been detected, the adsorption is disordered on stepped surfaces and there is evidence of dissociation of the molecule.

The unique properties of atoms at steps or kinks in steps may be due to a charge density which is different from that for atoms with high coordination number in low Miller index planes. There is evidence, both from work function measurements[40] and from theory,[41] for increased charge density on atoms at steps. The localized d electrons on atoms in steps may also be rehybridized[42] and provide a different interaction potential to the approaching adsorbate as compared to atoms in the terraces.

It appears that the different chemistry of atoms at surface irregularities is especially enhanced for transition metals such as platinum, iridium, and tungsten. For gold, on the other hand, atomic steps do not enhance chemisorption of various hydrocarbons. Conrad et al.[43]

have shown that, while stepped surfaces exhibit an enhanced initial heat of adsorption for hydrogen on palladium, the heat of adsorption of carbon monoxide was the same on both a (111) and a stepped surface.

Summary

In summary, ordered adsorption is observed for both atoms and molecules on low Miller index surfaces for appropriate conditions of temperature and pressure. Some adsorbates form more than one surface structure, including precursors to bulk phases such as sulfides, oxides, and nitrides. Through the use of LEED to study surface crystallography much very important information is gathered about the nature of the surface chemical bond. One can expect that our knowledge of surface properties will continue to grow very rapidly as surface research expands in the areas of surface crystallography of more complicated molecular adsorbates, studies of the large varieties of molecular crystals, and a more detailed understanding of the role of surface defects in surface chemistry.

(40) K. Besocke and H. Wagner, *Surf. Sci.*, **53**, 351 (1975).
(41) L. L. Kesmodel and L. M. Falicov, *Solid State Commun.*, **16**, 1201 (1975).
(42) Y. W. Tsang and L. M. Falicov, *J. Phys. C*, **9**, 51 (1976).
(43) H. Conrad, G. Ertl, J. Koch, and E. E. Latta, *Surf. Sci.*, **43**, 462 (1974).

Quasiclassical Trajectory Studies of Reactive Energy Transfer

Donald L. Thompson

Departments of Physics and Chemistry, University of Mississippi, University, Mississippi 38677, and University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

In recent years an abundance of data concerning energy transfer in molecular collisions has become available.[1] It is always desirable in cases where there is active production of experimental data to have access to a theory (or theories) which can be used to help interpret the data and to extend the results to regions that are inaccessible or prohibitively expensive by experimental means. Ideally, quantum mechanical calculations would be used for intermolecular energy-transfer studies.[2] However, the range of chemical systems and conditions that can be studied with current quantum mechanical methods is limited. Quantal calculations are not feasible for most of the energy-transfer problems that interest the experimentalist. As a result, energy-transfer studies are often made using classical mechanics.

Although application of classical mechanics to quantal processes such as energy transfer may be questioned, it has been found to be a good approxima-

tion in most of the cases where direct comparisons have been made with quantum mechanical results.[3] The most popular classical mechanics method is the quasiclassical trajectory method introduced by Karplus, Porter, and Sharma;[4] it is now well understood[5] and widely used. Excellent reviews[6] illustrate the success that has been attained with this approach for simulating molecular collisional processes, especially chemical reactions. The first attempt to apply this approach to the examination of chemical collisional processes was the hand calculation of a single H + H_2 trajectory by Hirschfelder, Eyring, and Topley[7] in the 1930's—long before fast

(1) For a recent review of experimental studies of energy transfer, see S. Ormonde, *Rev. Mod. Phys.*, **47**, 193 (1975).
(2) For a recent review of the progress in this area, see D. Secrest, *Annu. Rev. Phys. Chem.*, **24**, 379 (1973).
(3) See, for instance: (a) J. D. Kelley and M. Wolfsberg, *J. Chem. Phys.*, **44**, 324 (1966), and (b) D. Secrest and B. R. Johnson, *ibid.*, **45**, 4556 (1966); (c) C. C. Rankin and J. C. Light, *ibid.*, **51**, 1701 (1969), and (d) D. Russell and J. C. Light, *ibid.*, **51**, 4701 (1969); (e) R. LeBudde and R. B. Bernstein, *ibid.*, **59**, 3687 (1973), and (f) W. A. Lester, Jr., and J. Schaefer, *ibid.*, **59**, 3676 (1973).
(4) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3259 (1965).
(5) For a succinct description of the quasiclassical trajectory methodology, see R. N. Porter and L. M. Raff, "Classical Trajectory Methods in Molecular Collision", to be published in "Modern Theoretical Chemistry", Vol. III, W. H. Miller, Ed., Plenum Press, New York, N.Y., in press.
(6) (a) D. L. Bunker, *Methods Comput. Phys.*, **10**, 287 (1971); (b) J. C. Polanyi, *Acc. Chem. Res.*, **5**, 161 (1972); (c) R. N. Porter, *Annu. Rev. Phys. Chem.*, **25**, 317 (1974).
(7) J. O. Hirschfelder, H. Eyring, and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936).

Donald L. Thompson was born in Haskell County, Okla., in 1943. He received his B.S. degree from Northeastern Oklahoma State University and Ph.D. from the University of Arkansas. He was a research associate for 1 year at the University of California, Irvine, after which he joined the staff at the University of California, Los Alamos Scientific Laboratory, in 1971. He is presently a Visiting Associate Professor of Physics at the University of Mississippi while on leave from LASL. His main research interests are in the area of reaction dynamics, energy transfer, and potential-energy surface calculations.

digital computers were available to render such calculations tractable on a statistically significant scale.

In the quasiclassical approach it is assumed that the initial distributions of rotational and vibrational (and sometimes orbital angular momentum) states are described by quantum mechanical probability density functions. That is, at the start of the trajectory, before interaction of the collision partners, only quantum mechanically allowed states are available; however, *once the trajectory begins, all motion is classical,* and a continuum of states is allowed in the final state of the collision. Classically, energy can be transferred in every collision, and not in quantal amounts. Therefore, it is necessary to employ some arbitrary method for relating the final-state energies to quantum states. One procedure that has been used for computing transition probabilities $P_{i \rightarrow j}$ is to "count" as transfer collisions only those events in which the final-state energies fall within the boundaries that define a range that extends above and below the energy of state j some arbitrary distance, usually one-half of the quantum size. Then, the transition probability is calculated as

$$P_{i \rightarrow j} = \frac{N_j}{N_{\text{total}}}$$

where N_j is the number falling within the specified range about j and N_{total} is the total number of collisions. An alternative method is to define the transition probability as

$$P_{i \rightarrow j} = \langle \Delta E \rangle / h\nu$$

where $\langle \Delta E \rangle$ is the average energy transfer of all collisions and $h\nu$ is the energy spacing between i and j.

An important step in a quasiclassical trajectory study is the statistical averaging over the ensemble of collisions. From statistical mechanics we know the distribution of reactant states for a given set of experimental conditions, and by examining the final states of the collision trajectories we can determine the probability of a given type of outcome. But to compute a rate coefficient, cross section, or relaxation time from this information requires the execution of a multidimensional integral.[8] The usual methods of numerical integration (such as quadrature methods) are not adequate for this purpose. The most common approach used is Monte Carlo integration.[9] The procedure amounts to randomly selecting initial values from the appropriate probability density functions for the collision variables such as the molecular orientation relative to the direction of initial relative translation velocity, the impact parameter (the perpendicular distance from the center of mass of the molecule and the extension of the relative velocity vector), the internal state of the molecule specified by the vibrational and rotational quantum numbers v and J, respectively, the internuclear separation of the diatomic molecule (vibrational phase), and the relative velocity. A very appealing aspect of the Monte Carlo procedure is that it simulates the "random" process by which collisions in the laboratory actually occur. But most importantly, the method permits the integration to be done without determining the functional form of the dependence of the probability on the collision variables. Similar, but nonrandom, integration procedures[10] are sometimes used, and in many respects are as efficient as Monte Carlo; however, all the work discussed here employed the Monte Carlo method.

A theory such as quasiclassical trajectory analysis plays a dual role in the study of energy transfer. First, it can be used to interpret the experimental data. Although properly designed experiments can provide insight into the details of the processes, a theoretical calculation can often provide more detailed information at much less expense. In this regard, quasiclassical trajectory calculations have been most useful in determining the mechanisms by which energy is transferred. A mechanism includes such information as the characteristics of the collisions (are the encounters long-lived, short-lived, etc.?), the dependence of the energy transfer on the initial states of the collisions, and the fate of the energy being transferred (for example, it can be determined whether vibrational energy is transferred into the rotational or translational mode). Of course, the validity of the mechanism determined from trajectory calculations depends on the accuracy of the potential-energy surface.

In atom–diatomic molecule systems involving hydrogen and halogens, the systems to which we will direct our attention here, there are two basic types of collisional energy-transfer mechanisms: reactive and nonreactive. The nonreactive energy-transfer mechanism does not involve the breaking of a chemical bond. The reactive mechanism involves the chemical exchange of an atom between two identical species such that no net chemical change in the system occurs,[11] for example, the reaction $Cl + HCl \rightarrow ClH + Cl$, which is discussed below. It can be argued that vibrational relaxation can readily take place by a reactive mechanism. First, even though vibrational relaxation rates for the systems discussed here are high, many chemical reactions have comparable rates. Second, if we consider that vibrationally excited molecules often (though not always) react faster than molecules with a thermal distribution of energies,[12] then the reactive energy-transfer mechanism appears even more plausible. Also, one can add to this the fact that when internal energy is present in the reactants and acts to promote the passage of the system over a barrier to products, this internal energy usually appears as relative translational motion of the products.

The second function of quasiclassical trajectory calculations is to provide energy-transfer information in regions that are difficult or impossible to explore by experimental means. This type of calculation has been an important source of input for modeling studies of chemical lasers and other systems involving vibrationally excited molecules.[13]

(8) See ref 5 for a description of this problem.

(9) For comprehensive discussions of Monte Carlo methods, see (a) J. M. Hammersley and D. S. Handscomb, "Monte Carlo Methods", Wiley-Methuen, New York, N.Y., 1964; (b) "Monte Carlo Method", Yu. A. Schreider, Ed., Pergamon Press, Elmsford, N.Y., 1966; (c) and for a description of the application of Monte Carlo techniques to quasiclassical trajectories, see ref 5.

(10) (a) V. B. Cheng, Ph.D. Thesis, State University of New York, Stony Brook, N.Y., 1970; (b) H. H. Suzukawa, Jr., D. L. Thompson, V. B. Cheng, and M. Wolfsberg, *J. Chem. Phys.*, **59**, 4000 (1973); (c) H. H. Suzukawa, Jr., Ph.D. Thesis, University of California, Irvine, Calif., 1974.

(11) Obviously, for completely symmetrical exchange reactions the nonreactive and reactive processes are physically indistinguishable. Experimentally, isotopically labeled systems such as $^{82}Br + H^{79}Br$ have been used to study symmetric reactions.

(12) See, for example, ref 6b.

(13) See, for example, J. H. Sullivan, R. C. Feber, and J. W. Starner, *J. Chem. Phys.*, **62**, 1714 (1975).

Classical mechanics has been used for energy-transfer studies for many years. (An extensive review of the earlier work has been given by Rapp and Kassal.[14]) Many of the classical trajectory studies employed model interaction potentials and did not include full dimensionality of the motion. The studies that we discuss here involve a treatment of all degrees of freedom and employ potential-energy surfaces that can be considered sufficiently "realistic" and accurate so that a comparison between the trajectory results and experiments should be valid.

In this Account we shall be concerned with the study of vibrational, rotational, and translational energy transfer by quasiclassical trajectory methods. The results of these studies concerning energy-transfer mechanisms and the comparisons of computed relaxation rates with experimental results will be discussed. Our attention will be restricted primarily to atom–diatom systems involving hydrogen and the halogens because realistic semiempirical potential-energy surfaces are available for these systems.

Potential-Energy Surfaces

Energy transfer (excluding electronic energy) occurs on two basic types of potential-energy surfaces: nonreactive and reactive. A reactive energy-transfer potential-energy surface is illustrated in Figure 1. Since there can be no net chemical change in the system due to the reactions, the surface must be symmetrical, with the "reactant" and "product" valleys usually separated by a barrier. However, in some cases, for example Cl + HCl, the two valleys are separated by a well (see Figure 2) rather than a barrier. These surfaces, of course, may also have shallow wells representing long-range attraction of the atom and molecule.

Because of the lack of accurate and complete ab initio calculations[15] for most systems of interest, it is common practice to employ some version of the London[16] equation semiempirical formulism[17] to obtain potential-energy surfaces for studying reactive energy transfer. The analytical form of the London equation, for the A–B–C triatomic system, is

$$V = Q_{AB} + Q_{BC} + Q_{AC} - \{\tfrac{1}{2}[(J_{AB} - J_{BC})^2$$
$$+ (J_{BC} - J_{AC})^2 + (J_{AC} - J_{AB})^2]\}^{1/2}$$

where Q_{ij} and J_{ij} are the Coulomb and exchange integrals, respectively. Rather than solving these integrals, they are written in terms of the singlet- and triplet-state energies of the atom pairs using the Heitler–London equations:

$$Q_{ij}(r_{ij}) = \tfrac{1}{2}[^1E_{ij}(r_{ij}) + {}^3E_{ij}(r_{ij})]$$

and

$$J_{ij}(r_{ij}) = \tfrac{1}{2}[^1E_{ij}(r_{ij}) - {}^3E_{ij}(r_{ij})]$$

The potential-energy surface is defined by specifying the atom-pair potentials $^1E_{ij}$, using the Morse function, and $^3E_{ij}$, using either the anti-Morse function or the
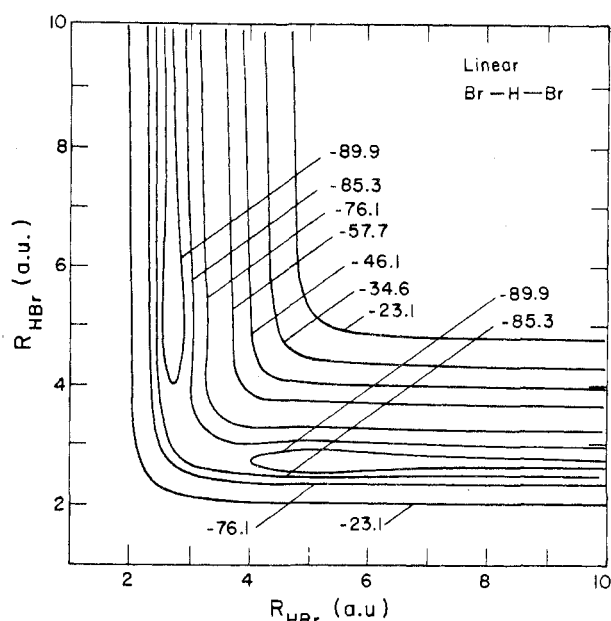
(14) D. Rapp and T. Kassal, *Chem. Rev.*, **69**, 61 (1969).

(15) For a recent example of the use of ab initio potential-energy surfaces in trajectory calculations, see: D. R. McLaughlin and D. L. Thompson, *J. Chem. Phys.*, **59**, 4393 (1973), and ref 5 therein.

(16) F. London, *Z. Elektrochem. Angew. Phys. Chem.*, **35**, 552 (1929).

(17) For a description of the basis of this semiempirical formulation, see H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", Wiley, New York, N.Y., 1944, Chapter 13.

Figure 1. Symmetric-reaction potential-energy surface with an energy barrier between the reactants and products: the collinear Br + HBr → BrH + Br reaction. (Contour energies are in kcal/mol.)
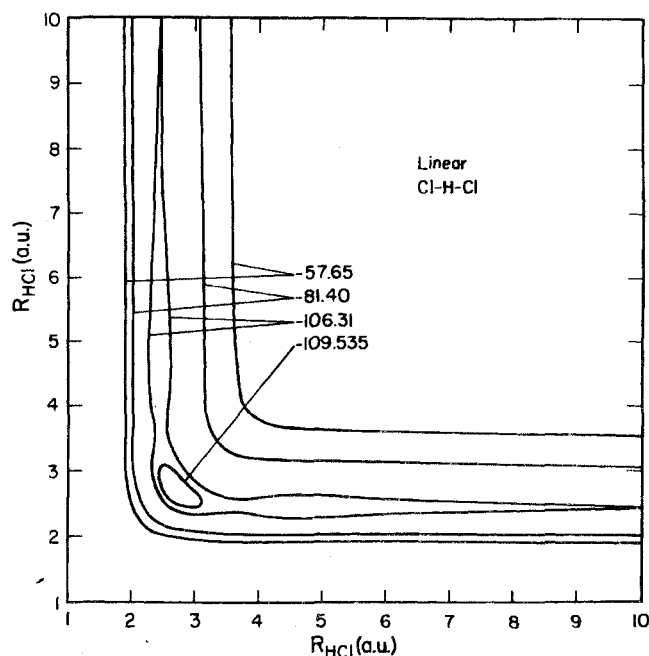

Figure 2. Symmetric-reaction potential-energy surface with a well between the reactants and products: the collinear Cl + HCl → ClH + Cl reaction. (Contour energies are in kcal/mol.)

Pedersen–Porter[18] function. The singlet-state curves are known in most cases. The triplet-state curves are usually determined by adjusting the reaction barrier height so that it is consistent with the reaction activation energy.[19]

The London equation is an approximate valence-bond solution for three one-electron atoms. There is little to justify its use for systems such as we discuss here (which consist of many electron monovalent atoms) except that when proper parameter adjustments are made trajectory results can be obtained that are in general accord with experiments. Because of the very

(18) L. G. Pedersen and R. N. Porter, *J. Chem. Phys.*, **47**, 4751 (1967).

(19) See, for example: (a) R. N. Porter and M. Karplus, *J. Chem. Phys.*, **40**, 1105 (1964), and (b) L. M. Raff, L. Stivers, R. N. Porter, D. L. Thompson, and L. B. Sims, *ibid.*, **52**, 3449 (1970).
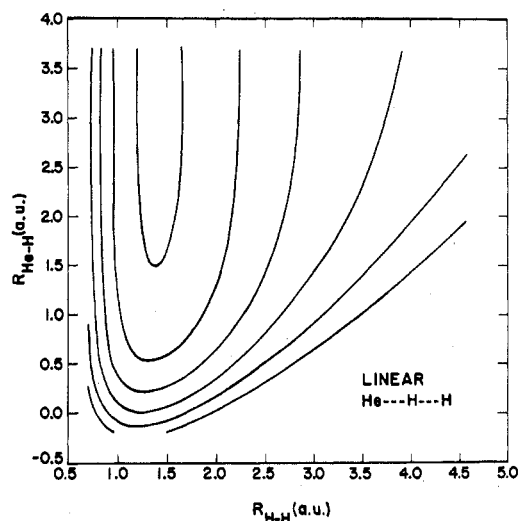
Figure 3. Contour plot of the collinear He–H$_2$ potential-energy surface.

approximate nature of these surfaces proof of accuracy depends on the comparison of computed results with experimental data. We include such comparisons in our discussion of the surfaces that have been used in energy transfer studies, which support the overall validity of the semiempirical approach.

On a nonreactive potential-energy surface chemical reaction, except molecular dissociation, is energy forbidden. The potential-energy surface contour map shown in Figure 3 is a typical example of nonreactive surfaces. The low-energy region of the surface corresponds to the atom (He in this example) well separated from the stable molecule (H$_2$). As the atom approaches the molecule the potential energy increases rapidly, and unless there is sufficient energy in the system to permit dissociation of the molecule, the system will be reflected back into the low-energy valley. The initial distribution of energy among the vibrational, rotational, and translational modes may be changed in this collision (inelastic scattering) or the system may return to its original state (elastic scattering).

A variety of analytical functions are used to represent nonreactive potential-energy surfaces. For example, SCF-CI potential-energy points for the system He–H$_2$ have been fit[20] using

$$V(X,R,\theta) = C \exp[-\alpha_0 X + \alpha_1 X r][A(\theta) + B(\theta)r]$$

where C, α_0, and α_1 are constants, X is the distance from the atom to the center of mass of the molecule, R is the molecular internuclear separation, θ is the angle made by X and R, and:

$$A(\theta) = 1 + 0.251 P_2 \cos \theta$$

$$B(\theta) = -0.316(1 - 0.778 P_2 \cos \theta)$$

$$r = R - R_e$$

The H$_2$ potential is usually represented by the Morse function.

A simpler type of function that has often been used to represent nonreactive surfaces is an additive pairwise potential, such as used by Kelley and Wolfsberg.[21] This potential is made up of unbound atom pair repulsions

represented by terms like $\exp(-r_{ij}/L)$ and a Morse or harmonic oscillator potential for the bound molecule.

Trajectory Results

The most important use that has been made of classical trajectory energy-transfer calculations is in the study of mechanisms, that is, the details of the collisional processes in which energy is transferred from one species to another or one mode to another. Some quantitative information has been computed using trajectories and can be evaluated by comparison with experimental data. In some cases the trajectory calculations have been the only source for needed quantitative information. Quasiclassical calculations have been particularly useful in providing detailed qualitative descriptions of atom–diatomic molecule energy-transfer processes.

Cl + HCl. Let us first consider the vibrational relaxation of HCl by chlorine atoms. This was the first system for which the reactive energy-transfer mechanism was investigated. The vibrational relaxation of HCl (v = 1, 2, and 3) by Cl was first studied experimentally using chemiluminescence techniques.[22] Two other experimental investigations of these systems have since been carried out using lasers.[23,24] The relaxation is very rapid; it is found that the relaxation of HCl (v = 1) by Cl is about 2000 times more efficient than is the relaxation by Cl$_2$.[23] Since the activation energy for the Cl + HCl symmetric atom exchange is about 5.4 kcal/mol,[25] and the first excited vibrational state of HCl possesses an energy of 8.24 kcal/mol, there is sufficient energy present in the excited molecule to surmount this reaction energy barrier. Therefore, it is reasonable to suggest that vibrational relaxation might involve chemical reaction.

The first quasiclassical trajectory study[26] of Cl + HCl vibrational relaxation was carried out using a semiempirical (London equation) potential-energy surface[27] derived from parameters computed for the related system Cl + H$_2$ → HCl + H. In Figure 2 an energy contour map of the interaction surface for the symmetric atom-exchange reaction along collinear reaction paths is shown. The most important characteristic of the surface in Figure 2 is the symmetrically located well which predicts ClHCl to be stable by 5 kcal/mol with respect to Cl + HCl. This is supported by experimental studies in which infrared spectra in hydrogen chloride–chlorine–argon mixtures obtained using matrix isolation techniques have been interpreted as due to bound ClHCl.[28,29] On the other hand, as we have already pointed out, there are the results of the reaction kinetics measurements which indicate an energy barrier for this

(22) B. A. Ridley and I. W. M. Smith, *Chem. Phys. Lett.*, **9**, 457 (1971).

(23) N. C. Craig and C. B. Moore, *J. Phys. Chem.*, **75**, 1622 (1971).

(24) R. G. Macdonald, C. B. Moore, I. W. M. Smith, and F. J. Wodarczyk, *J. Chem. Phys.*, **62**, 2934 (1975).

(25) This value for the activation energy is obtained from the work of F. S. Klein, A. Persky, and R. E. Weston, Jr., *J. Chem. Phys.*, **41**, 1799 (1964), and A. A. Westenberg and M. de Haas, *ibid.*, **48**, 4405 (1968).

(26) D. L. Thompson, *J. Chem. Phys.*, **56**, 3570 (1972).

(27) R. N. Porter, L. B. Sims, D. L. Thompson, and L. M. Raff, *J. Chem. Phys.*, **58**, 2855 (1973).

(28) P. N. Noble and G. C. Pimentel, *J. Chem. Phys.*, **49**, 3165 (1968).

(29) There is some controversy concerning this interpretation; see, for example: (a) L. Andrews, *Annu. Rev. Phys. Chem.*, **22**, 109 (1971); (b) G. C. Pimentel and A. L. McClellan, *ibid.*, **22**, 347 (1971); (c) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **53**, 2034 (1970); (d) D. E. Milligan and M. E. Jacox, *ibid.*, **55**, 2550 (1971); S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 104 (1974).

(20) M. D. Gordon and D. Secrest, *J. Chem. Phys.*, **52**, 120 (1970); **53**, 4408 (1970).

(21) J. D. Kelley and M. Wolfsberg, *J. Chem. Phys.*, **53**, 2967 (1970).

reaction.[25] Thus, there is some question as to whether there is a barrier or a well at the midpoint of the reaction path.[30]

Three-dimensional trajectories were calculated at collision energies given by a Boltzmann distribution for 300 K for the three vibrational states, $v = 1, 2,$ and 3, of HCl.[26] From these results, rate coefficients for vibrational relaxation due to reactions, nonreactive collisions, and the sum of these can be computed. The computed rate coefficient for the overall relaxation process $k_{1 \to 0}$ of $\simeq 8 \times 10^{12}$ cm^3/mol-s can be compared with the measured values of 6.5×10^{12} cm^3/mol-s from ref 23 and 5.1×10^{12} cm^3/mol-s reported[24] more recently. These quasiclassical trajectory results clearly illustrated that chemical reaction can be a mechanism for vibrational relaxation. The results also show that the atom-exchange process becomes less important as a vibrational relaxation mechanism as the initial vibrational excitation of HCl increases, even though the reaction rate increases as v increases. That is, increasing amounts of vibrational energy in the reactant enhances the rate of reaction, but is deposited in product vibration when present in amounts exceeding the barrier to reaction. This observation has also been made experimentally in a study of F + HCl → HF + Cl.[31]

The effect of a reaction energy barrier on the Cl + HCl atom-exchange vibrational relaxation is qualitatively the same as that of a potential well.[32] Calculations with a London–Eyring–Polanyi–Sato[33] (LEPS) potential-energy surface adjusted to give an energy barrier of 9.84 kcal/mol along the collinear reaction path show that the vibrational relaxation is due to both reactive and nonreactive encounters. Reactive encounters in which an atom is exchanged account for approximately one-half of the relaxation, while collisions in which the system of atoms passes into the energy barrier region of the surface and then recrosses back into the reactant region again (with the final result being no reaction) contribute the rest. Since the system potential-energy surface is symmetric and the reactants and products are identical for the same isotopes of Cl, the two types of processes are the same; they are separable only in a theoretical calculation. The significant point is that the dominant energy transfer is due to collisions that involve crossing (reaction) and recrossing (no reaction) of the region of strong interactions of the energy surface.

The vibrational relaxation rate coefficients for HCl ($v = 1$) and HCl ($v = 2$) computed on surfaces possessing an energy barrier[32] are not in accord with the results of either of the experimental studies.[22,23] This has been clearly demonstrated by a thorough trajectory study of Cl + HCl energy transfer on two empirical LEPS-type potential-energy surfaces with reaction energy-barrier heights of 7.05 and 9.84 kcal/mol.[34] Rate coefficients were computed from planar collision trajectories. The conclusion is that the efficient vibrational relaxation measured for Cl + HCl cannot be explained on the basis

of potential-energy surfaces of this type possessing a simple barrier to reaction. Comparison of the results obtained using potential surfaces with simple reaction energy barriers[32,34] with the results obtained using a surface with a well[26] suggests that the surface must possess a well if the computed relaxation rate coefficients are to be in accord with measured values.[23,24] Support is also added to this conclusion by a recent trajectory study[35] of this system employing a surface with a 0.77 kcal/mol well in which the computed vibrational relaxation rate coefficients are in good agreement with the measured values.[23,24]

F + HF and F + DF. The effect of the collision system crossing into the transition-state interaction region (for either a barrier or a well) of the surface is efficient transfer of energy from vibration, whether the collision is reactive or not. It might be inferred from this that the explanation of the rapid vibrational relaxation observed for other hydrogen halides by hydrogen or halogen atoms is to be found in atom exchange. This may be generally true; however, there appears to be at least one exception: F + HF ($v \leq 3$). A quasiclassical trajectory study[36] of F + HF and F + DF employing a semiempirical potential-energy surface[37] possessing a rather large reaction energy barrier gave results in very good accord with experiment.[38] At the time this calculation was done there had been no ab initio calculations of the FHF interaction potential. The surface used in the trajectory study possesses a barrier of about 25 kcal/mol, thus excluding the possibility of chemical reaction for the first two excited vibrational states at collision energies of experimental interest. Ab initio calculations of the potential surface have since been carried out for linear FHF.[39] This surface calculation, with a double-ζ plus polarization basis for the wave function, gave an energy barrier height of 23.9 kcal/mol.

The F + HF and F + DF nonreactive vibrational relaxation is due primarily to transfer of energy to rotation. A study of the reactive energy transfer, which occurs for $v \geq 3$, shows that, as is the case for Cl + HCl, the reactive and nonreactive mechanisms make approximately equal contributions to the overall rate of relaxation.[40] The most important conclusion made from these results is that the rapid rate of vibrational relaxation for $v = 1 \to v = 0$ is due to nonreactive collisions that do not involve collisions extending into the transition-state region of the potential-energy surface.

H + HBr and Br + HBr. The atom-exchange mechanism has also been shown to be a significant contributor to the vibrational relaxation of HBr by hydrogen and bromine atoms.[41] The semiempirical potential-energy surface formulism[19b,27] employed in the study of Cl + HCl[26] was used in the studies of H + HBr and Br + HBr. For the Br–H–Br system, collinear conformations are of lowest energy. The surface possesses only a slight energy barrier of approximately 4 kcal/mol with shallow attractive wells in the reactant

(30) F. S. Klein and A. Persky, *J. Chem. Phys.*, **59**, 2775 (1973).

(31) See, for example, L. J. Kirsch and J. C. Polanyi, *J. Chem. Phys.*, **57**, 4498 (1964).

(32) I. W. M. Smith and P. M. Wood, *Mol. Phys.*, **25**, 441 (1973).

(33) For a succinct discussion of the London–Eyring–Polanyi–Sato potential-energy surface formalism and characteristics, see C. A. Parr and D. G. Truhlar, *J. Phys. Chem.*, **75**, 1844 (1971).

(34) R. L. Thommarson and G. C. Berend, *Int. J. Chem. Kinet.*, **5**, 629 (1973).

(35) R. L. Wilkins, *J. Chem. Phys.*, **63**, 534 (1975).

(36) D. L. Thompson, *J. Chem. Phys.*, **57**, 4164 (1972).

(37) N. C. Blais, "Monte Carlo Trajectories: Dynamics of the Reaction H + F$_2$", Report No. LA-4687, University of California, Los Alamos Scientific Laboratory, Los Alamos, N. Mex., 1971.

(38) L. S. Blair, W. D. Breshears, and G. L. Schott, *J. Chem. Phys.*, **59**, 1582 (1973).

(39) S. V. O'Neal, H. F. Schaefer III, and C. F. Bender, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 104 (1974).

(40) N. C. Blais and D. L. Thompson, unpublished.

(41) J. M. White and D. L. Thompson, *J. Chem. Phys.*, **61**, 719 (1974).

and product valleys. The hypersurface is strongly angle dependent, with the energy barrier rising to 33 kcal/mol for the Br–H–Br angle equal to 90°.

Comparison of the potential-energy surfaces suggests that the H + HBr and Br + HBr energy-transfer processes should differ. The largest difference involves the details of the collisional processes. The Br + HBr collisions are characterized by complex encounters with orbiting and multiple H-atom exchange between the two bromine atoms. The Br + HBr encounter can be described as follows: The heavy bromine atoms determine the interaction time as they slowly move together and scatter. Simultaneously, the light hydrogen atom moves back and forth between them (multiple exchanges) and rotates around them within the confines of the steep potential walls. The process of orbiting and exchange of the hydrogen atom between the two bromine atoms continues until the bromine atoms have moved sufficiently far apart that the hydrogen atom can interact with only one of them. An example of these complex collisions is shown in Figure 4, which illustrates a typical trajectory that ends in atom exchange. The rotation (orbiting) of the hydrogen atom about the bromine atoms is shown by the large peaks; the H–Br vibrations cause the structure seen in these peaks. The impact of the hydrogen atom with the incoming bromine atom results in transfer of energy to the diatomic molecule, as seen by the increased amplitude of the vibration in the curve; this is then followed by orbiting and exchange. The computed product angular distributions show that the product is scattered mainly in the direction that the incident bromine atom moves (forward hemisphere).

In the reactive collisions of H with HBr the product molecule is scattered in the backward direction (opposite the direction of the incoming hydrogen atom), due primarily to the inertia of the heavy bromine atom. The collisions are simple, straightforward single encounters with no evidence of orbiting or multiple exchanges.

In spite of the rather striking differences in the H–Br–H and Br–H–Br potential-energy surfaces there are some important similarities in the energy transfer processes of the two systems. First, atom exchange is a significant mechanism for vibrational relaxation in both cases. Also the rate of the atom-exchange reactions, for both systems, is enhanced by both reactant vibration and rotation. In Br + HBr atom exchange for a thermal distribution of rotational states the rate of reaction for HBr (v = 5) is 28 times faster than for HBr (v = 1), and HBr (v = 2) is five times faster than HBr (v = 1). Furthermore, computed rate coefficients for Br + HBr (v = 2) show that there is a significant temperature dependence due to translation and rotation, even though the system possesses approximately 18 kcal/mol energy (including zero-point energy). Initial HBr rotational energy has a strong influence on the rate; there is an increase in the rate of about a factor six for both v = 1 and v = 2 as the initial rotational state of HBr is increased from J = 0 to J = 40. The behavior of the rate as a function of the rotational state J is essentially the same for all v > 0, especially for large J. (The same behavior is also seen for v = 0 for J > 10.)

The influence of the initial HBr vibrational energy on the rate of exchange is not as great in H + HBr as in Br + HBr; the rate of exchange for v = 5 is a factor of three greater than for v = 1. Similarly, there is a lesser
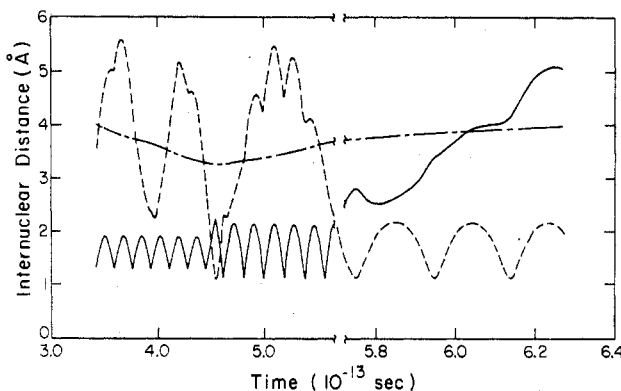

Figure 4. A plot of the internuclear separations as a function of collision time of a typical Br + HBr atom-exchange reaction trajectory. The Br–Br distances is denoted by — · — -, and the H–Br distances by the solid and dashed curves.

influence of initial rotation on the rate: For H + HBr (v = 2) with relative translational energies for 1000 K the increase in the rate is approximately a factor of six as J increases from 0 to 40. These results present the caveat that in studies of dynamics all possible influences on the collisions must be properly considered, even rotational energies which might seem inconsequential relative to the larger vibrational energies.

Cl + Cl₂ and I + I₂. At this point we have only considered vibrational relaxation of hydrogen halides. It is thus worthwhile, to avoid leaving the impression that the conclusions apply to this specific type of molecule, to discuss some results for homonuclear diatomic molecules. The pure halogens Cl + Cl₂ and I + I₂ are chosen for the following reasons: (1) There should be no extreme differences in the types of interactions from those in the systems we have been discussing. (2) These systems provide systematic changes in masses and interactions. (3) There are experimental data by which the accuracy of the I + I₂ potential may be judged.

The I + I₂ symmetric atom-exchange reaction rate has been measured[42] in solution and the semiempirical potential-energy surface used in studies of vibrational relaxation[43] gives a value for the exchange rate in excellent agreement with the reported value.[44] On this basis it is argued that the potential-energy surface realistically represents the system. The comparison of gas-phase and solution-phase rates is justified on the basis that the reaction is activation controlled and solution effects are negligible.[42] Though there is no similar test of the Cl + Cl₂ potential-energy surface, it is argued that it is equally "realistic" and accurate since it is based on the same formalism as the I + I₂ surface.

The most salient features of the Cl₃ potential-energy surface are the attractive wells along the collinear pathways, similar to those in the H–Br–H surface. The wells in the reactant and product valleys are 2.72 kcal/mol deep and occur for one chlorine atom at a distance of about 5.4 au from the closest atom of Cl₂. The symmetrically located well is approximately the same depth and occurs for the Cl–Cl separations approximately equal to 4 au. The potential is only slightly dependent on the Cl–Cl–Cl "bond" angle.

As could be guessed, atom-exchange plays an important role in Cl + Cl₂ vibrational relaxation. The vi-

(42) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).
(43) D. L. Thompson, *J. Chem. Phys.*, **60**, 4557 (1974).
(44) D. L. Thompson, *J. Chem. Phys.*, **62**, 4241 (1975).

Table I
Reactive (k_r) and Nonreactive (k_{nr}) Relaxation Rate
Coefficients for I + I$_2$ (v = 7) → I + I$_2$ (v') at 1100 K[a]

v'	k_r	k_{nr}
0	0.28 ± 0.20	0.48 ± 0.34
1	0.28 ± 0.20	1.40 ± 0.57
2	0.28 ± 0.20	2.55 ± 0.76
3	1.20 ± 0.40	2.78 ± 0.79
4	1.33 ± 0.42	0.93 ± 0.46
5	2.78 ± 0.59	2.08 ± 0.69
6	6.48 ± 0.88	3.00 ± 0.82
7	—	1.40 ± 0.57
8	7.28 ± 0.93	0.48 ± 0.34
9	1.85 ± 0.49	1.15 ± 0.51
10	0.93 ± 0.35	0.48 ± 0.34
11	0.40 ± 0.23	0.23 ± 0.23
12	0.53 ± 0.26	0.48 ± 0.34
13	0.40 ± 0.23	0.23 ± 0.23
14	0.28 ± 0.20	0.23 ± 0.23

[a] Units are 10^{12} cm^3/mol-s.

brational spacings in Cl$_2$ are relatively small, and since there is no barrier to reaction it is not surprising that the rates of exchange for Cl$_2$ (v = 0) and Cl$_2$ (v = 1) are approximately equal and the rate is increased only by a factor of 3 as v is increased to 14. The general results are essentially the same as for the other systems we have discussed: vibrational energy enhances reactions and the atom-exchange mechanism is a significant contributor to vibrational relaxation.

The I + I$_2$ potential-energy surface possesses a collinear reaction energy barrier of about 5.9 kcal/mol for the two I–I distances equal to 5.4 au. There are wells in the I + I$_2$ valleys about 1 kcal/mol deep for one I atom separated by a distance of 7.3 au from either of the other two. Because of the energy barrier, the v = 10 state (corresponding to 6.25 kcal/mol in energy) is the lowest state with sufficient energy to lead to reaction. An interesting result is seen in the rates of relaxation for v → v' at 1100 K and v = 7, 10, 12, and 14. The nonreactive rate of relaxation is greater than the reactive rate for v' greater than v and for the v' slightly less than v, but the reactive rate is greater for $v' \ll v$. However, for the overall rate of relaxation from v to all v' the nonreactive

and atom-exchange mechanisms are essentially equal contributors. The same general behavior is also true for Cl + Cl$_2$.

These systems serve to illustrate vibrational relaxation of highly excited molecules. For all systems for which information is available multiple-quantum jumps ($\Delta v > 1$) in energy occur with appreciable rates relative to $\Delta v = 1$ transfers. As one might expect, the rate for $\Delta v = 1$ is great, with the rate decreasing as Δv increases; this is true of both the reactive and nonreactive rates, as shown by the results from I + I$_2$ (v = 7) → I + I$_2$ (v') given in Table I.

Conclusions

Quasiclassical trajectory studies of the reactive vibrational relaxation mechanism in atom–diatom collisions and related aspects of energy transfer have been discussed. The goal of this work has been to obtain a detailed understanding of the mechanistic processes for energy transfer in simple systems, and to develop techniques for computing reliable energy transfer data. The quasiclassical trajectory approach has been shown to be a useful tool for accomplishing this goal. The usefulness does, however, rest upon the capability of computing accurate potential-energy surfaces. Carefully constructed semiempirical surfaces have been shown to be quite reliable for a large number of systems. Employment of ab initio surfaces is an important next step in this type of study.

Some of the mechanistic aspects of atom–diatomic molecule energy transfer are as follows: (1) Chemical reactions can play an important role in vibrational relaxation. (2) In systems that involve chemical reactions the reactive and nonreactive paths are approximately equal contributors due to the fact that in both cases the system crosses into the (transition) region of strong interactions. (3) In most cases vibration–rotation transfer is a greater contributor to vibrational relaxation than is vibration–translation. (4) Initial rotational energy has a significant influence on energy transfer. (5) Multiple quantum jumps occur when the molecule has initial vibrational excitation of $v > 1$.