

A comparison of exact classical and quantum mechanical calculations of vibrational energy transfer. II. The effect of long-lived collision complexes

Robert J. Gordon

Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680
(Received 8 September 1977)

Exact classical and quantum mechanical calculations of V - T relaxation were carried out for the model system $\text{He} + \text{O}_2(v=1)$. The diatomic molecule was treated as a harmonic oscillator, and a spherically symmetric Lennard-Jones intermolecular potential was assumed. The bin and two-moment methods were used to quantize the classical energy transfer. For a deep well both classical and quantal calculations showed evidence of complex formation. In this case inelastic transitions were classically allowed even at low collision energies. The classical transition probabilities generally agreed within a factor of 2 with the quantal results. The final energy distribution of the complex trajectories was not completely random, as compared with the information-theoretic prior expectation.

I. INTRODUCTION

Classical mechanics provides an accurate description of molecular collisional processes under a wide range of conditions.¹ The assumption of the validity of classical mechanics is the basis for the widespread use of trajectory calculations to describe scattering phenomena.² However, only a limited number of comparisons of exact classical and quantum mechanical scattering calculations have been carried out.^{3,4} In order to put trajectory calculations on a firmer footing, it is important to determine the conditions under which classical mechanics breaks down.

In a previous paper³ (hereafter referred to as Paper I) we compared exact classical and quantum mechanical calculations of vibrational energy transfer for collisions of an atom with a spherically symmetric diatomic oscillator. It was found that for a repulsive exponential intermolecular potential, the average classical and quantal energy transfer were in excellent agreement at collision energies exceeding the vibrational spacing of the oscillator, $h\nu$. However, the determination of classical transition probabilities presented a problem. The usual histogram or bin method was inaccurate because of the existence of a large classical threshold. That is, for the particular problem studied [$\text{He} + \text{O}_2(v=1)$], at translational energies less than $3h\nu$ no trajectories produced an energy transfer greater than $h\nu/2$. On the other hand, a moment method based on the information theoretic techniques of Levine, Bernstein, and co-workers^{5,6} and of Truhlar and Duff⁷ was quite successful. It was speculated that for less repulsive potential functions the classical threshold may be lower and the bin method may be applicable.

In the present paper we compare calculations of classical and quantum mechanical energy transfer for collisions of an atom and a harmonic oscillator with a spherically symmetric Lennard-Jones potential. A number of exact quantum mechanical calculations have been reported for collinear collisions with an attractive intermolecular potential.⁸⁻¹⁷ Several semi-classical approximations¹⁸⁻²⁰ have been tested against two of the quantal calculations,^{9,11} with generally satisfactory results. To our knowledge, purely classical calculations with an at-

tractive potential have never been tested, aside from a brief study in Paper I.

Our objectives here are twofold. It is well known that if the well depth in the intermolecular potential is comparable in magnitude to the translational energy, a long-lived collision complex may be formed.²¹ Our first objective is to test the validity of classical mechanics when such complexes occur. Second, we wish to gain insight into the effects of collision complexes on vibrational energy transfer. Such complexes play a central role in unimolecular kinetics,²² and are important in a large number of bimolecular reactions as well.²³ Recent experimental evidence has shown that long range attractive forces can greatly enhance the rate of vibrational relaxation.²⁴⁻³¹

II. METHODS

The classical and quantum mechanical calculations were described in Paper I. The classical equations of motion were integrated by standard methods. The quantum scattering problem was solved by the method of R. G. Gordon,³² using a program written by A. F. Wagner.¹⁵

In the present study a spherically symmetric Lennard-Jones potential.

$$V(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], \quad (1)$$

was used throughout. As in Paper I we calculated the vibrational energy transfer for the system $\text{He} + \text{O}_2(v=1)$. The nominal potential parameters¹⁵ are $\sigma = 115.5$ and $\epsilon = 0.01593$. The unit of length is one-half of the zero point vibrational amplitude, while the unit of energy throughout this paper is the vibrational spacing of the harmonic oscillator. In order to increase the incidence of complex formation, in some of the calculations we set $\epsilon = 2$ or 3 . A table of typical values of ϵ for neutral scattering partners is given in Ref. 14.

The classical transition probabilities P_{10} and P_{12} , for final states $j=0$ and 2 , were calculated by the bin method and the two moment method discussed in Paper I. In the bin method P_{10} is defined as the fraction of initial oscillator phases leading to an energy transfer ΔE be-

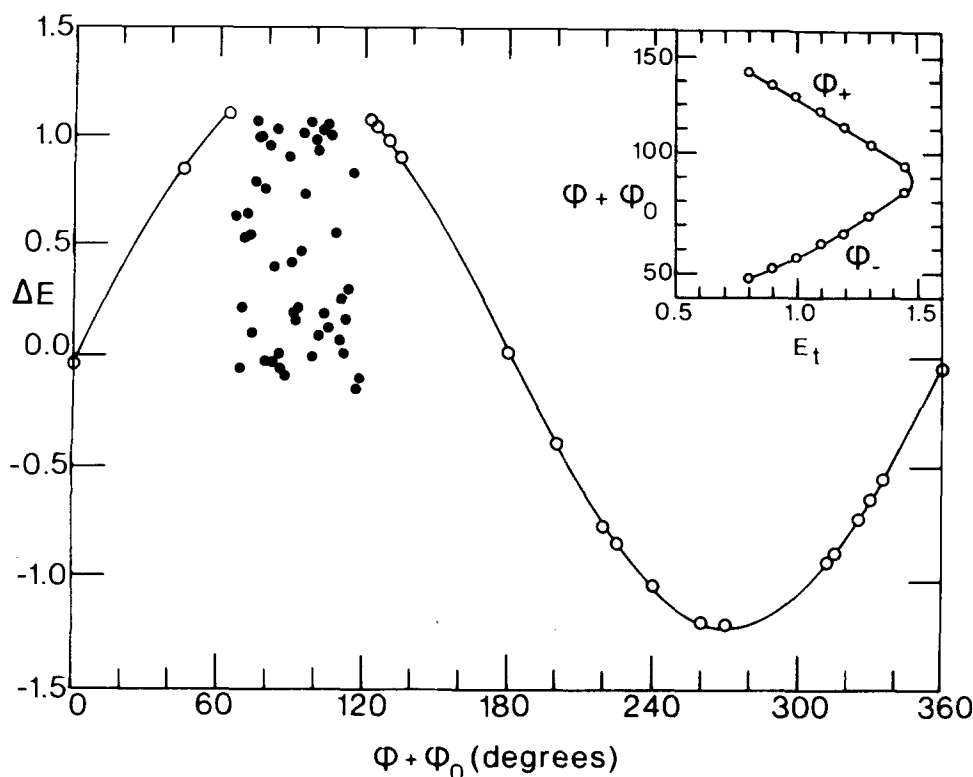


FIG. 1. Final vibrational energy, E_v' , as a function of initial oscillator phase, ϕ , for $\text{He} + \text{O}_2$ ($v=1$), with $\epsilon=2.0$, $E_t=1.1$, and $l=0$. The curve is a sine function, defined by Eq. (6), with ϕ_0 a least squares parameter. The open circles correspond to trajectories with only one turning point. The solid circles correspond to complex trajectories (i.e., trajectories having more than one turning point). The insert is a plot of the upper (ϕ_+) and lower (ϕ_-) phases defining the complex region.

tween -0.5 and -1.5 , while P_{12} is the corresponding fraction of phases with $0.5 \leq \Delta E < 1.5$.

The key assumption of the moment method is that the classical moments are a good approximation to the exact quantum values. Quantum mechanically, the n th moment for N states with the oscillator initially in state i is defined by

$$\langle \Delta^n E \rangle = \sum_{j=0}^N (j-i)^n P_{ij}. \quad (2)$$

The zeroth moment is just unity. In principle, if $n=N$ and n independent moments (in addition to the zeroth moment) are known, Eq. (2) can be solved for all the transition probabilities. In practice³ even small uncertainties in some of the moments can cause very large errors in solving sets of equations for $n > 2$. A way around this dilemma is to use fewer than n moments to calculate the least biased (in the information-theoretic sense) probability distribution.⁵ In Paper I two moments were found to be adequate for most purposes. For an initial state $i=1$, three different cases occur. For translational energy, E_t , less than 1,

$$P_{10} = -\langle \Delta E \rangle \quad (3a)$$

and

$$P_{12} = 0. \quad (3b)$$

For $1 \leq E_t < 2$,

$$P_{10} = (\langle \Delta^2 E \rangle - \langle \Delta E \rangle^2) / 2 \quad (4a)$$

and

$$P_{12} = (\langle \Delta^2 E \rangle + \langle \Delta E \rangle^2) / 2. \quad (4b)$$

For $E_t \geq 2$, the least biased probability distribution is used, namely,

$$P_{vv'} = \exp\{-[\lambda_0 + \lambda_1(v' - v)]\}, \quad (5)$$

where λ_0 and λ_1 are the usual Lagrangian multipliers.⁶

III. RESULTS

It has been shown by a number of authors that for direct collisions of an atom with a harmonic oscillator the energy transferred is a sinusoidal function of the initial oscillator phase.^{3,20,21} In contrast, the amount of energy transferred in a complex trajectory varies in a very complicated fashion with the initial phase. This behavior is illustrated in Fig. 1 for a collinear collision with $E_t=1.1$ and $\epsilon=2$. The curve has the functional form

$$\Delta E = \delta + A \sin(\phi + \phi_0), \quad (6)$$

where ϕ is the initial phase of the oscillator, and δ , A , and ϕ_0 are least-squares parameters. The trajectories used for this fit (open circles) all have a single turning point, while the trajectories in the complex region (solid circles) have at least three and as many as 93 turning points. In calculating the classical moments, contributions from both direct and complex trajectories must be included. The former was obtained from a least-squares fit of Eq. (6) to the direct trajectories, while the latter was evaluated by computing typically 20 evenly spaced trajectories in the complex region. The width of the complex region decreases with E_t . In collinear collisions with $\epsilon=2$, no complexes are formed for $E_t > 1.48$. This fact is illustrated in the insert of Fig. 1, where the minimum and maximum phases defining the complex region are plotted against initial translational energy. For a spherically symmetrical potential the width of the complex region also decreases with increasing impact parameter.

The quantum mechanical calculations also show evi-

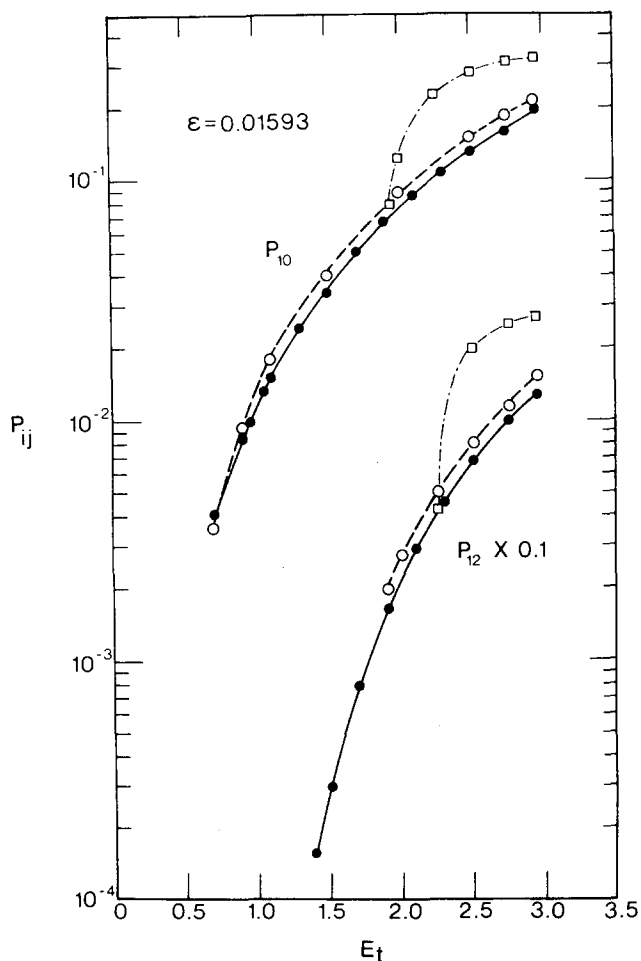


FIG. 2. Classical and quantal transition probabilities for collinear collisions with $\epsilon = 0.01593$, as a function of initial translational energy, E_t . The solid circles and solid curves are the quantal results. The open circles and dashed curves are the moment calculations. The squares and dot-dashed curves are the bin results. Note the shift in scale for P_{12} .

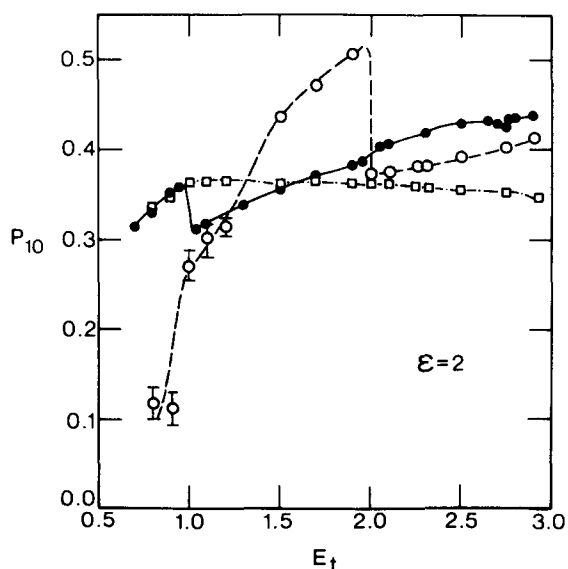


FIG. 3. Classical and quantal calculations for P_{10} for $\epsilon = 2$, as a function of initial translational energy. Symbols are the same as in Fig. 2. Error bars for $E_t \leq 1.2$ are the standard errors due to sampling of trajectories in the complex region.

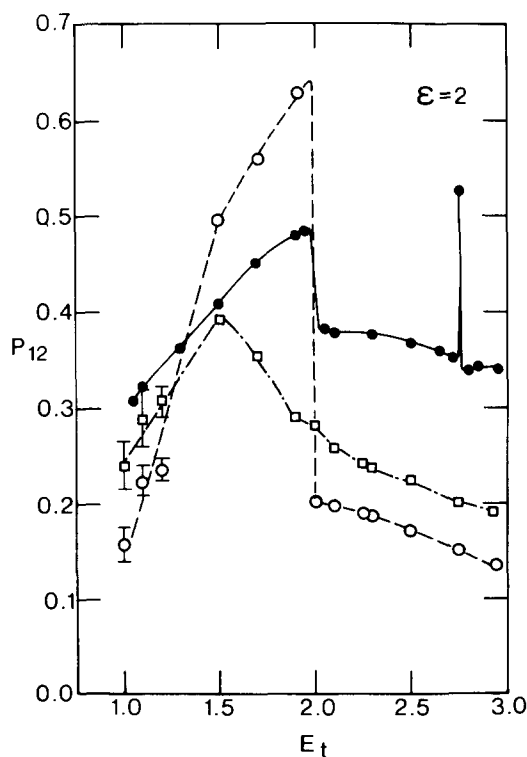


FIG. 4. Classical and quantal calculations of P_{12} for collinear collisions with $\epsilon = 2$, as functions of initial translational energy. Symbols are the same as in Figs. 2 and 3.

dence of complex formation, although there is no sharply defined complex region as there is in the classical case. The number of virtual states needed for convergence increases with ϵ , and these states must be retained far into the asymptotic region. Moreover, the transition probabilities have increasingly complicated energy dependences as ϵ is increased. This behavior is illustrated in Figs. 2–5 for collinear collisions. For $\epsilon = 0.01593$ (Fig. 2) P_{10} and P_{12} increase smoothly and monotonically with E_t . Both transition probabilities vary by several orders of magnitude over the energy range studied. In contrast, for $\epsilon = 2$ (Figs. 3 and 4) P_{10} and P_{12} have erratic behavior, but on the average vary only slightly with energy. At $E_t = 1$ there is a discontinuity in the quantal calculation of P_{10} . At $E_t = 2$ there is a similar jump in P_{12} and a weaker step in P_{10} . These variations are caused by the opening of new vibrational states. In addition there is a strong resonance at $E_t = 1.753$ with a FWHM = 0.007. Oscillations in P_{ij} have been observed in many other studies, but only in a few cases of non-reactive scattering with an attractive potential have sharp resonances been reported.^{12,16,33} We did not make a systematic attempt to locate all such peaks in the present study. The structure observed for $\epsilon = 2$ is greatly enhanced for $\epsilon = 3$ (Fig. 5), with many undulations apparent in P_{ij} .

The classical and quantal transition probabilities are compared in Figs. 2–4. For $\epsilon = 0.01593$ there are no collinear complexes in the energy range studied. The classical threshold for P_{10} (i. e., for $\Delta E \leq -0.5$) occurs at $E_t = 1.95$, while for P_{12} ($\Delta E \geq 0.5$) the threshold is at $E_t = 2.25$. Although these thresholds are smaller than in the case of a repulsive exponential potential,³ they are

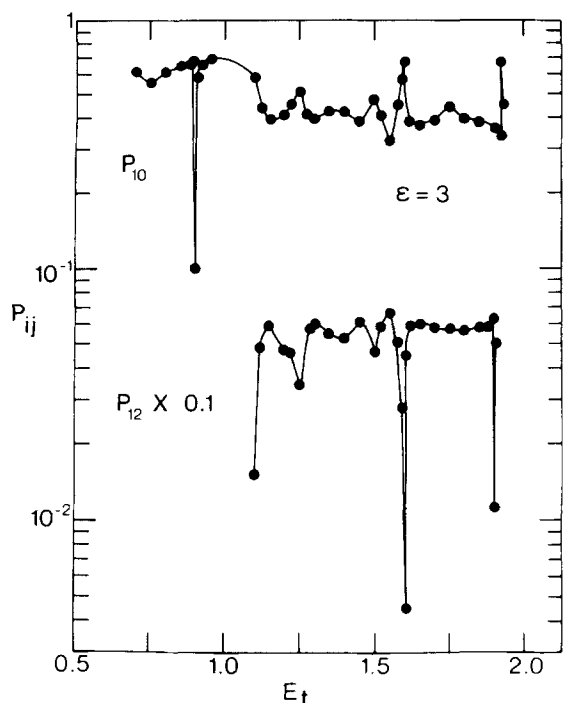


FIG. 5. Quantal calculations of transition probabilities for collinear collisions with $\epsilon = 3$, as a function of initial translational energy. Note the shift in scale for P_{12} .

sufficiently large that the bin method would produce significant errors in calculations of cross sections and rate coefficients. The moment method, on the other hand, is in excellent agreement with the quantum results.

When ϵ is increased to 2 the situation is quite different. In this case there are no classical thresholds, and the bin method actually fares slightly better than the moment analysis. The moment method, however, does predict the discontinuity at $E_t = 2$. The moments used in these calculations are shown in Fig. 6. We note that the classical values of $\langle \Delta E \rangle$ are accurate for $E_t > 1.5$, while the classical $\langle \Delta^2 E \rangle$ is accurate only for $E_t > 2$. The factor of 2 discrepancy between the exact quantal calculations and the classical moment approximations of P_{12} for $E_t > 2$ implies that at higher translational energies more than two moments are needed to describe the probability distribution.

The variation of P_{ij} with orbital angular momentum, l , is shown in Fig. 7 for $E_t = 1.1$. The quantum transition probabilities have several interesting features. At $l = 49$ there is an abrupt decrease in P_{12} . This jump is due to the fact that at $l = 49$ the centrifugal barrier calculated with the potential energy matrix elements for $i = 1$ and $j = 2$ lies above the initial translational energy. Also there are a number of resonances, most of which occur for $l > 49$. The origin of these resonances, and the role of the centrifugal barrier, are under further investigation.

In the corresponding classical calculations, collision complexes were formed for $l \leq 35$. For $l \geq 72$, P_{12} is classically forbidden, and for $l \geq 79$ P_{10} is also forbidden. The moment analysis predicts nonzero P_{ij} at large-

er values of l ; however, for $l \geq 90$ it predicts negative values of P_{12} . The reason for this is that for strongly forbidden transitions the constraints

$$P_{12} - P_{10} = \langle \Delta E \rangle \quad (7a)$$

and

$$P_{12} + P_{10} = \langle \Delta^2 E \rangle, \quad (7b)$$

are inconsistent when the classical moments are used to approximate the true ones. In this case we used Eqs. (3) to calculate P_{ij} .³⁴

The integral cross sections for the transitions shown in Fig. 7 are listed in Table I. For the $1-0$ transition the classical moment cross section is in excellent agreement with the quantal result. The bin calculation, however, is 50% too large, despite the fact that the transitions for large l are classically forbidden (i. e., $|\Delta E| < 0.5$). For the $1-2$ transition the agreement for both classical methods is poorer because of the centrifugal falloff at $l = 49$ in the quantal calculation.

It is interesting to compare these integral cross sections with similar calculations for a shallow well where classical complexes do not occur. For $\epsilon = 0.01593$ and $E_t = 1.1$ (see Table I) inelastic transitions are classically forbidden for all l . That is, the bin method predicts cross sections of zero. The moment method does the

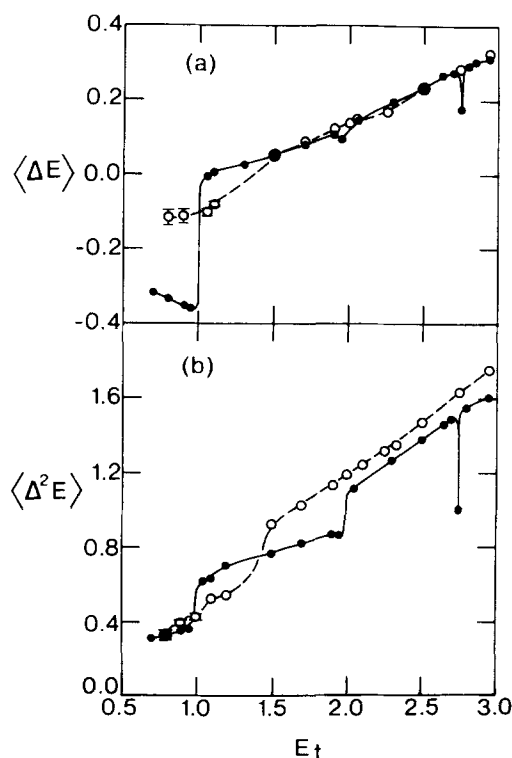


FIG. 6. First two moments of the transition probability distribution, as defined by Eq. (2), for collinear collisions with $\epsilon = 2$. The solid circles and solid curves are the quantal results, while the open circles and dashed curves are the classical calculations. (a) Average energy transfer vs initial translational energy. (b) Average of the square of the energy transfer vs initial translational energy.

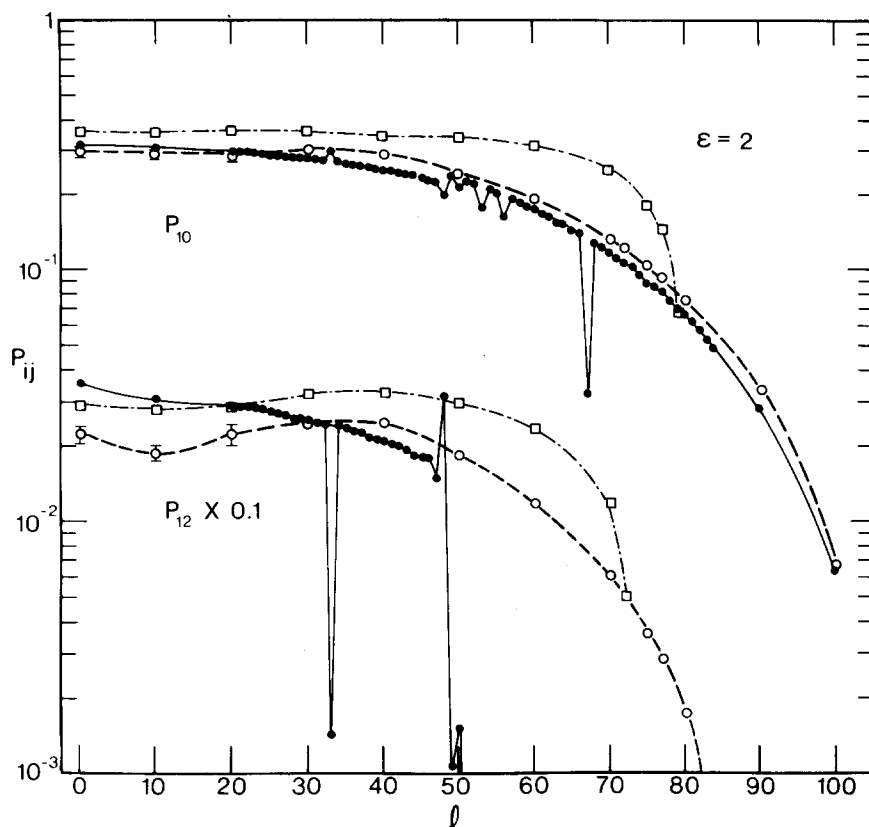


FIG. 7. Classical and quantal transition probabilities as a function of orbital angular momentum, l , for $\epsilon=2$ and $E_t=1.1$. Symbols are the same as in Figs. 2-4. Note the shift in scale for P_{12} .

same for the $1 \rightarrow 2$ transition, but for $1 \rightarrow 0$ (using Eq. [3a]) it is in excellent agreement with the quantal result.

IV. DISCUSSION

The grouping of initial oscillator phases into two bands, one containing only direct trajectories and the other only complex ones, was first noted by Rankin and Miller³⁵ for collinear reactive scattering of $H + Cl_2$. As in the present case, they found that the complex region is centered about the phase of maximum energy transfer ($\phi + \phi_0 = \pi/2$ in Fig. 1). The energy dependence of the upper and lower bounds of the complex region (ϕ_+ and ϕ_- in Fig. 1) is reminiscent of the reactivity maps found by Laidler, Tan, and Wright³⁶ for $H + H_2$ collisions. In their case reactive trajectories occur only in a well defined band of phases. The trajectories in this band are all direct, while on the boundaries multiple collisions occur. In the present calculations trajectories on the boundaries of the complex region have very long collision times, and generally were not completed in 2 min of IBM 370/158 cpu time. The analogy with the reactivity bands should not be taken too literally, however, because the fitted value of ϕ_0 in Eq. (6) varies erratically with energy, and it is only the width of the complex region that has a smooth energy dependence.

There is a simple way of locating the phases ϕ_+ and ϕ_- . Note in Fig. 1 that the quantity $A + \delta$ [defined in Eq. (6)] is larger than the collision energy, E_t . Since ΔE cannot exceed E_t , there must be a range of phases in which Eq. (6) does not hold. The upper and lower bounds of this range, given by

$$\phi_{\pm} = \sin^{-1}[(E_t - \delta)/A], \quad (8)$$

turn out to be the same as the bounds of the complex region.³⁷

A matter of some interest is the energy distribution after the complex redissociates. Gottdiener²¹ showed that ΔE is not a random function of ϕ . Rather, the complex region consists of many parabolically shaped, piecewise continuous segments with $d^2\Delta E/d\phi^2 > 0$. On each parabola the number of turning points in the trajectories is constant. The overall structure of the complex region is very complicated, with apparent discontinuities between parabolas. Because of this complexity, it is possible that the distribution of final energies might turn out to be nearly random.

The randomness of the final distribution can be tested with information theory.⁶ The usual assumption is that

TABLE I. Integral cross sections for $E_t = 1.1$.^a

Transition	ϵ	Quantum Result	Moment Method	Bin Method
$1 \rightarrow 0$	2.0	45	51	66
$1 \rightarrow 2$	2.0	20	31	47
$1 \rightarrow 0$	0.01593	0.28	0.30	0
$1 \rightarrow 2$	0.01593	1.8-4	0	0

^aEnergies are expressed in units of $h\nu$. Cross sections are in \AA^2 . 1.8-4 means 1.8×10^{-4} .

TABLE II. Comparison of prior and actual moments of the final energy distribution in collinear complexes.

E	$\langle f_v \rangle$	$\langle f_v^2 \rangle$	$\langle \Delta E \rangle$	$\langle \Delta^2 E \rangle$
2.3	0.74 ± 0.03^a (0.67) ^b	0.56 ± 0.05 (0.53)	0.02 ± 0.08 (0.033)	0.12 ± 0.04 (0.47)
2.4	0.80 ± 0.04 (0.67)	0.66 ± 0.06 (0.53)	0.42 ± 0.09 (0.10)	0.28 ± 0.07 (0.52)
2.5	0.74 ± 0.03 (0.67)	0.56 ± 0.05 (0.53)	0.34 ± 0.08 (0.17)	0.22 ± 0.06 (0.58)
2.6	0.75 ± 0.02 (0.67)	0.59 ± 0.03 (0.53)	0.45 ± 0.06 (0.23)	0.37 ± 0.06 (0.66)
2.7	0.73 ± 0.05 (0.67)	0.56 ± 0.09 (0.53)	0.48 ± 0.14 (0.30)	0.39 ± 0.14 (0.74)

^aMoments of the actual distribution with $\epsilon = 2$. Uncertainties are the standard errors.

^bPrior moments are in parentheses.

the prior detailed transition rate $i \rightarrow j$ at total energy E is given by⁵

$$k^0(i \rightarrow j; E) = R\rho(E_t'), \quad (9)$$

where ρ is the density of states of the products, E_t' is the final translational energy, and R is a constant independent of energy. For collinear collisions³⁸

$$\rho(E_t') = A_c E_t'^{-1/2}, \quad (10)$$

where A_c is a constant. If f_v is the fraction of the total energy in product vibration, Eqs. (9) and (10) yield the prior distribution function

$$P(f_v) = 1/2(1 - f_v)^{-1/2}, \quad (11)$$

with the first two moments

$$\langle f_v \rangle = 2/3 \quad (12)$$

and

$$\langle f_v^2 \rangle = 8/15. \quad (13)$$

The prior and actual moments of f_v for the complex region at a number of different energies are compared in Table II. The prior values of $\langle f_v \rangle$ and $\langle f_v^2 \rangle$ are close to the actual values, differing on the average by only -0.08 and 0.05 , respectively. The first two moments of ΔE are related to the moments of f_v by the expressions

$$\langle \Delta E \rangle = E \langle f_v \rangle - E_v \quad (14)$$

and

$$\langle \Delta^2 E \rangle = E^2 \langle f_v^2 \rangle - 2E_v E \langle f_v \rangle + E_v^2, \quad (15)$$

where E_v is the initial vibrational energy and E is the total energy. As shown in Table II, the prior moments of ΔE differ substantially from the actual values.

The actual and prior distributions of f_v for $E_t = 1.1$ are plotted in Fig. 8. In both distributions most of the energy is retained in vibration. The actual distribution, however, appears to be bimodal, and has no trajectories with $f_v < 0.5$. These features indicate a bias in the distribution, which arises from the minima of the parabolic

regions described by Gottdiener.²¹ Since approximately half of the complex trajectories have only three turning points (i. e. two bounces), some nonrandom behavior in ΔE is not unreasonable. Nonrandom unimolecular dissociation of larger molecules has been found in other trajectory calculations.^{39,40}

The quantal transition probabilities vary nonmonotonically with energy, displaying greater complexity as the well depth is increased. This trend, illustrated in Figs. 2-5, has been observed previously with a variety of potential functions.⁸⁻¹⁷ A further point of interest is the size of the transition probabilities. For a shallow well the inelastic transition probabilities are fairly small (Fig. 2). As the well depth is increased, inelastic transitions become more probable than elastic ones, even at low collision energies (Figs. 3-5). This tendency holds for integral cross sections as well, as shown in Table I, and is consistent with experimental observations that vibrational relaxation is significantly enhanced when complexes are formed.⁴¹

We have shown in this paper that both the moment and bin methods are useful in approximating quantal transition probabilities. For shallow wells the existence of a classical threshold makes the bin method highly inaccurate at thermal energies. For deep wells there is no threshold, and the bin probabilities are in fairly good agreement with the quantal values. However, the bin method (at least as formulated here) then suffers from the difficulty that it predicts nonzero probabilities for endoergic transitions that are energetically inaccessible. (E. g., for $E_t < 1$ there are some trajectories with $\Delta E > 0.5$.) The moment method does not have these shortcomings. However, it is more sensitive to the classical estimate of the average energy transfer, especially at low collision energies. On the whole the mo-

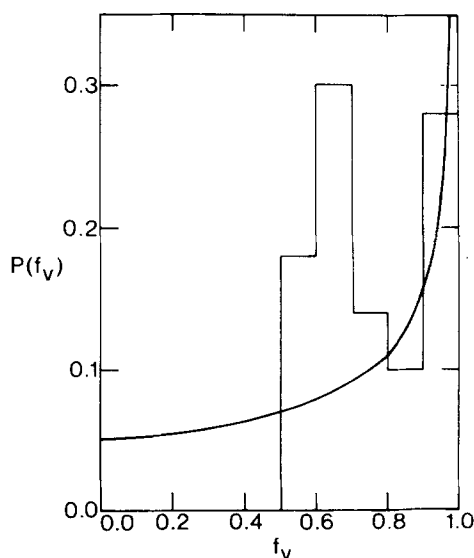


FIG. 8. Probability of a fraction f_v of the total energy appearing in final vibration. The histogram is the actual distribution calculated from 50 trajectories with $\epsilon = 2$. The curve is the prior distribution divided by 10 to correspond to a histogram bin size of 0.1.

ment method appears to be the more reliable of the two. Nevertheless, errors of up to a factor of 2 are likely in calculations of integral cross sections. This is in contrast with the case of direct collisions, where greater accuracy is achievable with classical mechanics.³

ACKNOWLEDGMENTS

We wish to thank Dr. Albert F. Wagner for use of his quantum mechanical scattering program and for many illuminating discussions. Support by the Computer Center of the University of Illinois at Chicago Circle and by the National Science Foundation are gratefully acknowledged.

- ¹R. G. Gordon, Faraday Discuss. Chem. Soc. **55**, 22 (1973).
- ²R. N. Porter, Ann. Rev. Phys. Chem. **25**, 317 (1974).
- ³R. J. Gordon, J. Chem. Phys. **65**, 4945 (1976); and references cited.
- ⁴G. C. Shatz and A. Kuppermann, J. Chem. Phys. **65**, 4668 (1976).
- ⁵R. D. Levine and R. B. Bernstein, Adv. At. Mol. Phys. **11**, 215 (1975).
- ⁶I. Procaccia and R. D. Levine, J. Chem. Phys. **63**, 4261 (1975) and **64**, 808 (1976).
- ⁷D. G. Truhlar and W. Duff, Chem. Phys. Lett. **36**, 551 (1975)
- ⁸D. J. Diestler, J. Chem. Phys. **52**, 2280 (1970).
- ⁹V. P. Gutschick, V. McKoy, and D. J. Diestler, J. Chem. Phys. **52**, 4807 (1970).
- ¹⁰D. J. Wilson, J. Chem. Phys. **54**, 540 (1971).
- ¹¹D. J. Diestler and P. Feuer, J. Chem. Phys. **54**, 4626 (1971).
- ¹²E. J. Shipsey, J. Chem. Phys. **56**, 1179 (1972).
- ¹³R. E. Roberts and D. J. Diestler, J. Chem. Phys. **57**, 2998 (1972).
- ¹⁴D. Secrest and W. Eastes, J. Chem. Phys. **56**, 2502 (1973).
- ¹⁵A. F. Wagner and V. McKoy, J. Chem. Phys. **58**, 2604 and 5561 (1973).
- ¹⁶W. Eastes and R. A. Marcus, J. Chem. Phys. **59**, 4757 (1973).
- ¹⁷J. H. Clarke and D. J. Wilson, J. Chem. Phys. **50**, 713 (1974).
- ¹⁸R. J. LaBrecque and R. J. Morse, J. Chem. Phys. **56**, 546 (1972).
- ¹⁹W. R. Gentry and C. F. Giese, J. Chem. Phys. **63**, 3144 (1975).
- ²⁰J. N. L. Connor and H. R. Wayne, Mol. Phys. **32**, 1123 (1976).
- ²¹L. Gottdiener, Mol. Phys. **29**, 1585 (1975).
- ²²P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, London, 1972).
- ²³S. Stolte, A. E. Proctor, and R. B. Bernstein, J. Chem. Phys. **65**, 4990 (1976); and references cited therein.
- ²⁴J. E. Breen, R. B. Quay, and G. P. Glass, J. Chem. Phys. **59**, 556 (1973).
- ²⁵K. Glazner and J. Troe, J. Chem. Phys. **63**, 4352 (1975); **65**, 4324 (1976).
- ²⁶J. E. Spencer and G. P. Glass, Chem. Phys. **15**, 35 (1976).
- ²⁷J. Billingsby and A. B. Callear, Trans. Faraday Soc. **467**, 257 (1970).
- ²⁸P. F. Zittel and C. B. Moore, J. Chem. Phys. **59**, 6636 (1973).
- ²⁹R. A. Lucht and T. A. Cool, J. Chem. Phys. **60**, 1026 (1974); and references cited therein.
- ³⁰J. C. Stephenson, J. Chem. Phys. **60**, 4289 (1974).
- ³¹J. A. McGarvey, Jr., N. E. Friedman, and T. A. Cool, J. Chem. Phys. **66**, 3189 (1977).
- ³²R. G. Gordon, J. Chem. Phys. **51**, 14 (1969).
- ³³E. J. Heller, Chem. Phys. Lett. **23**, 102 (1973).
- ³⁴An alternative is to use the least biased distribution with only one moment. While the resulting P_i lie between zero and one, they are very much larger than the quantal values.
- ³⁵C. C. Rankin and W. H. Miller, J. Chem. Phys. **55**, 3150 (1971).
- ³⁶(a) J. S. Wright, K. G. Tan, and K. J. Laidler, J. Chem. Phys. **64**, 970 (1976); (b) J. S. Wright and K. G. Tan, J. Chem. Phys. **66**, 104 (1977).
- ³⁷For similar behavior see R. J. Gordon and A. Kupperman, J. Chem. Phys. **58**, 5776 (1973).
- ³⁸W. A. Wassam, Jr. and R. D. Levine, J. Chem. Phys. **64**, 3118 (1976).
- ³⁹C. S. Sloan and W. L. Hase, J. Chem. Phys. **66**, 1523 (1977).
- ⁴⁰J. D. McDonald and R. A. Marcus, J. Chem. Phys. **65**, 2180 (1976).
- ⁴¹M. Quack and J. Troe, Ber. Bunsenges. Phys. Chem. **81**, 160 (1977).