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CLASSICAL MODEL FOR ELECTRONICALLY NON-ADIABATIC
COLLISION PROCESSES: RESONANCE EFFECTS IN
ELECTRONIC-VIBRATIONAL ENERGY TRANSFER

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November 1980

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Abstract

A recently developed classical model for electronically non-adiabatic collision processes is applied to electronic-vibrational energy transfer in a collinear atom-diatom system, $A + BC(v=1) \rightarrow A^* + BC(v=0)$, which closely resembles $Br-H_2$. This classical model, which treats electronic as well as heavy particle (i.e., translation, rotation, and vibration) degrees of freedom by classical mechanics, is found to describe the resonance features in this process reasonably well. The usefulness of the approach is that it allows one to extend standard Monte Carlo classical trajectory methodology to include electronically non-adiabatic processes in a dynamically consistent way.

I. Introduction

A series of papers[1] over the last few years has developed and applied a classical model for treating electronically non-adiabatic processes in molecular collisions. The novel feature of this model is that electronic, as well as heavy particle (i.e., translation, rotation, and vibration), degrees of freedom are described by classical mechanics, and its attractiveness from a practical point of view is that calculations can be carried out within the framework of standard Monte Carlo classical trajectory methodology.[2]

One of the motivations for developing this completely classical model was the realization[3] that "mixed" dynamical models--i.e., those which characterize some degrees of freedom by classical mechanics and others by quantum mechanics--fail to describe some features of the dynamics correctly. The very popular and often successful surface-hopping model,[4] for example, which treats heavy particle motion classically but electronic degrees of freedom quantum mechanically (as states, i.e., distinct potential energy surfaces), is unable to describe resonance effects between electronic and heavy particle degrees of freedom. Such resonance effects are important in the quenching of excited fluorine atoms ($^2P_{\frac{1}{2}}$) by collision with H_2[5] because the 404 cm^{-1} excitation energy of fluorine is roughly equal (within $\sim$ 10%) to the energy of the 0→2 rotational excitation of H_2. Similarly, $Br^*(^2P_{\frac{1}{2}})$ is thought[6] to be quenched efficiently by H_2 because the vibrational quantum of H_2 approximately matches the 3685 cm^{-1} excitation energy of bromine. Since the classical model[1]

treats all degrees of freedom on the same dynamical footing, i.e., by classical mechanics, it has been reasoned that it should be able to describe these aspects of resonance energy trasfer at least qualitatively correctly. To see how quantitative the model is, however, requires numerical applications, and such is the purpose of this paper.

Earlier calculations[1d] have shown that the classical model does indeed provide a reasonably good description of the resonance effect between electronic and rotational degrees of freedom in $F-H_2$ collisions,

$$F^*(^2P_{1/2}) + H_2(j=0) \rightarrow F(^2P_{3/2}) + H_2(j=2) \quad ; \quad (1.1)$$
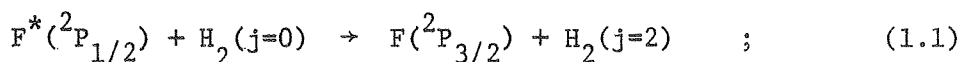
The cross section for this process is much larger at low collision energies than for quenching by a comparable rare gas atom that does not have rotational degrees of freedom. The present paper considers a simple model of electronic-vibrational energy transfer that would pertain, for example, to the quenching of Br^* by H_2,

$$Br^*(^2P_{1/2}) + H_2(v=0) \rightarrow Br(^2P_{3/2}) + H_2(v=1) \quad . \quad (1.2)$$
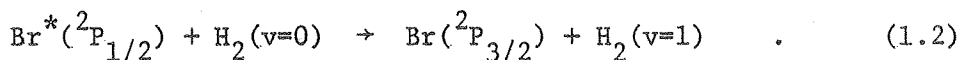
The particular example we consider is the collinear version of such a system for which Lee, Lam, DeVries, and George[7] have recently carried out quantum mechanical coupled channel calculations. Lee et al.'s calculations provide the exact results for this model problem, which can thus serve as a benchmark to see how well the classical model is able to describe such non-adiabatic processes.

Section II defines the system treated by Lee et al. and briefly
summarizes the classical model as it applies to this example. The
results are discussed in Section III.

II. The Model

Lee et al.[7] consider a collinear atom-diatom collision system, A + BC, with two potential energy surfaces, i.e., two electronic states, corresponding to ground and excited states of the atom A. The 2 × 2 diabatic interaction potential surface matrix is

$$
\begin{pmatrix} V_{00}(R,r) & , & V_{01}(R,r) \\ V_{10}(R,r) & , & V_{11}(R,r) \end{pmatrix} = \begin{pmatrix} \dfrac{\lambda}{3} & , & \dfrac{\sqrt{2}\,\lambda}{3} \\ \dfrac{\sqrt{2}\,\lambda}{3} & , & \dfrac{2\lambda}{3} \end{pmatrix}
$$

$$
+ \, e^{-\alpha(R - \frac{1}{2} r - \rho_0)} \begin{pmatrix} A_0 & , & 0 \\ 0 & , & A_1 \end{pmatrix} \quad , \quad (2.1)
$$

where r is the vibrational coordinate of BC and R the translational coordinate, the distance of A to the center of mass of BC. It is useful to make a unitary transformation of this potential matrix to diagonalize the first term, the atomic part of the interaction that survives as $R \rightarrow \infty$. The appropriate unitary transformation matrix is

$$
\underset{\sim}{U} = \begin{pmatrix} \sqrt{\dfrac{2}{3}} & , & \sqrt{\dfrac{1}{3}} \\ -\sqrt{\dfrac{1}{3}} & , & \sqrt{\dfrac{2}{3}} \end{pmatrix} \quad , \quad (2.2)
$$

and for the transformed potential matrix $\bar{\underset{\sim}{V}}$,

$$
\bar{\underset{\sim}{V}} \equiv \underset{\sim}{U}^{\dagger} \cdot \underset{\sim}{V} \cdot \underset{\sim}{U} \quad , \quad (2.3)
$$

one obtains

$$\begin{pmatrix} \bar{V}_{00} \; , \; \bar{V}_{01} \\ \bar{V}_{10} \; , \; \bar{V}_{11} \end{pmatrix} = \begin{pmatrix} 0 \; , \; 0 \\ 0 \; , \; \lambda \end{pmatrix} + e^{-\alpha(R - \frac{1}{2}r - \rho_0)} \begin{pmatrix} \bar{A}_{00} \; , \; \bar{A}_{01} \\ \bar{A}_{10} \; , \; \bar{A}_{11} \end{pmatrix} , \quad (2.4)$$

where

$$\bar{A}_{00} = \frac{2}{3} A_0 + \frac{1}{3} A_1 \qquad (2.5a)$$

$$\bar{A}_{11} = \frac{1}{3} A_0 + \frac{2}{3} A_1 \qquad (2.5b)$$

$$\bar{A}_{01} = \bar{A}_{10} = \frac{\sqrt{2}}{3} (A_1 - A_0) \qquad . \qquad (2.5c)$$

The classical model[1] for the electronic degrees of freedom replaces the diabatic potential matrix $\bar{V}_{N,N'}(R,r)$, $N,N' = 0,1$ of Eq. (2.5) by a classical electronic Hamiltonian $\bar{V}(R,r,N,Q)$ which is defined in terms of the matrix elements by

$$\bar{V}(R,r,N,Q) = N\bar{V}_{11}(R,r) + (1-N)\bar{V}_{00}(R,r)$$

$$+ 2 \bar{V}_{01}(R,r) \sqrt{(N+\frac{1}{2})(\frac{3}{2} - N)} \; \cos Q \qquad . \qquad (2.6)$$

(N,Q) are the classical action-angle variables[8] for the electronic degrees of freedom; i.e., N is the classical electronic quantum number. With Eq. (2.4) one notes that as $R \rightarrow \infty$ Eq. (2.6) becomes

$$\bar{V}(R \rightarrow \infty, r, N, Q) = N\lambda \qquad ; \qquad (2.7)$$

thus N is a conserved quantity in the asymptotic region, with N=0 corresponding to the ground electronic state of atom A (with energy 0) and N=1 to the excited state A^* (with energy λ).

To obtain the classical Hamiltonian for the complete system one adds to $\bar{V}(R,r,N,Q)$ the potential energy for free vibrational motion of BC and the kinetic energy for vibration and translation, and with Eqs. (2.4) and (2.6) this gives

$$H(P,R,p,r,N,Q) = \frac{P^2}{2\mu} + \frac{p^2}{2m} + \frac{1}{2} m\omega^2 (r-r_0)^2$$

$$+ N\lambda + e^{-\alpha(R - \frac{1}{2}r - \rho_0)} [(1-N)\bar{A}_{00} + N\bar{A}_{11}$$

$$+ 2 \bar{A}_{01} \sqrt{(N+\frac{1}{2})(\frac{3}{2}-N)} \; \cos Q] \qquad , \qquad (2.8)$$

where m and μ are the reduced masses for BC vibration and A–BC translation, respectively. To obtain the final form of the classical Hamiltonian one replaces the vibrational coordinate and momentum (r,p) by their action-angle variables[8] (n,q),

$$r-r_0 = \sqrt{\frac{2n+1}{m\omega}} \cos q \qquad\qquad\qquad (2.9a)$$

$$p = -\sqrt{(2n+1)m\omega} \; \sin q \qquad , \qquad\qquad (2.9b)$$

giving

$$H(P,R,n,q,N,Q) = \frac{P^2}{2\mu} + (n+\frac{1}{2})\omega + N\lambda$$

$$+ \exp\{-\alpha[R-R_0-\frac{1}{2}\sqrt{\frac{2n+1}{m\omega}}\cos q]\}\ [(1-N)\bar{A}_{00} + N\bar{A}_{11}$$

$$+ 2\,\bar{A}_{01}\sqrt{(N+\frac{1}{2})(\frac{3}{2}-N)}\ \cos Q] \quad . \tag{2.10}$$

The results presented in the next section correspond to implementation of the classical model within the framework of the standard quasiclassical histogram approach.[2,9] Thus to compute the probability for the following vibration-to-electronic transition,

$$A + BC(n=1) \rightarrow A^* + BC(n=0) \quad , \tag{2.11}$$

one integrates Hamiltonian's equations (generated from the Hamiltonian of Eq. (2.10)) with initial conditions

$$n(t_1) = 1 \equiv n_1$$

$$N(t_1) = 0 \equiv N_1$$

$$q(t_1) = 2\pi\xi_1$$

$$Q(t_1) = 2\pi\xi_2$$

$$R(t_1) = \text{large}$$

$$P(t_1) = -\sqrt{2\mu[E_{tr}-(n_1+\frac{1}{2})\omega-N_1\lambda]} \quad , \tag{2.12}$$

where ξ_1 and ξ_2 are random numbers in $(0,1)$ and E_{tr} is the initial translational energy. The final values of n and N that correspond to Eq. (2.11) are n=0, N=1, and the quasiclassical approximation to the probability of this transition is the fraction of trajectories with the above initial conditions that have their actual final values of n and N within a "box" of unit width about these values n=0, N=1.

The parameters in the classical Hamiltonian, Eq. (2.10), which correspond to Lee et al.'s[7] calculations are

$$\omega = 0.02 \qquad\qquad \alpha = 3$$
$$R_0 = 4.7 \qquad\qquad \bar{A}_{00} = \frac{11}{3} \times 10^{-5}$$
$$m = 1000 \qquad\qquad \bar{A}_{11} = \frac{13}{3} \times 10^{-5}$$
$$\mu = 3896.1 \qquad\qquad \bar{A}_{01} = \frac{2\sqrt{2}}{3} \times 10^{-5} \ . \quad (2.13)$$

These values, in atomic units, correspond roughly to the Br-H_2 system. The parameter λ, the A $\rightarrow$ A* excitation energy, is varied in these model calculations to assess the significance of resonance in the electronic-vibrational energy transfer. Exact resonance, for example, corresponds to $\lambda = \omega = 0.02$, so for very low translational energies, where resonance considerations are most important, one would expect the transition probability for Eq. (2.11) to be largest for $\lambda \simeq 0.02$. By varying λ one can see how prominent the resonance effect is and how well the classical model is able to describe it.

III. Results and Discussion

Figures 1-3 show the transition probability for Eq. (2.11) as a function of the atomic energy gap λ for translational energies of 0.01 eV, 0.035 eV, and 0.055 eV, respectively. The solid curves are the exact quantum mechanical results computed by Lee et al.,[7] and the broken curves the present results of the classical model. As expected, the resonance structures is sharpest at the lowest translational energy; i.e., in Figure 1 the transition probability peaks sharply at $\lambda \simeq 0.02$. At higher translational energy the resonance structure broadens and shifts.

The significant point to note is that this classical model does describe the resonance features in this process reasonably well. The position and width of the resonance peak are described well over the entire energy range considered. Used in this primitive histogram mode, however, the classical results do have shortcomings: the peak heights are too large (by a factor of two in the worst case, Figure 1) and the classical results do not describe the wings of the resonance line shape well. This latter failing is typical of all quasiclassical histogram treatments, namely the inability to describe weak (classically forbidden) processes.[9]

The encouraging note is that the quasiclassical results for this electronically inelastic process are no worse than typical quasi-classical results for rotationally and vibrationally inelastic processes.[10] Thus the classical model for electronic degrees of freedom seems to do about as well (or as poorly, depending on one's

point of view) in describing electronically inelastic processes as
classical mechanics does for inelastic processes involving only
heavy particle degrees of freedom. To the extent that this level
of accuracy is sufficient one thus has a consistent dynamical model
for treating both electronically non-adiabatic as well as adiabatic
collision processes.

Acknowledgments

References

1. (a) W. H. Miller and C. W. McCurdy, J. Chem. Phys. 69, 5163 (1978); (b) C. W. McCurdy, H.-D. Meyer, and W. H. Miller, J. Chem. Phys. 70, 3177 (1979); (c) H. D. Meyer and W. H. Miller, J. Chem. Phys. 70, 3214 (1979); (d) 71, 2156 (1979); (e) 72, 2272 (1980).

2. See, for example, R. N. Porter and L. M. Raff, in Dynamics of Molecular Collisions Part B (Vol. II of Modern Theoretical Chemistry), ed. W. H. Miller, Plenum, N.Y., 1976, p. 1.

3. W. H. Miller, J. Chem. Phys. 68, 4431 (1978).

4. J. C. Tully and R. K. Preston, J. Chem. Phys. 55, 562 (1971); see also, J. C. Tully, in Dynamics of Molecular Collisions Part B (Vol. II of Modern Theoretical Chemistry), ed. W. H. Miller, Plenum, N.Y., 1976, p. 217.

5. (a) A. L. DeVries and T. F. George, J. Chem. Phys. 66, 2421 (1977); (b) F. Rebentrost and W. A. Lester, J. Chem. Phys. 67, 3367 (1977).

6. (a) I. H. Zimmerman and T. F. George, Chem. Phys. 7, 323 (1976); (b) David J. Nesbitt and Stephen R. Leone (to be published).

7. H. W. Lee, K. S. Lam, P. L. DeVries, and T. F. George, J. Chem. Phys. 73, 206 (1980).

8. H. Goldstein, Classical Mechanics, Addison-Wesley, Reading, Mass., 1950, p. 288.

9. See also, W. H. Miller, <u>Adv. Chem. Phys.</u> 25, 69 (1974).

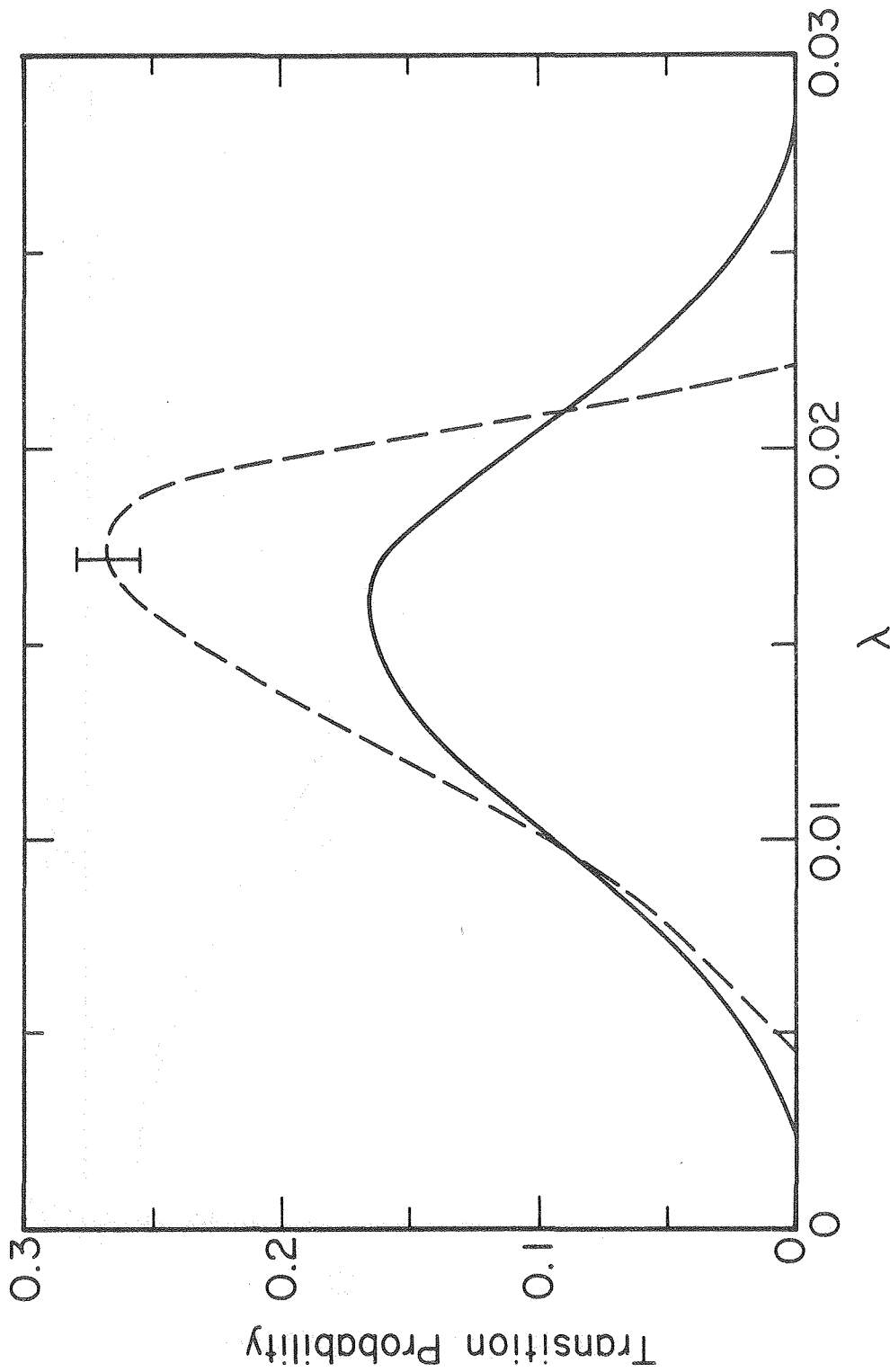10. See, for example, S. Chapman and S. Green, <u>J. Chem. Phys.</u> 67, 2317 (1977).

Figure Captions

1. Transition probability for Eq. (2.11) as a function of the atomic
   excitation energy λ, for an initial translational energy $E_{tr} =$
   0.01 eV. The solid curve is the exact quantum result of Lee _et al._
   (reference 7) and the broken curve the results of the present
   classical model; the error bar is the usual Monte Carlo error
   estimate.

2. Same as Figure 1 except $E_{tr} = 0.035$ eV.

3. Same as Figure 1 except $E_{tr} = 0.055$ eV.
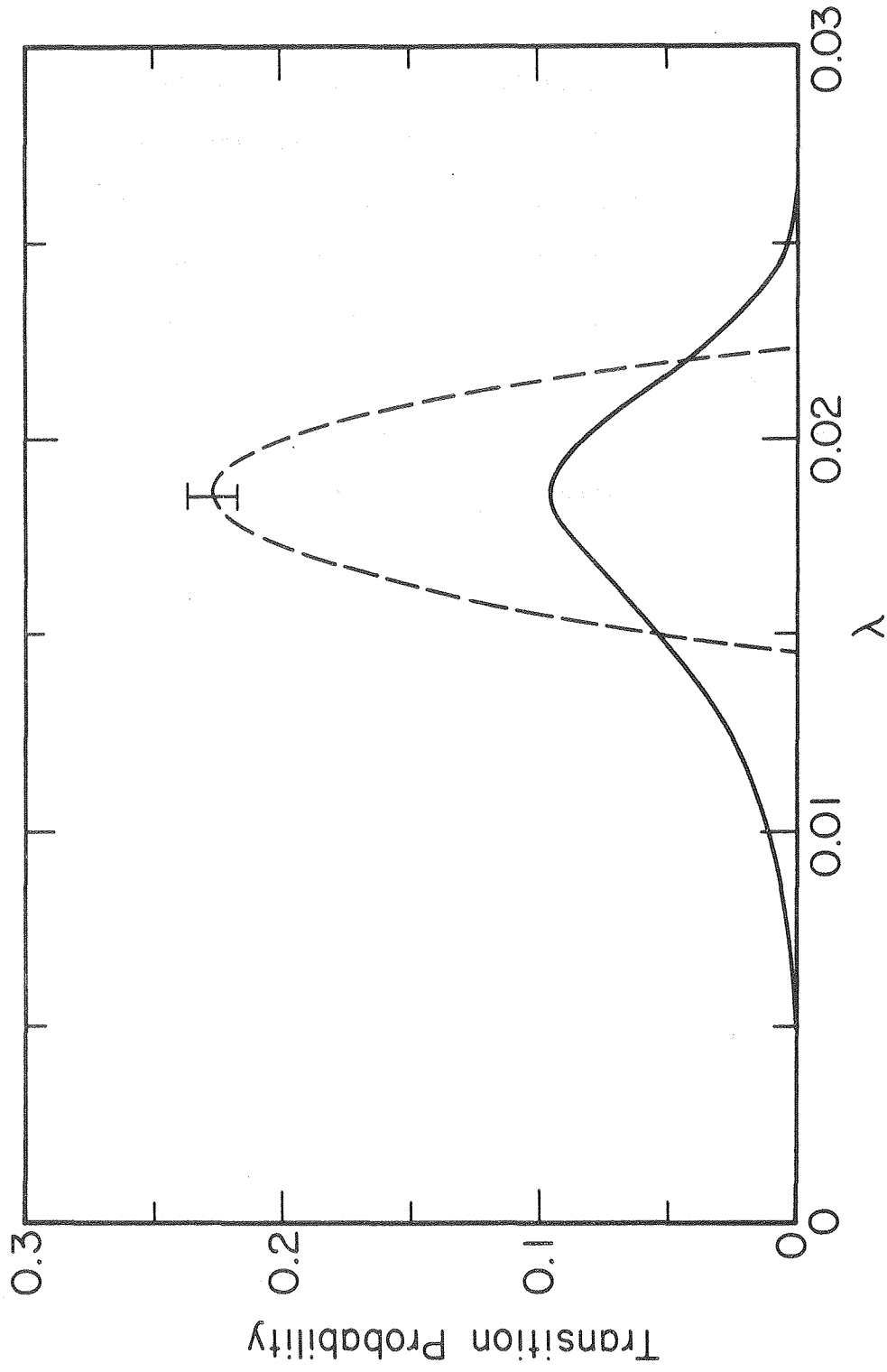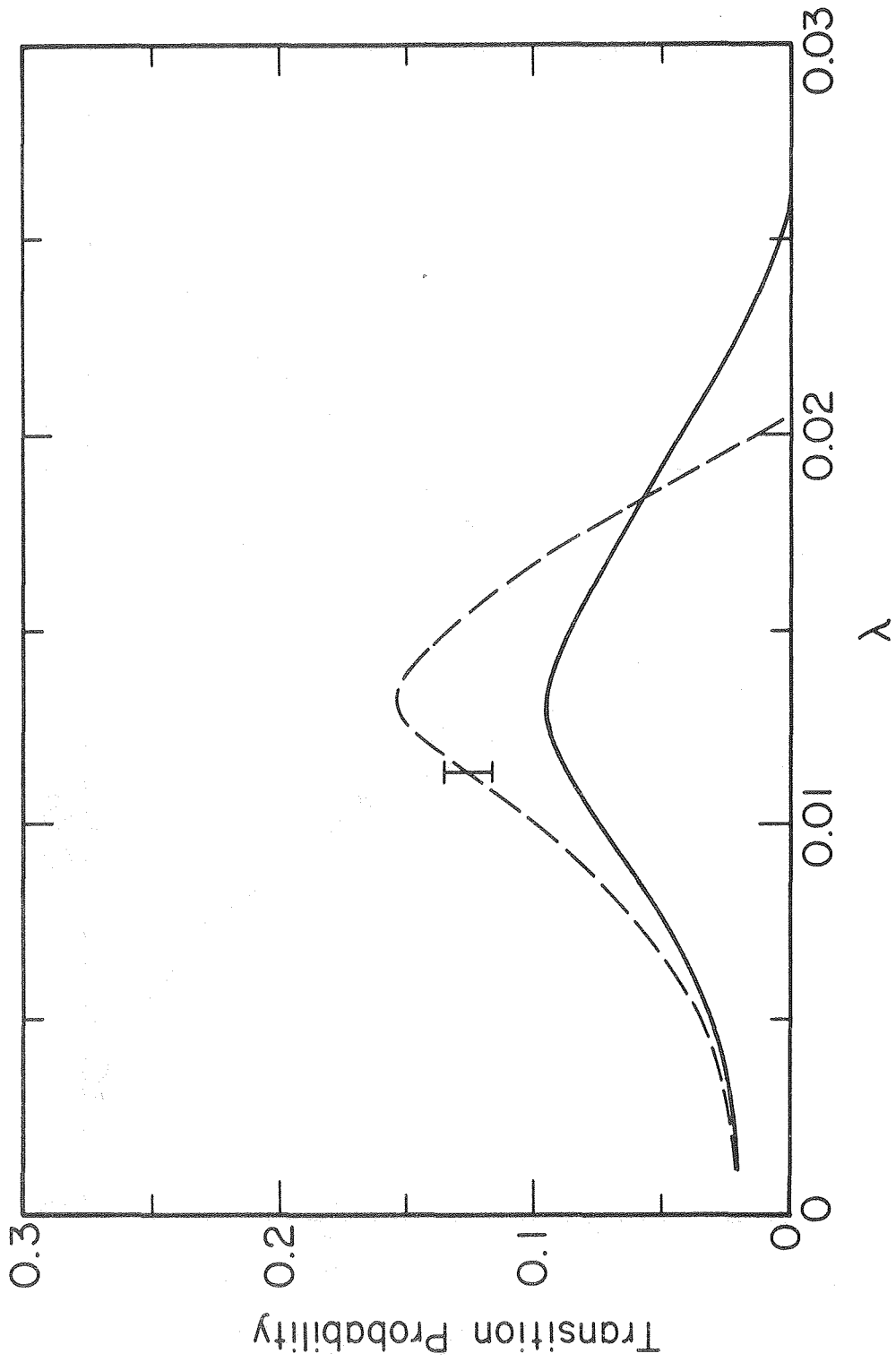
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Figure 1

Figure 2

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Figure 3