I_2 potential curve for $V(r)$ in Eq. (2.1), curve T utilizes the thermally averaged potential of Eq. (2.10) for $V(r)$, and curve S uses the semiclassical surface-hopping model to allow $V(r)$ to change as the electronic state of the system changes.

3. Average relative population of the 10 electronic states (state 1 is the ground state) as obtained in the stochastic surface-hopping trajectory calculation (points connected by solid lines) and as given by a Boltzmann distribution (broken curve). (A) is for a region of large r (7-8 Å), and (B) for a region of smaller r (4-5 Å).

4. Dissociation probability, $P_\infty \equiv P(t \to \infty)$, with $P(t)$ as shown in Figure 2 for 300°K. The labels G, T, and S have the same meaning as in Figure 2.

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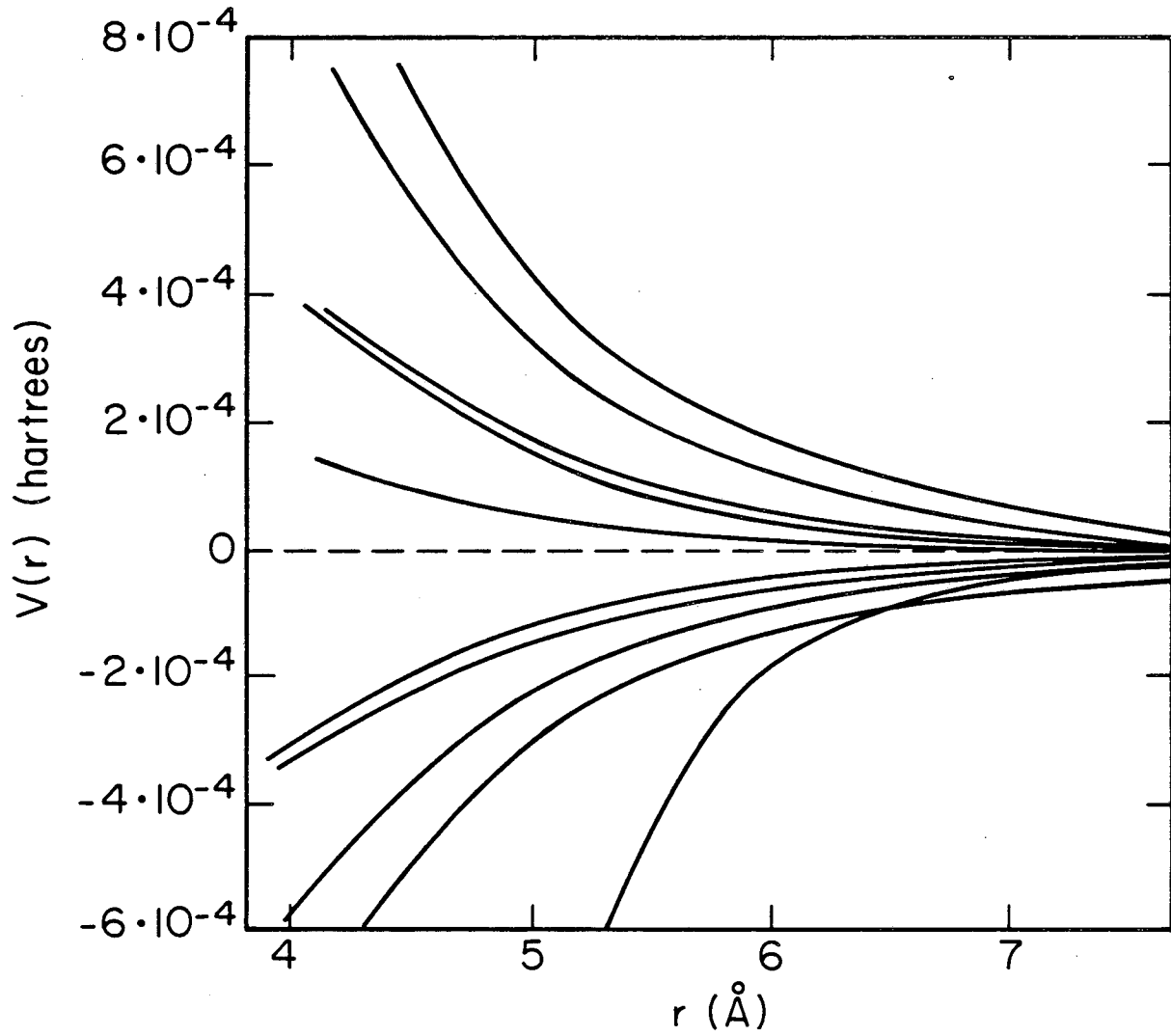19. J. C. Tully and R. K. Preston, J. Chem. Phys. 55, 562 (1971).

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Table I. Potential Parameters[a]

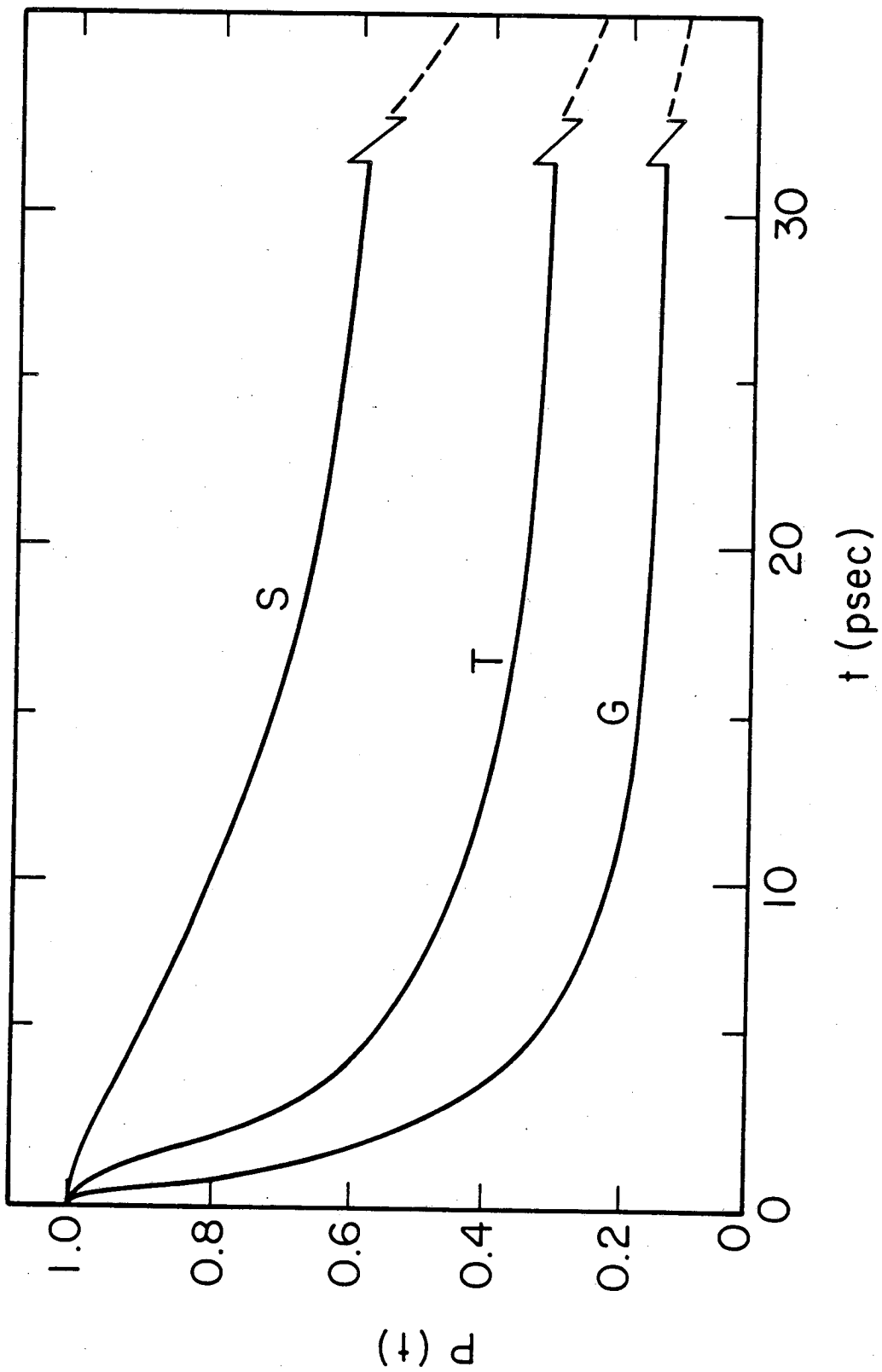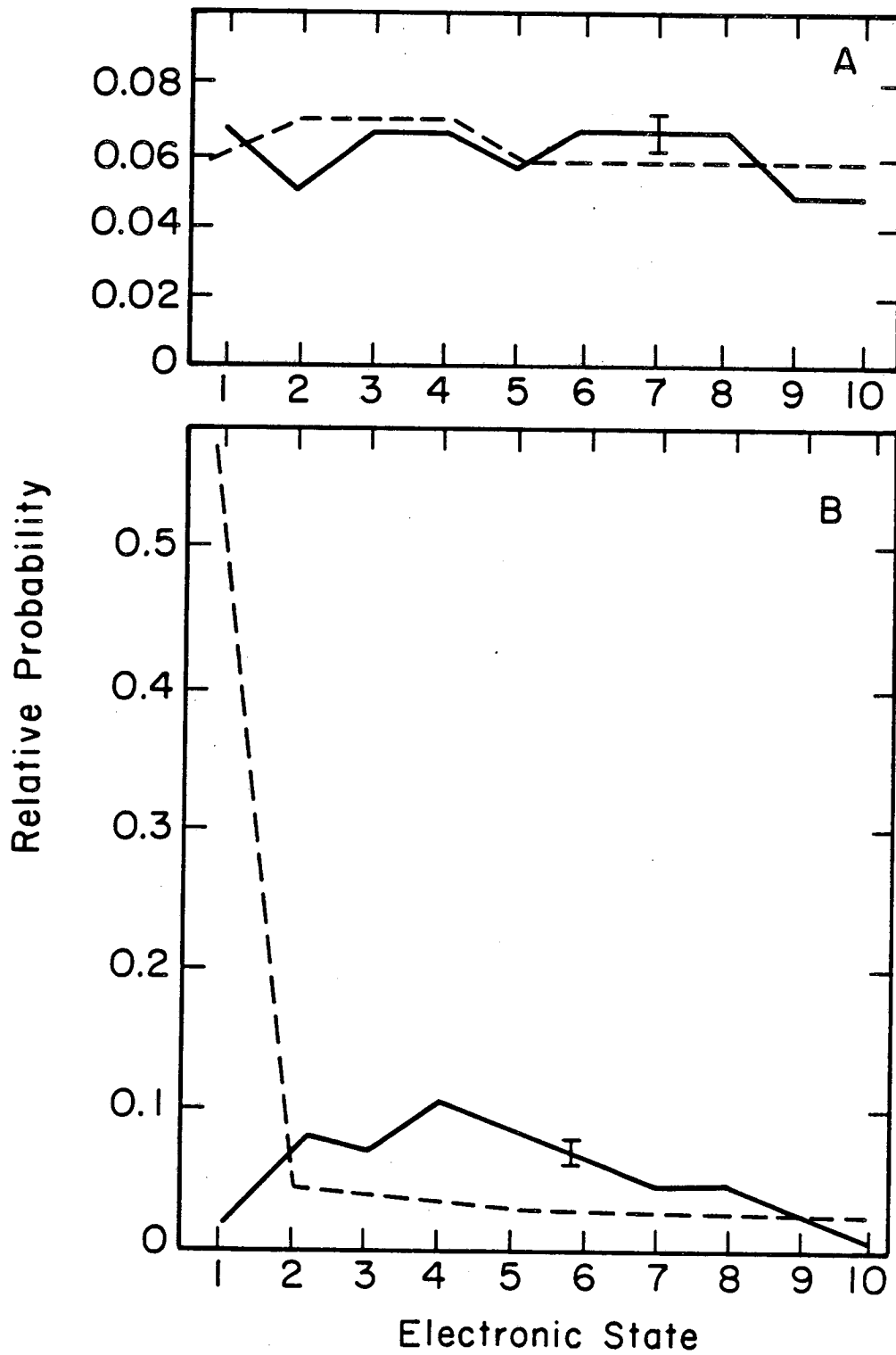| Electronic State	C_i[b]	Degeneracy
$^1\Sigma_g^+$	0.00	1
$^3\Pi_{2u}$	-28.99	2
$^3\Pi_{1g}$	-16.58	2
$^3\Pi_{1u}$	- 8.35	2
$^3\Pi_{0^-u}$	- 8.35	1
$^3\Pi_2$	4.17	2
$^1\Pi_u$	12.41	2
$^3\Delta_3$	12.41	2
$^3\Sigma_g^-$	24.82	1
$^3\Sigma_u^+$	33.16	1

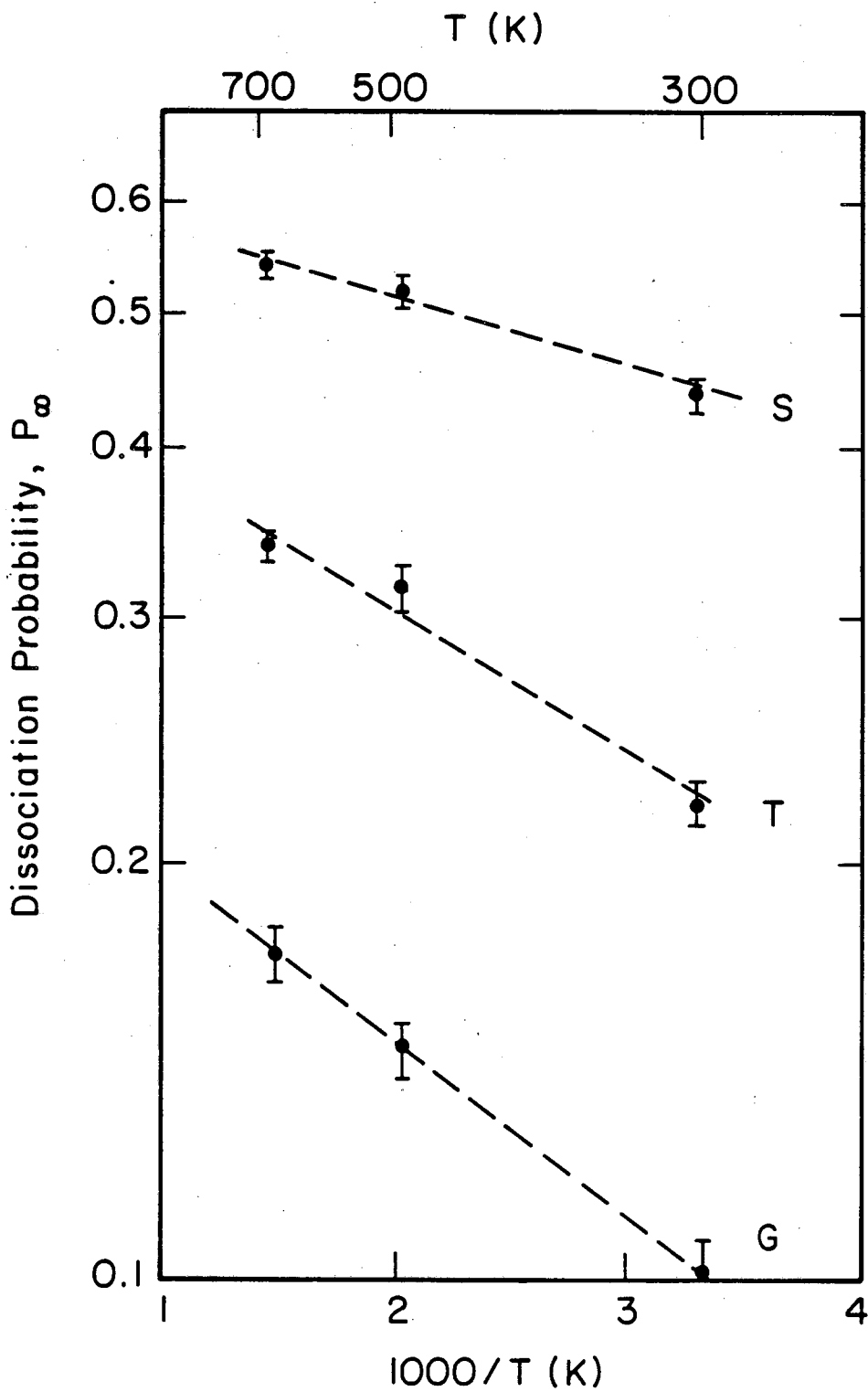[a]See Eq. (2.12).

[b]Units are hartree·bohr^5.

Figure 1

XBL 8212-12226

Figure 2

XBL 8212-12227

Figure 3

Figure 4

XBL 8212-12228