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# Effect of electronic transition dynamics on iodine atom recombination in liquids

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The Langevin stochastic trajectory model used by Hynes, Kapral, and Torrie [J. Chem. Phys. 72, 177 (1980)] to describe secondary recombination 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<sup>1</sup> 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,<sup>2-6,14</sup> and there have also been a number of experimental<sup>7,8</sup> and theoretical<sup>9-11</sup> studies of the process in the gas phase. Of particular importance are the picosecond experiments<sup>2-6,14</sup> 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<sup>12-14</sup> and stochastic trajectory,<sup>15,16</sup> 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,<sup>15</sup> where the focus is on *secondary recombination*<sup>17</sup> of the iodine atoms; i.e., one considers the iodine atoms that, after photoexcitation of  $I_2$ , have separated to a distance of  $\sim 4-6$  Å, from which they either recombine (on a time scale of  $\sim 10-30$  ps) 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,<sup>18</sup> 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,<sup>9</sup> who discussed it only on statistical grounds, and that of Martire and Gilbert,<sup>16</sup> 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 in dealing with the effects of electronic transitions, one would like to have a less phenomenological approach that is also tractable 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

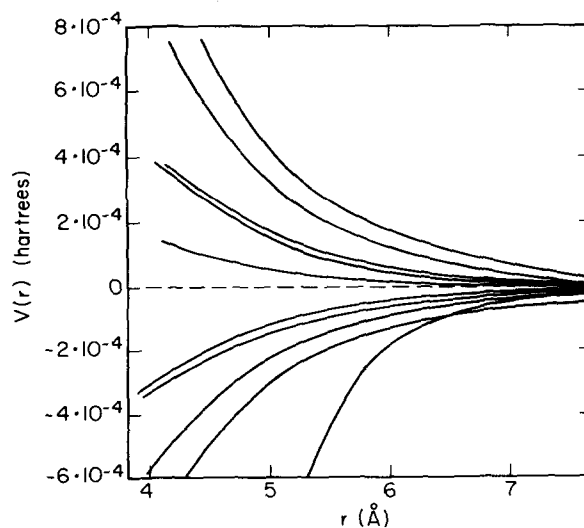


FIG. 1. Potential curves for the ten electronic states arising from two ground state ( $^2P_{3/2}$ ) iodine atoms.

I<sub>2</sub>. Specifically, we utilize the Tully–Preston surface-hopping model<sup>19</sup> 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.<sup>20</sup> 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 Sec. 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 Sec. 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.*,<sup>15</sup> we describe the relative motion of two iodine atoms by a Langevin equation

$$\frac{d}{dt} \mathbf{r}(t) = \mathbf{p}/\mu, \quad (2.1a)$$

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

where  $\mathbf{r}$  is the relative coordinate vector,  $\mathbf{p}$  the conjugate momentum,  $V(\mathbf{r})$  the potential function for the I–I interaction,  $\xi$  the friction constant, and  $\mathbf{R}(t)$  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<sup>21</sup>; 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.,  $\mathbf{R}(t)$  is assumed to be Gaussian random, its correlation function is related to the friction coefficient through the fluctuation-dissipation theorem<sup>22</sup>

$$2\xi\delta(t) = \langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle, \quad (2.2)$$

and the friction constant is related to the self-diffusion constant  $D_0$  by

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

According to Enskog theory<sup>23</sup> the temperature dependence of  $D_0$  is  $T^{1/2}$ , so one has

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

and  $D_0(300)$  is taken as

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

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.<sup>24</sup>

As noted in the Introduction, the new aspect of the present work is that we allow the potential function  $V(\mathbf{r})$  (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  $V(\mathbf{r})$  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<sup>20</sup> version of the surface-hopping model,<sup>19</sup> an electronic transition from state  $i$  to state  $j$  is localized to the time (or times) at which  $\Delta V_{ij}(t) = \Delta V_{ij}[\mathbf{r}(t)] \equiv |V_i(t) - V_j(t)|$  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

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

where

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

$$\Delta \ddot{V}_{ij} = \Delta V''_{ij}(t_0).$$

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

$$|V_i(\mathbf{r}) - V_j(\mathbf{r})|$$

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

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

and

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

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  $\Delta V_{ij}(t)$  *simultaneously* 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  $V(\mathbf{r}) = V_i(\mathbf{r})$ ; when  $\mathbf{r}(t)$  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  $V(\mathbf{r}) = V_j(\mathbf{r})$ , until  $\mathbf{r}(t)$  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

$$P_{j \rightarrow i} = P_{i \rightarrow j} . \quad (2.7)$$

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 deexcitation transitions  $i \rightarrow j$ , and then invoke *detailed balance* to obtain the probabilities of excitation transitions:

$$P_{j \rightarrow i} = (g_j/g_i) P_{i \rightarrow j} \exp[-\beta(V_j - V_i)] , \quad (2.8)$$

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:

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

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  $V_i(r)$ ,

$$\bar{V}(r) = \sum_i g_i V_i(r) \exp[-\beta V_i(r)] / \sum_i g_i \exp[-\beta V_i(r)] . \quad (2.10)$$

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 used a standard Morse potential

$$V_1(r) = D_e \{ \exp[-2\alpha(r - r_e)] - 2 \exp[-\alpha(r - r_e)] \} , \quad (2.11)$$

with

$$D_e = 5.7144 \times 10^{-2} \text{ hartree} ,$$

$$\alpha = 0.98819a_0^{-1} ,$$

$$r_e = 5.03962a_0 ,$$

for the ground electronic state, and all the others are described as quadrupole-quadrupole interactions<sup>18</sup>

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

$i = 2, \dots, 10$ ; the constants  $C_i$  are given in Table I,

TABLE I. Potential parameters.<sup>a</sup>

Electronic state	$C_i^b$	Degeneracy
$1\Sigma_g^+$	0.00	1
$3\Pi_{2\mu}$	-28.99	2
$3\Pi_{1g}$	-16.58	2
$3\Pi_{1u}$	-8.35	2
$3\Pi_{0-\mu}$	-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

<sup>a</sup>See Eq. (2.12).

<sup>b</sup>Units are hartree bohr<sup>5</sup>.

along with their symmetry labels and degeneracies. Since we only need to follow the I-I dynamics for  $r \geq 4$  Å (see Sec. III), 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 Fig. 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 Sec. III), 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  $p$  selected at random from a Boltzmann distribution. We have used two different initial distances  $r_0 = 5.5$  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  $T = 500^\circ$  and  $700^\circ$ . There is only 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; these values are 4 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 suffi-

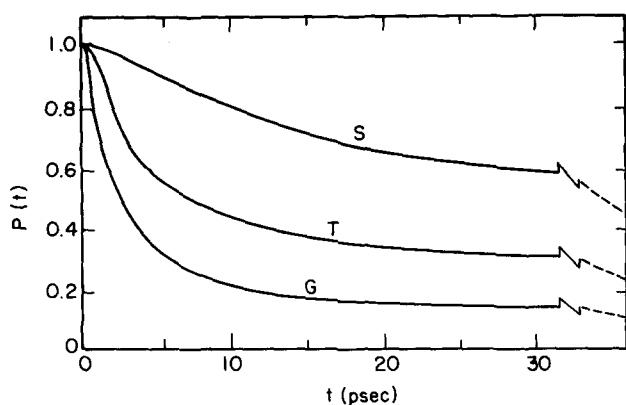


FIG. 2. Probability that at time  $t$  the two iodine atoms have not recombined;  $T = 300\text{ K}$ ,  $r_0 = 5.5\text{ \AA}$ . All results are from the stochastic trajectory model; curve G (the results of Ref. 15) utilizes the ground state  $\text{I}_2$  potential curve for  $V(r)$  in Eq. (2.1), curve 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.

ciently large that no further transitions occur. Trajectories are followed until  $r(t)$  reaches one of these cutoff points, up to a total time of 150 ps; 99% of the trajectories have reached one of the cutoffs by this time limit. Specifics of the numerical integration procedure are discussed by Turq, Lantelme, and Friedman.<sup>25</sup>

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  $\text{I}_2$  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<sup>26</sup>

$$Z \approx Z_g g(r),$$

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  $\sim 20$  to 30 collisions per picosecond as  $T$  varies from 300 to 700 K, while the average number of outer classical turning points in our stochastic trajectory surface-hopping calculations varies from  $\sim 20$  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 poten-

tial, 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 Fig. 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 3(a) is for a region of large  $r$  (7–8  $\text{\AA}$ ), 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  $\text{\AA}$ ), however, Fig. 3(b) shows that the surface-hopping model produces much less population in the ground electronic state (state No. 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 Fig. 2 are for initial separation  $r_0 = 5.5\text{ \AA}$  and temperature  $T = 300\text{ K}$ . 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.,  $P(\infty)$ , the dissociation probability, does of course depend on  $r_0$  and  $T$ . The temperature dependence of  $P(\infty)$  is shown in Fig. 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 to 6.67  $\text{\AA}$  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 ex-

cited 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<sup>3</sup>/mols from their calculations using only the ground state I-I potential curve,<sup>15,27</sup> compared to the experimental value of  $\sim 1-2 \times 10^{13}$  cm<sup>3</sup>/mols of Troe and co-workers.<sup>28</sup> Hynes *et al.*, attribute this difference to curve-crossing effects in the I<sub>2</sub> electronic levels. If we crudely relate the rate to the time it takes  $P(t)$  to fall to one-half its asymptotic value, then Fig. 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.

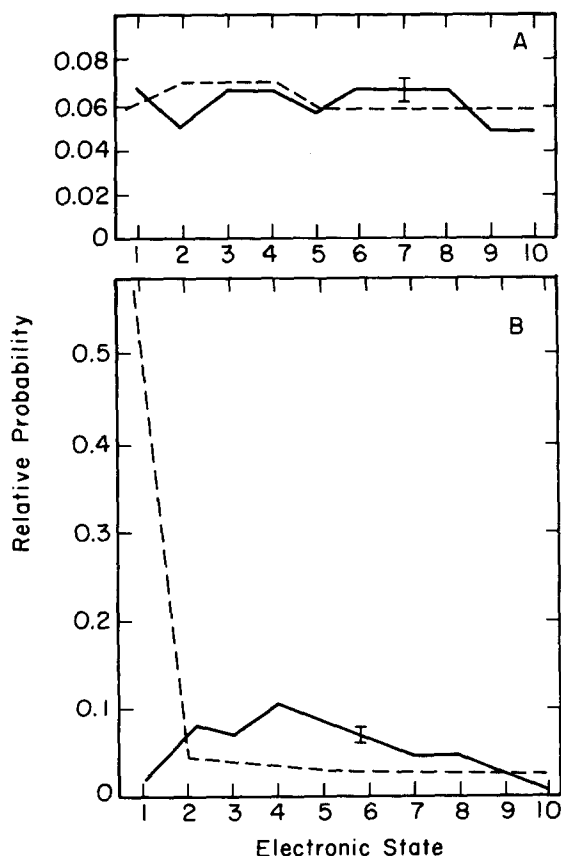


FIG. 3. Average relative population of the ten electronic states (state 1 is the ground state) as obtained in the stochastic surface-hopping trajectory calculation (points connected by solid lines) and as given by a Boltzmann distribution (broken curve). (A) is for a region of large  $r$  (7-8 Å), and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

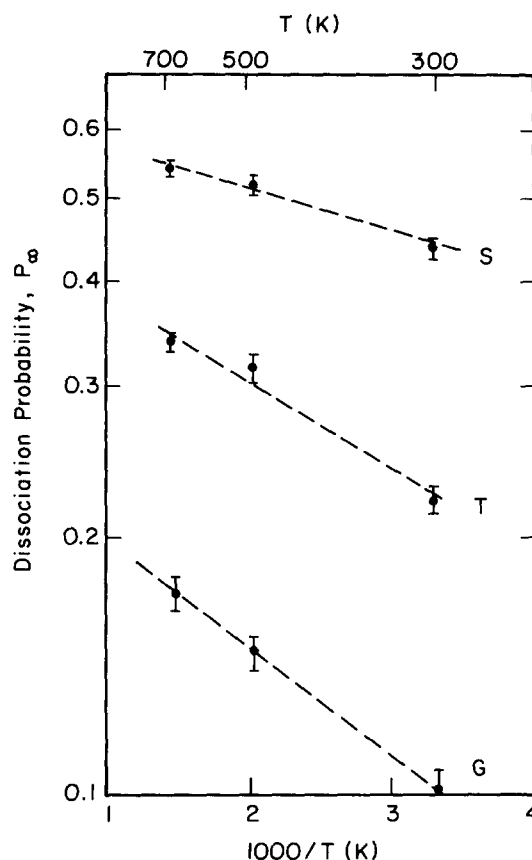


FIG. 4. Dissociation probability  $P_\infty \equiv P(t \rightarrow \infty)$ , with  $P(t)$  as shown in Fig. 2 for 300 K. The labels G, T, and S have the same meaning as in Fig. 2.

#### 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 interplay 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 Sec. III, 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<sub>2</sub> 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 cutoff at  $r = 4 \text{ \AA}$ , 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  $4 \text{ \AA}$ . 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.

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