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## Theoretical Approaches to the Reaction Dynamics of Clusters

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### 1.1. INTRODUCTION

The theoretical treatment of cluster kinetics borrows most of its concepts and techniques from studies of smaller and larger systems. Some of the methods used for such smaller and larger systems are more useful than others for application to cluster kinetics and dynamics, however. This chapter is a review of specific approaches that have found fruitful use in theoretical and computational studies of cluster dynamics to date. The review includes some discussion of methodology; it also discusses examples of what has been learned from the various approaches, and it compares theory to experiment. A special emphasis is on microsolvated reactions—that is, reactions where one or a few solvent molecules are clustered onto gas-phase reactants and hence typically onto the transition state as well.

Both analytic theory and computer simulations are included, and we note that the latter play an especially important role in understanding cluster reactions. Simulations not only provide quantitative results, but they provide insight into the dominant causes of observed behavior, and they can provide likelihood estimates for assessing qualitatively distinct mechanisms that can be used to explain the same experimental data. Simulations can also lead to a greater understanding of dynamical processes occurring in clusters by calculating details which cannot be observed experimentally.

One interesting challenge that reactions in van der Waals and hydrogen-bonded clusters offer is the possibility of studying specifically how weak interactions or microsolvation bonds affect a chemical reaction or dissociation process. In that sense, theoretical studies of weakly bound clusters have proved to be useful in learning about the “crossover” in behavior from that of an isolated nonsolvated molecule in the gas phase to that for a molecule in a liquid or solid solvent.

It is very common to begin reviews with a disclaimer as to completeness. Such a disclaimer is, we hope, not required for this chapter because it is not a comprehensive review but a limited-scope discussion of selected work that illustrates some issues that we perceive to be especially important.

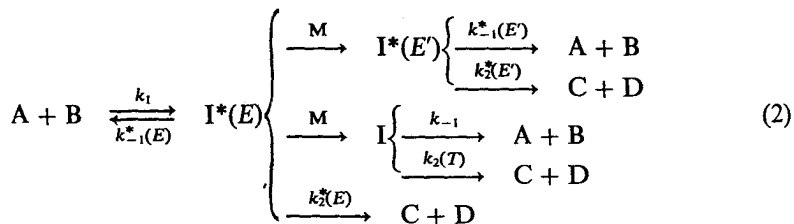
The chapter is divided into three parts. Section 1.2 discusses collisional and statistical theories for cluster reactions. This section is mainly (though not entirely) concerned with ion kinetics. It is well known that the chemistry of ions is strongly influenced by solvation. Thus, the reactivity of cluster ions is particularly interesting in defining the influence and role of solvent molecules on the chemistry of ions. The study of the reactivity of ions can be especially illuminating with respect to the molecular origin of solvation effects for which condensed phase studies only show the collective effect of solvent. With the development of experimental techniques for studying cluster ion dynamics in the gas phase, it has become possible to quantitatively explore the transition in the kinetics of ion-molecule reactions from their solvent-free behavior to their behavior in solution; thus, this kind of study is one of the purest examples of using cluster chemistry to bridge the gap between the gas phase and condensed matter (for representative examples, see Bohme and Mackay 1981; Bohme and Raksit 1984; Bohme and Young 1970; Castleman and Keesee 1986a,b; Hierl et al. 1986a,b; Jortner 1992; Leutwyler and Bösiger 1990; Syage 1994).

Section 1.2 has a particular emphasis on capture rate coefficients for exchange and association reactions, and it begins a discussion of the related issue of unimolecular dissociation of the association complexes. This provides a bridge into section 1.3 which considers the question of energy transfer in clusters from a more general point of view. Section 1.4 returns to the subject of reaction rates emphasized in section 1.2, but now considering cases where the theoretical model involves detailed consideration of the short-range forces in the vicinity of a tight dynamical bottleneck.

Most bimolecular cluster reactions can proceed through complexes. If A and B denote reactants and C and D denote products, at low pressure one has only direct reaction,



because there are no collisions to stabilize the intermediate, where  $k_0$  is the rate coefficient. At higher pressures one has



where  $k_1$  is called either the collision rate coefficient or the capture rate coefficient,  $I^*(E)$  and  $I^*(E')$  are activated intermediates with energy  $E$  and  $E'$  (or energy distributions centered at  $E$  or  $E'$ ), and  $I$  is a thermalized intermediate. Either  $I^*$  or  $I$  can convert to product by a unimolecular reaction, which is assumed to pass through a tight transition state. Assuming that every collision of  $I^*(E)$  with  $M$  produces  $I$  eliminates the need to consider  $I^*(E')$ . This is called the strong collision approximation. A somewhat weaker approximation is to set the rate coefficient for  $I^*(E) + M \rightarrow I + M$  equal to an empirical constant (usually called the collision

efficiency or  $\beta$ ) times the collision rate coefficient but again to neglect  $I^*(E')$  [or, equivalently, to take  $k_2^*(E) = k_2^*(E')$  and  $k_{-1}^*(E) = k_{-1}^*(E')$ ]. With or without these additional assumptions, in the high pressure limit, mechanism (2) yields an overall rate coefficient

$$k_0 = k_1 k_2 / k_{-1}. \quad (1-1)$$

At low pressure it would yield,

$$k_0 = k_1 \frac{k_2^*(E)}{k_{-1}^*(E) + k_2^*(E)}; \quad (1-2)$$

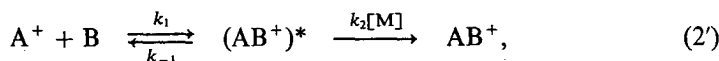
however, this low pressure limit has meaning only for molecules that internally randomize their energy well enough to serve as their own heat bath; otherwise  $k_2^*(E)$  and  $k_{-1}^*(E)$  are not physically meaningful as kinetic constants. A more appropriate formulation of the low pressure limit involves only a single rate coefficient for converting reactants to products. We call this  $k_0$  in eq. (1-1).

Transition state theory plays an important conceptual role in discussing such mechanisms. The transition state assumption is that there exists a perfect dynamical bottleneck somewhere along the reaction path. A perfect dynamical bottleneck is a hypersurface in coordinate space or phase space that separates reactants R from products P and has the property that any trajectory through it in the R  $\rightarrow$  P direction originated on the R side and will proceed to products without recrossing it. In terms of the reaction we have been discussing, the low pressure  $k_0$  would be expected to equal the capture rate coefficient  $k_1$  of the mechanism shown in reaction (2) if the transition state assumption is exact for a dynamical bottleneck that occurs early in the collision, whereas it would equal the  $k_0$  of eq. (1-1) if transition state theory at a tight dynamical bottleneck is exact. In general, the transition state assumption might not be perfect for either of these choices, and then one must consider recrossing effects at one or both imperfect dynamical bottlenecks. One (approximate) way of doing this is the unified statistical model (Garrett and Truhlar 1979c, 1982; Miller 1976; Truhlar et al. 1985b), which is based on the branching analysis of Hirschfelder and Wigner (1939). The only completely reliable way to estimate recrossing effects is to compute the full dynamics and compare to quantized transition state theory calculations. A popular approximation is to carry out a dynamical simulation using classical trajectories.

The situation is slightly different for an association reaction,



Then, making the strong collision approximation, one considers the mechanism



where again an asterisk denotes an unequilibrated (hot, excited) species.

In terms of these mechanisms, section 1.2 is primarily concerned with theoretical models of  $k_1$ ,  $k_{-1}$ ,  $k_2^*$ , and  $k_2$  that do not require a full potential energy surface. Section 1.3 is concerned with  $I^*(E) \xrightarrow{M} I^*(E')$  or I and with energy transfer within  $I^*(E)$  itself. Section 1.4 is primarily concerned with the calculation of  $k_0$  from potential energy surfaces.

## 1.2. COLLISIONAL AND STATISTICAL THEORIES FOR CLUSTER REACTION RATES

### 1.2.1. Bimolecular Rate Coefficients

#### a. Theory

In the early development of chemical kinetics, it was often assumed that bimolecular reactions occur upon every encounter between a pair of reactants. Then the encounter becomes a capture event, and the reaction rate is the capture rate. Although it is well known that this assumption is usually not true, the concept of a "collision" or "capture" rate is useful for establishing an approximate upper bound on measured reaction rates. This approximate bound is particularly useful in ion-molecule chemistry where strong long-range forces dominate the early stages of the reaction dynamics. The capture approximation can be applied to calculate approximate rate coefficients for exothermic reactions which contain no potential barriers and which are dominated by attractive, long-range intermolecular forces. For example, if the long-range potential is dominated by a charge-induced dipole interaction, then the capture rate coefficient is given by the familiar Langevin (1905)/Gioumousis-Stevenson (1958) expression. According to this model, the reactants are treated as point particles, and the rate coefficient is that for passing the maximum in the effective potential consisting of a positive centrifugal potential added to negative ion-induced dipole potential. This is an "orbiting transition state" (McDaniel 1964). The rate coefficient then depends on the electric properties of the ion (charge and polarizability), is inversely proportional to the square root of the colliding pair's reduced mass, and is independent of temperature.

For systems with anisotropic potentials, such as the reactions of ions with molecules having permanent dipole moments, the application of capture theories is not as simple as for collision partners interacting by central potentials, since the rotational motion of the molecules becomes hindered by the presence of the ion as it approaches, and this strong perturbation of the rotational motion has to be included in any realistic theory (Moran and Hamill 1963). A variety of theoretical approaches have been developed to simplify this problem. The first of these approximations that could be generally applied was the average dipole orientation (ADO) theory of Su and Bowers (Bass et al. 1975; Su and Bowers 1973a,b, 1975). This theory used statistical methods to calculate the average orientation of the polar molecule in the ion field and a Langevin procedure to calculate the rate of passage over the resulting entrance channel effective barrier. Ridge and coworkers (Barker and Ridge 1976; Celli et al. 1980) treated the competition between free rotation and collision-induced calculated alignment differently; they calculated an average interaction energy between the ion and the dipole and then again used the Langevin procedure to calculate the rate coefficient. The major assumption in the original formulation of the ADO theory is that there is no angular momentum transfer between the rotating molecule and the ion-molecule orbital motion. While this assumption may be quite good at large ion-molecule separations it becomes less valid as the separation distance decreases. Conservation of angular momentum was considered in the formulation of an improved theory called angular-momentum-conserved ADO theory or AADO (Su et al. 1978).

A further advance occurred when Chesnavich et al. (1980) applied variational transition state theory (Chesnavich and Bowers 1982; Garrett and Truhlar 1979a,b,c,d; Horiuti 1938; Keck 1967; Wigner 1937) to calculate the thermal rate coefficient for capture in a noncentral field. Under the assumptions that a classical mechanical treatment is valid and that the reactants are in equilibrium, this treatment provides an upper bound to the true rate coefficient. The upper bound was then compared to calculations by the classical trajectory method (Bunker 1971; Porter and Raff 1976; Raff and Thompson 1985; Truhlar and Muckerman 1979) of the true thermal rate coefficient for capture on the ion-dipole potential energy surface and to experimental data (Bohme 1979) on thermal ion-polar molecule rate coefficients. The results showed that the variational bound, the trajectory results, and the "experimental upper bound" were all in excellent agreement. Some time later, Su and Chesnavich (Su 1985; Su and Chesnavich 1982) parameterized the collision rate coefficient by using trajectory calculations.

At low temperature the classical approximation fails, but a quantum generalization of the long-range-force-law collision theories has been provided by Clary (1984, 1985, 1990). His capture-rate approximation (called adiabatic capture centrifugal sudden approximation or ACCSA) is closely related to the statistical adiabatic channel model of Quack and Troe (1975). Both theories calculate the capture rate from vibrationally and rotationally adiabatic potentials, but these are obtained by interpolation in the earlier work (Quack and Troe 1975) and by quantum mechanical sudden approximations in the later work (Clary 1984, 1985).

The abundant experimental data on ionic clusters reacting with neutral molecules has been used to test some of these collision theories. In the next subsection, we briefly review several papers where comparisons between measured and theoretical rate coefficients have been made, and we summarize some of the important conclusions concerning the reactivity of clusters.

## b. Comparison to experiment

i. *Exchange reactions.* In an early paper, Smith et al. (1981) studied the temperature dependence of the rate coefficients of the proton transfer and ligand exchange reactions  $\text{H}^+(\text{H}_2\text{O})_n + \text{CH}_3\text{CN}$  with  $n = 1-4$  at  $T = 200-300$  K. A slightly positive or zero temperature dependence was found; this result agrees well with collision theory calculations that predicted only a 1% rise in the rate coefficient with temperature. However, later improved theories do not agree so well. For example, the parameterized trajectory calculations of Su and Chesnavich (1982) predict a negative temperature dependence (approximately  $T^{-1/2}$  as expected from the analytic models) of the collision rate coefficients for an ion-molecule reaction in which the neutral reactant has a permanent dipole moment. Viggiano et al. (1988a) studied the reactions  $\text{H}^+(\text{H}_2\text{O})_n + \text{CH}_3\text{CN}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{COCH}_3$  and  $\text{C}_5\text{H}_5\text{N}$  with  $n = 2-11$ . They found that the rate coefficients displayed a stronger temperature dependence, varying as  $T^{-1}$ , than the just-mentioned theoretical prediction of  $T^{-1/2}$ . The authors explained the observed discrepancy between experiment and theory as being due to a failure of the theory to account for the dipole-induced dipole interaction and the nonuniform distribution of charge in the clusters at low temperatures. The former interaction is more

important for cluster ions than for bare ones because of the large polarizability of the ion. In later work (Viggiano et al. 1988b), the rate coefficients for proton transfer from  $\text{H}^+(\text{NH}_3)_m \cdot (\text{H}_2\text{O})_n$  with  $m + n \leq 5$  were found to vary as  $T^{-\lambda}$  with  $\lambda = 0.3-1.7$ . In more recent work, Yang and Castleman (1991a) analyzed the kinetics of  $\text{H}^+(\text{H}_2\text{O})_n + \text{acetone}$ , acetonitrile, and methyl acetate with  $n = 1-60$ , both at room temperature and at  $T = 130$  K. The measured rate coefficients were found to agree within experimental error with values calculated using the Su-Chesnavich (1982) method for the entire range of cluster sizes and at both temperatures. In a following paper, Yang and Castleman (1991b) reported detailed experimental studies and theoretical calculations of the temperature and cluster size dependence of  $\text{H}^+(\text{H}_2\text{O})_n$  with  $\text{CH}_3\text{CN}$ , with  $n = 1-30$ , for temperatures in the range 130–300 K. Very good agreement was found between the experiments and Su-Chesnavich theory for both proton transfer and switching reactions for all the accessible cluster sizes at room temperature. The agreement of theory and experiment was also found to be very good for the dependence of the rates on temperature and cluster size. The same kind of good agreement was found for larger clusters,  $\text{H}^+(\text{H}_2\text{O})_n$  with  $n = 4-45$ , in their association reactions with  $\text{CH}_3\text{CN}$  (Yang and Castleman 1989).

Hierl et al. (1986a) studied the proton transfer ( $\text{X}^- + \text{HY} \rightarrow \text{HX} + \text{Y}^-$ ) between  $\text{OH}^-(\text{H}_2\text{O})_n$  and HF with  $n = 0-3$  as a function of hydration number and temperature in the range 200–500 K. Their experimental data agree within experimental error with theoretical predictions for collision rate coefficients derived using the ACCSA method introduced above. They included only ion-dipole and ion-induced dipole interactions and omitted the dipole-dipole interactions, which are estimated to raise the rate coefficient in the case analyzed by up to 30%. The agreement with other theoretical predictions (Su and Chesnavich 1982) was about 20%. From these comparisons, Hierl et al. (1988) concluded that intermolecular proton transfer was occurring on essentially every collision throughout the ranges of hydration and temperature studied, and that the product tends to be hydrated. The former observation is consistent with other works—that is, proton transfer is usually fast (see, e.g., Viggiano et al. 1988a). The latter observation was explained by postulating a transition state structure of the form  $\text{HOH} \cdots \text{OH}^- \cdots \text{HF}$ , such that the formal transfer of a proton to the left and a water to the right is accomplished in actually by the transfer of an  $\text{OH}^-$  to the right. One may consider the proton as coming not from the donor but from the acceptor's solvation shell (kinetic participation of the solvation shell), and the reaction pathway is favorable (can occur at low energy) because the polar solvent molecule can stay close to the center of charge.

Hierl et al. (1986b) also studied the nucleophilic displacement reactions ( $\text{X}^- + \text{CH}_3\text{Y} \rightarrow \text{CH}_3\text{X} + \text{Y}^-$ ) between  $\text{OD}^-(\text{D}_2\text{O})_n$  and  $\text{CH}_3\text{Cl}$  with  $n = 0-2$  as a function of hydration number and temperature at 200–500 K. The reaction efficiencies (the reaction efficiency is defined as the ratio of the experimental rate coefficient to the theoretical collision rate coefficient) evaluated using ACCSA collisional rates showed that, in contrast to the proton transfer discussed above, nucleophilic displacement does not occur on every collision, and efficiencies decrease with increasing hydration and temperature. In fact, three water molecules were found to be sufficient to quench the reaction altogether, which is consistent

with the much higher activation energies observed for  $S_N2$  reactions in the condensed phase. The results were interpreted in terms of the model discussed by Olmstead and Brauman (1977), which views  $S_N2$  reactions as proceeding along a potential energy profile with a double minimum; one minimum corresponding to the reactant ion-dipole complex and one to the product ion-dipole complex. These may be called the precursor and successor complexes. The efficiency of a reaction in the Olmstead-Brauman model results from the trade-off between two effects in the reactivity of the precursor ion-dipole complex: (1) differences in entropies of activation for the dynamical bottleneck between reactants and the precursor complex and the dynamical bottleneck near the central barrier between the minima, and (2) the magnitude of the central barrier resulting from the differential solvation of the reactants and the transition state. The central transition state involves Walden inversion. Solvent transfer was considered energetically unfavorable because it was assumed to require an energetically and entropically unfavorable transition state. We will return to this question in section 1.4. Related work (Bohme and Mackay 1981; Bohme and Raksit 1985; Henschman et al. 1983, 1985, 1987; Hierl et al. 1988) has been discussed in terms of the relative energetics of unsolvated and microsolvated species. Some experimentally observed microsolvation effects may be understood quantitatively in terms of the attractive idea that cluster-ion studies in the gas phase bridge the gap between unsolvated gas phase reactions on one hand and the condensed phase reactions on the other hand. However, this is not always true (Bohme and Raksit 1984; Henschman et al. 1983, 1988; Hierl et al. 1988).

In early studies, Fehsenfeld and Ferguson (1974) determined the room-temperature rate coefficients for the reactions of  $CO_2$  and other molecules with  $OH^-(H_2O)_n$ ,  $n = 0$  and 2-4, and with  $O_3^-(H_2O)_n$ ,  $n = 0-2$ . In a later paper, Fahey et al. (1982) examined the reaction of  $CO_2$  and other molecules  $O_2^-(H_2O)_n$  with  $n = 1-4$ . Hierl and Paulson (1984) analyzed the energy dependence of the cross sections for the reactions of  $OH^-(H_2O)_n$  with  $n = 0-3$ . More recently, Viggiano et al. (1990) have studied the temperature dependence of rate coefficients for reaction of  $O^-(H_2O)_n + H_2$  or  $D_2$  with  $n = 0-2$ . All these investigations deal with small hydrated clusters, and the reaction paths are those expected for gas phase species. For example, Hierl and Paulson (1984) found that  $CO_2$  replaces water molecules in the hydrated cluster  $OH^-(H_2O)_{n=1-2}$  to form  $HCO_3^-(H_2O)_n$  with a rate coefficient nearly equal to the gas phase collision limit as evaluated with the AADO formalism introduced above. Interestingly, when  $n = 3$  the measured rate coefficient was reported to be significantly lower than the calculated value (the reason was not discussed in the paper). In more recent work (Yang and Castleman 1991c), the reactions of large clusters  $X^-(H_2O)_{n=0-59}$ ,  $X = OH, O, O_2$  and  $O_3$  with  $CO_2$  were studied by Yang and Castleman. For the smaller solvated cluster ions, the rate coefficients are very close to the Langevin collision limit, and they vary as the negative square root of the reduced mass of the collision complex, as predicted by theory. The rate coefficients for those reactions that proceed at near the gas phase collision limits do not display any temperature dependences, as predicted by Langevin theory for the case where the neutral (here  $CO_2$ ) has no permanent dipole moment. The differences between experimentally measured rate coefficients and the theoretical calculations become larger as cluster size increases.

For  $O_2^-$  and  $O_3^-$  clusters, these are explained by a change in sign of the reaction enthalpy, whereas reactions of hydrated  $OH^-$  with  $CO_2$  are exothermic for all degrees of solvation, and the large discrepancy between the experimentally measured rate coefficients and the theoretically calculated values, also attributable to solvation, was explained by an association mechanism in which the unimolecular dissociation rate coefficient of the reaction intermediate increases and the rate coefficient for conversion to product decreases for progressively larger cluster sizes. (We will review theoretical treatments of association reactions in the next subsection.) Yang et al. (1991) made a similar comparison between experimental and theoretical collision rate coefficients (in this case evaluated by the Su-Chesnavich method) and showed that  $OH^-(H_2O)_n$  with  $n = 0$  or 1 reacts with  $CH_3CN$  via proton transfer and ligand switching reactions at nearly the collision rate. Further hydration greatly reduces the reactivity of  $OH^-(H_2O)_n$  with  $n > 1$ , in disagreement with the collision theory. On the contrary, for all the cluster sizes studied,  $O^-(H_2O)_n$  reacts with  $CH_3CN$  at nearly the collision rate via hydrogen transfer from acetonitrile to the anionic clusters. Hierl and Paulson (1984) had found their measured rate coefficients for the reactions between  $OH^-(H_2O)_n$  and  $SO_2$  to be comparable to those predicted by the AADO theory. The authors explained that  $SO_2$  reacts more rapidly than  $CO_2$  according to that theoretical formalism because  $SO_2$  possesses a permanent dipole moment. The collision theory of Su and Chesnavich was also shown (Yang and Castleman 1991d) to correctly predict the rates of  $X^-(H_2O)_n$  with  $n = 1-3$  and  $X = OH, O, O_2$  and  $O_3$ , with  $SO_2$ ; these reactions proceed via ligand switching at room temperature. For larger clusters at low temperature, where association dominates the reaction mechanism, the measured rate coefficients are also very close to the collision limit, showing very little dependence on pressure, temperature, and cluster size, as predicted by the collision theory. In another study, Yang and Castleman (1990) analyzed the switching reactions  $NaX_n^+ + L \rightarrow NaX_{n-1}L^+ + X$  with  $X = H_2O, NH_3$ , and  $CH_3OH$ ,  $n = 1-3$ , and  $L = NH_3$  or various organic molecules at room temperature. All of the measured rates are very fast, proceeding at or near the collision rate predicted by the parameterized trajectory calculations of Su and Chesnavich. Furthermore, the rate coefficients do not show a pressure dependence, and the type of ligand bound to the sodium ion has little effect on the reaction rate. These features agree well with expectations (Castleman and Keesee 1986b) since all the reactions are exothermic and barrierless, and the parent ions can be treated as point charges due to their small physical size compared with the distance at which the maximum of the centrifugal barrier in the Langevin model occurs.

ii. *Association reactions.* Ion-molecule association reactions have received an increasing amount of attention over the years. Initially, the primary emphasis was thermochemical (Hogg et al. 1966), and later interest turned to the association rate coefficients. Simple clustering reactions provide good systems for testing theoretical models. Theoretical developments have been made concurrently with the experimental work.

Our discussion is based on the overall reaction (3) and the mechanism in reaction (2') presented above. The second step of reaction (2') has a bimolecular



rate coefficient of  $\beta$  times the  $(AB^+)^* + M$  collision rate coefficient, where  $\beta$  is the stabilization efficiency, usually assumed to be temperature independent, with a value between 0 and 1 depending on the nature of the third body, M, and the reacting system,  $A^+ + B$ .

Although the general mechanism of cluster formation is well understood, the redistribution of energy in the intermediate excited complex  $(AB^+)^*$  and the lifetime against dissociation back to the original reactants are major questions requiring further work. Therefore, theory can contribute by providing a better understanding of the unimolecular dissociation in terms of the statistical redistribution of energy within the excited intermediate. Although Rice–Ramsperger (1927)/Kassel (1928) (RRK) theory is sometimes used, the more sophisticated Rice–Ramsperger–Kassel–Marcus (RRKM) formulations (Forst 1983; Marcus 1952; Marcus and Rice 1951; Robinson and Holbrook 1972) and phase space theory (Bass et al. 1979; Bass and Jennings 1984; Caralp et al. 1988; Chesnavich and Bowers 1977; Light 1967; Light and Lin 1965; Nikitin 1965; Pechukas and Light 1965; Truhlar and Kuppermann 1969) give more insight because of their closer connection to the true molecular dynamics. In particular, RRKM theory is equivalent to transition state theory (Kreevoy and Truhlar 1986; Magee 1952; Rosenstock et al. 1952), and it allows an arbitrarily detailed description of the transition state. Phase space theory, in contrast, assumes that the collisional rate coefficient  $k_1$  and the rate coefficient  $k_{-1}$  for dissociation of the complex are governed by an orbiting or other type of loose transition state (requiring less information but sometimes introducing error when the assumption is invalid), but—unlike the usual formulation of RRKM theory—it rigorously conserves angular momentum. Especially interesting fundamental questions are related to the effectiveness of collisions and radiation in removing energy from complexes, leading to stable clusters. Other interesting questions are the effect of competing reaction channels on clustering, and the pressure and temperature dependences of association reactions. These questions have been discussed in the literature (Castleman and Keesee 1986b; Viggiano 1986).

Some of the initial work dealt with the formation of proton-bound dimers in simple amines. Those systems were chosen because the only reaction that occurs is clustering. A simple energy transfer mechanism was proposed by Moet-Ner and Field (1975), and RRKM calculations performed by Olmstead et al. (1977) and Jasinski et al. (1979) seemed to fit the data well. Later, phase space theory was applied (Bass et al. 1979). In applying phase space theory, it is usually assumed that the energy transfer mechanism of reaction (2') is valid and that the collisional rate coefficients  $k_1$  and  $k_{-1}$  can be calculated from Langevin or ADO theory and equilibrium constants.

Bass et al. (1981) published phase space theory models of the reaction  $CH_3^+ + HCN \rightarrow (CH_3^+ \cdot HCN) + h\nu$ , analyzing, in particular, radiative stabilization of the complex. Important work on radiative stabilization has also been published by Dunbar (1975), Herbst (1976) and Woodin and Beauchamp (1979).

In more recent work, Bass et al. (1983) applied the statistical phase space theory to clustering reactions of  $CH_3OH_2^+$ ,  $(CH_3)_2OH^+$ , and  $(CH_3OH)_2H^+$  with  $CH_3OH$ . Generally good agreement was found between the experimental and the

theoretical rate coefficients. The authors also modeled molecular elimination, back dissociation, collisional stabilization, and sequential clustering reactions.

The capture theories are most directly useful for exothermic reactions whose reverse reaction is also bimolecular. For association reactions, the reverse reaction is unimolecular. Equating the association rate coefficient to the capture one is only valid in the high pressure limit where all complexes are stabilized by third-body collisions. If the association reaction is treated as bimolecular, the apparent second-order rate coefficient becomes independent of pressure only in this limit. This problem has been widely studied for the reverse dissociation reactions, and specialized techniques have been developed (Troe 1977b, 1979) for theoretical treatment of the "falloff" regime between the high pressure second-order and low pressure third-order limits. Chang and Golden (1981) discussed this issue using Troe's simplified model in which the requisite information for the low pressure limit is the collision efficiency  $\beta$  and the density of states of the association complex. The low pressure model is equivalent to calculating the bimolecular dissociation rate coefficient and combining it with the equilibrium constant. The results are similar to those obtained by the somewhat more complicated RRKM theory of dissociation reactions.

The falloff region was treated for cluster reactions by Lau et al. (1982), who considered  $\text{H}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{H}^+(\text{H}_2\text{O})_n$  with  $n = 2-6$  and by Bass et al. (1983), who treated  $\text{H}^+(\text{CH}_3\text{OH})_{n-1} + \text{CH}_3\text{OH} \rightarrow \text{H}^+(\text{CH}_3\text{OH})_n$  with  $n = 2$  and 3.

The association reactions  $\text{CF}_3 + \text{O}_2$  and  $\text{CCl}_3 + \text{O}_2$ , although not cluster reactions, may be used to illustrate the issues. Ryan and Plumb (1982) and Danis et al. (1991) studied the kinetics of these reactions, the former in helium at  $1.6 \times 10^{16}$ – $2.7 \times 10^{17}$  molecules  $\text{cm}^{-3}$  and the latter in nitrogen in the 1–12 torr pressure range, as well as at 760 torr. Both groups carried out RRKM calculations for modeling the experimental results, and their results seem to be in reasonable agreement once the third-body efficiencies are taken into account. However, Danis et al. reported a strong temperature dependence for the rate coefficients at low pressure that could not be easily described using RRKM calculations. More recently, Fenter et al. (1993a) published new results on the same association reaction and they fit the experimental data by means of an RRKM calculation. This calculation was carried out using the strong collision hypothesis ( $\beta = 1$ , Troe 1977a), and a modified Gorin model (Davies and Pilling 1989; Garrett and Truhlar 1979d; Gorin 1938; Smith and Golden 1978) was used to represent the activated complex. The modified Gorin model is a phenomenological surrogate for variational transition state theory (see, e.g., Rai and Truhlar 1983) that does not require realistic potential functions. The analyzed experimental data were collected in the falloff region of the association reaction. Comparison of extrapolations with low and high pressure limiting rate coefficients from data taken in this region illustrates the state of the art of this kind of treatment. The same kind of calculations were reported by Caralp et al. (1988) for the association of peroxy radicals with  $\text{NO}_2$  and by Fenter et al. (1993b) for the association reactions of  $\text{CHCl}_2$  and  $\text{CH}_2\text{Cl}$  with molecular oxygen.

A more realistic treatment of the low pressure limit of the association rate coefficient requires a more complete treatment of energy transfer collisions, going

beyond the assumption that all such effects can be subsumed under the guise of a constant collision efficiency. These more sophisticated treatments of energy transfer are discussed in section 1.3.

Further discussion of ion-molecule association reactions and cluster formation is provided in chapter 6 in this volume by Wei and Castleman.

## 1.2.2. Unimolecular Dynamics

One approach to examining the dynamics of reactive bimolecular collisions that proceed through a complex is to study the unimolecular dissociation of a species that corresponds to the reaction intermediate. Clearly, in considering the mechanism of reaction (2), the unimolecular rate coefficients  $k_{-1}$  and  $k_2$  are just as essential to a complete picture as is the association rate coefficient  $k_1$ . These unimolecular rate coefficients are sometimes amenable to direct study. For instance, a stable intermediate for a gas phase  $S_N2$  reaction was isolated and photolyzed by Wilbur and Brauman (1991), and product was formed with significantly higher efficiency in the photolysis than in bimolecular kinetics studies. Because of large-impact-parameter collisions, the bimolecular reaction proceeds with larger average angular momentum than the species observed in the photolysis experiments, and statistical models were used to determine whether the higher angular momentum in the bimolecular reaction could account for its low efficiency. The orbital angular momentum in the bimolecular reaction raises the average effective barrier by  $2.5 \text{ kcal mol}^{-1}$  when a fixed value of  $8.6 \text{ \AA}$  is used for the distance between the centers of mass of the reactants at the association transition state. A variational transition state theory calculation of the transition state for association predicts that angular momentum raises the average effective barrier by approximately  $1.5 \text{ kcal mol}^{-1}$ , resulting in an efficiency change which accounts for about 30% of the effects seen. Calculations indicate that angular momentum also plays a significant role in the efficiency of product formation and lead one to expect differences in product energy distributions. In the energization of an intermediate, there is an energy regime in which an activated species has enough energy to cross the barrier to products but not enough energy to access the entrance channel. For species in this regime, formation of products has unit efficiency. For a low pressure bimolecular reaction, the reactants have energy at or above both channels of decay of the complex. Thus, the intermediate energy range is not accessed, and the efficiency is reduced. In related work, Graul and Bowers (1991) showed that the dissociation dynamics of  $\text{Cl}^-(\text{CH}_3\text{Br})$  is nonstatistical. Comparison of the experimental kinetic energy release distribution for metastable dissociation of the  $\text{Cl}^-(\text{CH}_3\text{Br})$  species with the distribution predicted by phase space theory revealed significant deviations, attributed to vibrational excitation of the  $\text{CH}_3\text{Cl}$  product.

Monomer evaporation from clusters has been studied extensively by Lifshitz and coworkers and interpreted in terms of transition state theory (Lifshitz 1993).

Sunner et al. (1989) used a semiempirical treatment to theoretically evaluate the rate coefficients of hydride transfer reaction  $\text{sec-C}_3\text{H}_7^+ + \text{iso-C}_4\text{H}_{10} \rightarrow \text{C}_3\text{H}_8 + \text{tert-C}_4\text{H}_9^+$ . Their kinetic scheme is based on a loose and excited chemically activated complex  $(\text{C}_3\text{H}_7^+ \cdot \text{C}_4\text{H}_{10})^*$  formed at the Langevin rate. The complex can decompose back to reactants or form the products of the hydride transfer

process [following the association mechanism of reaction (2)]. However, Hartree-Fock calculations with the STO-3G basis set and modified neglect of differential overlap (MNDO) semiempirical molecular orbital calculations indicate that the potential surface for this hydride transfer reaction does not have a central barrier—that is, is not of the double-minimum type.

Unimolecular dynamics of smaller clusters has also been studied. The HF dimer provides a particularly interesting system because it involves a highly quantal degenerate rearrangement consisting of a concerted double hydrogen-bond switch (Quack and Suhm 1991; Truhlar 1990).

### 1.3. ENERGY TRANSFER PATHWAYS IN CLUSTERS

Most of the models of ion-molecule association reviewed here do not consider the energy transfer process involved in stabilizing the intermediate of reaction mechanism (2'). Instead, the association rate coefficient is simply equated to that for ion-molecule capture, which is assumed to occur if the system passes the entrance-channel centrifugal barrier or entrance-channel vibrational transition state. However, there are two important dynamical steps in the mechanism of reaction (2'). One is the initial ion-molecule capture step, and the second is transfer of the reagent relative translational energy to vibrational and/or rotational modes of the complex. This energy transfer is necessary for formation of the excited complex ( $AB^+$ ). Similar energy transfer issues occur in photodissociation (both direct photofragmentation and predissociation from a photoexcited resonance state), in cage effects, and in exchange reactions; and all these issues are discussed in this section.

#### 1.3.1. Energy Transfer in Association

We begin by returning to the question of the low-pressure third-order rate coefficient for association reactions. A steady-state treatment of reaction mechanism (2') leads to a bimolecular rate coefficient

$$k = k_1 \frac{k_2[M]}{k_{-1} + k_2[M]}, \quad (1-3)$$

which at low pressure becomes

$$k_0 = \left( \frac{k_1}{k_{-1}} \right) k_2[M]. \quad (1-4)$$

A considerable amount of work (Adams and Smith 1981, 1983; Bass and Jennings 1984; Bates 1979a,b; Böhringer and Arnold 1982; Böhringer et al. 1983; Headley et al. 1982; Herbst 1979, 1980, 1981; Jennings et al. 1982; Liu et al. 1985; Moet-Ner 1979; Moet-Ner and Field 1975; Nielson et al. 1978; Patrick and Golden 1985; van Koppen et al. 1984; Viggiano 1984; Viggiano et al. 1985) has been addressed to the evaluation of this low pressure limit—that is, the termolecular rate coefficient

$$k_{\text{ter}} = (k_1/k_{-1})k_2 \quad (1-5)$$

and especially its temperature dependence. The theoretical treatments differ mainly in how the states of  $(AB^+)^*$  are counted in calculating the equilibrium constant  $(k_1/k_{-1})$ .

Typically, experimental data is analyzed by assuming  $k_{\text{ter}} = AT^{-n}$ , and the value of  $n$  is found to be small (e.g., 2–4) for diatomics and triatomics but considerably larger (e.g., 10) for polyatomics (Adams and Smith 1981; Bass et al. 1983; Bass and Jennings 1984; Böhringer et al. 1983; Headley et al. 1982; Jennings et al. 1982; Moet-Ner 1979; Neilson et al. 1978; van Koppen et al. 1984; Viggiano 1984).

The “thermal” and “modified thermal” models of Herbst (1979, 1980, 1981) and Bates (1979a,b) predict a small value of  $n$  and appear to be consistent only with the data for small molecules. Phase space theory calculations seem to be more successful (Bass et al. 1979, 1983), both in predicting larger  $n$  and in reproducing the curvature of the  $\log k$  vs.  $\log T$  plots. Phase space modeling has shown that the large temperature dependence and the nonlinear shape of  $\log k$  vs.  $\log T$  is principally due to vibrational excitation of the reactants, in agreement with the conclusions of Bass and Jennings (1984) for smaller systems. Viggiano (1984) found that the log–log slopes for the clustering reactions  $\text{NO}_3^-(\text{HNO}_3)_n + \text{HCl}$ , with  $n = 1$  and 2 deviated considerably from the value of 2.5 predicted by Bates’ theory, and these results were attributed to the low energy vibrations and internal rotations of the clusters. Similar conclusions were obtained for the association reactions  $\text{HSO}_4^-(\text{HNO}_3)_n + \text{HCl}$  with  $n = 1$  and 2 (Viggiano et al. 1985).

A modification to the theories of Herbst and Bates for ion–molecule association rate coefficients was proposed by Viggiano (1986). In the low pressure limit, the modified theory of Viggiano is similar to phase space theory and predicts a similar temperature dependence. This theory was applied to several systems, and good agreement with experiment was obtained (Morris et al. 1991). The steepness of the negative temperature dependences of association reactions, increasing with increasing complexity of the system, can be correlated with the increasing number of active vibrational degrees of freedom as either the temperature or the size of the cluster is increased (Adams and Smith 1981, Viggiano et al. 1985).

A potentially important question in association reactions is the temperature dependence of the collisional stabilization step. While this dependence is usually small, it is not always negligible. The primary evidence for this temperature dependence is that results obtained with different buffers show appreciably different temperature dependences. This problem has received considerable theoretical attention (Bates 1979a; Böhringer et al. 1983; Herbst 1982; Moet-Ner 1979; Patrick and Golden 1985; Smith et al. 1984; Viggiano 1986; Viggiano et al. 1985).

Bates (1984) interpreted the temperature dependence of  $\text{O}_2^+ + 2\text{O}_2 \rightarrow \text{O}_4^+ + \text{O}_2$  in terms of the energy randomization rate in the complex.

Ion–molecule association is seemingly well suited for the application of the quasiclassical trajectory (QCT) method (Porter and Raff 1976; Raff and Thompson 1985; Truhlar and Muckerman 1979). Since there is no potential barrier and the centrifugal potential is broad, quantum mechanical tunneling is typically unimportant. Energy transfer from relative translational to vibrational and/or rotational motions of the complex should be reasonably classical because of the

large density of states involved. Furthermore, since the variational transition state has an early location along the reaction path, quantization of reactant vibrational motions should result in a reasonably correct treatment of these motions at the transition state; however, we will return to this issue a few paragraphs later. (And we will return to the energy transfer issue in subsection 1.3.2.)

The earliest use of classical trajectory studies to provide insight into the dynamics of possible energy transfer processes in association reactions was by Dugan et al. (Dugan and Canright 1971; Dugan and Palmer 1972; Dugan et al. 1969). Their study involved rigid molecules and so energy transfer occurred by a translation-to-rotation (T-R) mechanism. Later, Brass and Schlier (1988) studied the exchange of energy between relative translation and reagent vibration (T-V). In other other studies, Schelling and Castleman (1984) and Babcock and Thompson (1983a,b) used trajectories to study enhancement of T-R energy transfer and successful association events by anisotropy in the long-range portion of the ion-molecule interaction potential and by reagent internal energy. The most extensive series of trajectory studies of association reactions was carried out by Hase and coworkers, and some of these studies are discussed next.

Classical trajectory studies of the association reactions  $M^+ + H_2O$  and  $M^+ + D_2O$  with  $M = Li, Na, K$  (Hase et al. 1992; Hase and Feng 1981; Swamy and Hase 1982, 1984),  $Li^+(H_2O) + H_2O$  (Swamy and Hase 1984),  $Li^+ + (CH_3)_2O$  (Swamy and Hase 1984; Vande Linde and Hase 1988), and  $Cl^- + CH_3Cl$  (Vande Linde and Hase 1990a,b) are particularly relevant to cluster dynamics. In these studies, the occurrence of multiple inner turning points in the time dependence of the association radial coordinate was taken as the criterion for complex formation. A critical issue (Herbst 1982) is whether the collisions transfer enough energy from translation to internal motions to result in association. Comparison of association probabilities from various studies leads to the conclusion that "softer" and/or "floppier" ions and molecules that have low frequency vibrations typically recombine the most efficiently. Thus, it has been found that  $Li^+ + (CH_3)_2O$  association is more likely than  $Li^+ + H_2O$  association, and similarly  $H_2O$  association with  $Li(H_2O)^+$  is more likely than with the bare cation  $Li^+$ . The authors found a nonmonotonic dependence of association probability on the assumed  $H_2O$  bend frequency and also a dependence on the impact parameter, the rotational temperature, and the orientation of the  $H_2O$  dipole during the collision.

Classical trajectory calculations do not include quantum effects such as tunneling, interference, and zero point energy (ZPE), although in quasiclassical trajectory calculations ZPE effects are included approximately by quantizing reactant energies at the start of the trajectory (see, e.g., Agrawal et al. 1988; Truhlar and Muckerman 1979). Hase and coworkers have discussed the sensitivity of trajectory results to the treatment of zero point energy. In particular, comparisons (Clark and Collins 1990; Gomez Llorente et al. 1990; Lu and Hase 1989) of trajectory simulations with experiments and quantum dynamics, as well as arguments (Torres-Vega and Frederick 1990) based on classical quantum correspondence, indicate that it may be better to omit the reactant molecule's zero point energy or include only a small fraction of it in choosing trajectory initial conditions. This is because classical mechanics allows zero point energy to flow

freely within the molecule, both incorrectly simulating an increased density of states and also allowing physically unrealistic processes to occur. As an example of the latter, trajectory studies on endothermic bimolecular reactions lead to incorrect threshold behavior (Gray et al. 1978, 1979a) and violations of detailed balance (Gray et al. 1979b). One approach for enforcing physically realistic quantization at dynamical bottlenecks is to find the dynamical bottleneck by variational transition state theory, quantize there, and run trajectories forwards and backwards from this point. When tunneling is included by a consistent transmission coefficient, this is called the unified dynamical model (Truhlar and Garrett 1987; Truhlar et al. 1982, 1985b); this model has been applied to reactions with tight transition states but not—so far—to loose dynamical bottlenecks.

Issues particularly germane to this chapter arise in the association of an ion, atom, or molecule with a cluster to form a larger cluster. One interesting issue is whether a cluster is large enough to act as its own heat sink. Another interesting issue is the mechanism by which a new molecule, added to a cluster, becomes "solvated" by moving to the interior. Cluster add-on and growth collisions have been studied by classical trajectory techniques with the aim of answering these and other questions (Alimi et al. 1990; Chartrand et al. 1991; de Pujo et al. 1993; Del Mistro and Stace 1992; Marks et al. 1991; Perera and Amar 1990). Reactive adsorption has also been studied (Adams 1990; Jellinek and Güvenç 1991; Raghavan et al. 1989). The kinetics of steady-state nucleation have been treated by Freeman and Doll (1988).

Hu and Hase (1992a,b, 1993) simulated association reactions of H in  $\text{HAr}_n$  microclusters with  $\text{CH}_3$  to form  $\text{CH}_4$  in order to study microscopic solvation dynamics. Classical trajectories and reaction path calculations were carried out for the  $\text{CH}_3 + \text{HAr}_n$  systems with  $n = 2, 4, 12$ , and 13 and with H initially on the surface of the cluster. In addition, they studied collisions of  $\text{CH}_3$  with an  $\text{Ar}_6\text{HAr}_6$  cluster in which H is completely solvated in the interior of an  $\text{Ar}_{12}$  shell. Solvating the H atom with  $\text{Ar}_n$  was found to have three important effects on the association dynamics. (1) Caging of H by  $\text{Ar}_n$  attenuates the association probability by keeping H from coming into close contact with  $\text{CH}_3$ . Solvent shells isolate reactants, so that their opportunities for contact are reduced. (2) Since  $\text{HAr}_n$  has a larger polarizability than H, the long-range attractive forces are greater, and the collision cross section is increased at low temperature. (3) Trapping by  $\text{CH}_3$  by  $\text{Ar}_n$  increases the probability of association. In collisions with low relative translational energy, the collision partners are trapped in a van der Waals well for long times. Physisorption of  $\text{CH}_3$  on the surface of the  $\text{Ar}_6\text{HAr}_6$  cluster provides sufficient time for the argon cage to relax, so that H and  $\text{CH}_3$  can associate. If the H atom is initially attached to the surface of the  $\text{Ar}_n$  cluster this relaxation is not necessary, since reaction can occur by both direct (the  $\text{CH}_3$  strips off the H in passing, or it initially hits the site where H is adsorbed on  $\text{Ar}_n$ ) and hopping (the  $\text{CH}_3$  is physisorbed elsewhere on the  $\text{Ar}_n$  surface and migrates to the H) mechanisms. (4) The solvation shell can serve as a chaperon. When a vibrationally and rotationally hot  $\text{CH}_4$  is formed,  $\text{Ar}_n$  acts as an energy sink to stabilize the excited  $\text{CH}_4$ .

Schulte et al. (1993) calculated classical trajectories for the collision of thermal  $\text{MO}_3$  clusters with Ne, Ar, and Xe. The simulation studied the dependence

of the energy transfer rate on collision mass and atom-cluster interaction potential.

Kaplan et al. (1993) have carried out classical trajectory calculations of high energy collisions of  $\text{He}^+$  and  $\text{Li}^+$  with  $\text{C}_{60}$  in free space and on an iron substrate. The simulations demonstrate the implantation of  $\text{He}^+$  to form endohedral  $\text{He}^+\text{C}_{60}$  at various energies, but  $\text{Li}^+$  collisions with  $\text{C}_{60}$  do not form  $\text{Li}^+\text{C}_{60}$ . For  $\text{Li}^+\text{C}_{60}$ , the authors found insertion and fragmentation to form  $\text{Li}^+\text{C}_{54}$  and  $\text{Li}^+\text{C}_{56}$ . The authors studied the yields as functions of incident energy, incident angle, point of impact, and whether the  $\text{C}_{60}$  is on the substrate or in free space.

Many of the issues that arise in cluster growth collisions are well known from the study of accommodation and sticking coefficients for gaseous molecules colliding with, or adsorbing at, solid surfaces (see, e.g., Adamson 1982; Kiselev and Krylov 1985; Weinberg 1991; Zangwill 1988). A related new area of study, intermediate between cluster growth and bulk solution, is the phenomenon of molecular scattering by the surface of a liquid. For example a recent study of the collision of a  $\text{D}_2\text{O}$  molecule with the surface of liquid  $\text{H}_2\text{SO}_4$  (Govoni and Nathanson 1994) involves the same competition of impulsive recoil, energy accommodation, trapping, desorption, and dissolution in the interior of the liquid as occurs when a molecule strikes a large cluster.

### 1.3.2. Energy Transfer in Dissociation

For a statistical approach to be valid for dissociation reactions, internal energy exchanges between modes should occur on time scales that are short compared with the dissociation time (Hase 1981; Truhlar et al. 1983). However, when the vibrational frequency spectrum has a gap, the high frequency modes may exchange energy slowly with the low frequency ones. Energy-gap (Beswick and Jortner 1981) and momentum-gap (Ewing 1979) "laws" have been proposed to quantify this effect. In one study of a system exhibiting such an effect, Desfrancois and Schermann (1991) investigated the classical dynamics of energy exchanges in a tetraatomic van der Waals cluster and found very long time scales for relaxation of high frequency degrees of freedom. Tardiff et al. (1990) studied energy transfer from the CH and OH stretch modes of  $\text{CF}_3\text{H}(\text{H}_2\text{O})_3$  into the dissociative mode leading to  $\text{CF}_3\text{H} + (\text{H}_2\text{O})_3$  and found that the OH mode leads to more rapid dissociation, probably because the water trimer is structurally coupled to the C-F bonds but not to the C-H bond.

A particularly important difficulty for classical theories arises in cases where the large ZPE from high frequency (stiff) vibrational modes (or part of it) is illegally transferred to other, soft modes. Consider a classical simulation of a van der Waals (vdW) cluster containing a diatomic molecule with a high frequency stretch. Not putting ZPE in the diatomic stretch may result in an incorrect description of various system properties, since the effective coupling among vibrational modes is changed, but giving the diatomic an energy equal to the quantum ZPE will allow part of the energy to flow to the weak bonds leading to unphysical dissociation of the cluster. There have been several theoretical attempts to devise methods that force the classical calculation to retain at least zero point energy in each mode (Bowman et al. 1989; Miller et al. 1989; Varandas and Marques 1994),



but these methods may lead to unphysical chaotic behavior (Sewell et al. 1992). One method was proposed by Alimi et al. (1992) specifically for molecules held in weakly bound clusters. This method treats the high frequency modes by semiclassical Gaussian wavepackets and the soft modes by classical dynamics using the time dependent self-consistent field approach (Alimi et al. 1990; Barnet et al. 1988) to couple the classical and the semiclassical modes. The resulting algorithm is very similar in form to a classical trajectory calculation, is stable, and appears to be free of unphysical effects. The method was illustrated by test applications to models of the van der Waals clusters  $I_2He$  and  $(HBr)_2$  in their ground states, which dissociate at the expense of their ZPE in classical trajectory calculations but that remain stable in the new method.

Quantum mechanical methods do not suffer these difficulties, and they have been widely applied to predissociative vibrational energy transfer in dimers (see, e.g., Balint-Kurti 1990; Chu 1984; Clary 1989, 1991; Hutson 1990; LeRoy 1984; Tucker and Truhlar 1988; Zhang and Zhang 1993), but they become impractical for larger ones.

Intracluster reactions are often induced by photons, as discussed in several chapters in this volume. One reason for the strong interest in such processes is that the relative geometries of the reagents are dictated by the cluster geometry so that one can, in principle, control the stereochemistry between them as if carrying out bimolecular collisions with oriented reactants (Wittig et al. 1988).

The process of predissociation in a cluster involves breaking a weak intermolecular bond following a high energy excitation of one of the molecular constituents of the complex. A central conclusion emerging from theoretical studies of this process is that statistical unimolecular rate theories are inapplicable to the predissociation of small van der Waals clusters. The most widely studied example is  $X \cdots BC$ , where X is a rare gas atom and BC is a chemically bonded diatomic molecule. In this process, which has been studied in hundreds of papers, part of the internal energy of BC is transferred to the van der Waals bond, causing its dissociation (Beswick and Jortner 1981). Larger clusters, such as  $X \cdots BC \cdots Y$ , with Y also being a rare gas atom,  $X_n BC$  with  $n = 2$ , and  $B_2 X_n$  with  $n = 17-71$ , have also been studied (Bačić et al. 1992; Delgado-Barrio et al. 1987; García-Vela et al. 1990a,b, 1991b; Le Quéré and Gray 1993; Potter et al. 1992; Schatz et al. 1983; Shin 1988; Villareal et al. 1989). The presence of at least two substituents weakly bonded to BC leads to complex dynamical behavior, and, as  $n$  increases, a transition to statistical liquid-like behavior may occur (García-Vela et al. 1990b, 1991b).

### 1.3.3. Cage Effect

A very fundamental difference between reactions in condensed matter and isolated molecular processes in the gas phase is the cage effect: when a reaction or excitation process occurs in a cluster or in a condensed phase, the surrounding solvent molecules may prevent the separation of the reaction products or excited interacting species or delay such separation, confining the nascent species to the initial "cage" for an extended period of time. As in the work reviewed in subsection 1.3.2, this involves the interplay of dissociation and energy transfer. There, the emphasis was

on transfer of energy into a dissociative mode; here, it is on transfer out of such a mode. If one can study the dynamics as a function of the size of the clusters, one can ask several interesting questions. For example, how does the probability for caging and the associated energy relaxation dynamics depend on cluster size, structure, and temperature? At what size cluster is bulk-like behavior observed?

Experimental evidence for caging has been found with even a single solvent atom. This effect has been the subject of several theoretical studies which have appeared in the literature (Beswick et al. 1987; García-Vela et al. 1991a, 1992a,b, 1993; Noorbach et al. 1984; Segall et al. 1993). For example, in a classical trajectory study of the photodissociation dynamics of HCl in the Ar...HCl cluster, García-Vela and coworkers have shown that a significant cage effect appears in the presence of even one solvent atom. The light atom has a high probability of colliding up to several times with the two heavy atoms that form the walls of the cage. There is substantial probability of transferring up to 25% of its initial kinetic energy. The cage effect leads to broad kinetic energy distributions and isotropic angular distributions of the fragments. A quasiclassical treatment led to the same qualitative results and conclusions as the fully classical simulation, although there were some significant differences between them (García-Vela et al. 1991a). In a later study, García-Vela et al. (1992a,b) used an approach that treats the hydrogen atom quantum mechanically while the heavy atoms are described classically. The time dependent self-consistent field approximation (Gerber et al. 1982a,b, 1986) was used to couple the quantum and classical modes. On the whole, qualitatively good agreement was found between the results of the (partly quantum) hybrid method and the purely classical ones of the earlier paper, despite the light mass of H. However, quantum diffraction oscillations were found in the angular distribution of the hydrogen fragment, and interference effects were found in its kinetic energy distribution. The peaks in the kinetic energy distribution are directly related to the resonance levels, which are not, however, seen in the absorption spectrum, which is structureless.

McCoy et al. (1993) extended this kind of study to (HCl)<sub>2</sub>. In this case, they again used a quasiclassical method in which quantal initial conditions were combined with classical trajectories; now, however, the quantal initial conditions were simulated by a Wigner transform of an anharmonic quantal ground state vibrational probability density obtained by the diffusion Monte-Carlo method. This initial condition was lifted to the repulsive excited state for one of the monomers, and trajectories were calculated. Although caging was observed, there were, at most, two internal collisions of H between HCl and Cl, as compared with up to six for H between Ar and Cl. The difference is due to the possibility of H + HCl reaction in the (HCl)<sub>2</sub> system. McCoy et al. observed that trajectories reaching the reactive part of the potential energy surface led to very efficient energy transfer, a well known effect (Thompson 1976) in noncluster dynamics.

Caging has also been studied in larger clusters. For example, Amar and Berne (1984) simulated caging of photoexcited Br<sub>2</sub> in neutral clusters of between 8 and 70 argon atoms. Caging was found to be particularly effective when the cluster structure had solvent atoms along the diatomic axis. The transition from a single shell of cluster atoms around the chromophore (Br<sub>2</sub>Ar<sub>20</sub>) to a two-shell cluster (Br<sub>2</sub>Ar<sub>70</sub>) gave little difference in caging behavior, which already approximates

bulk behavior, but two shells were required for relaxation behavior to become similar to that of the condensed phase, where the diatomic relaxes without significant dissociation. Scharf et al. (1986, 1988) observed a similar phenomenon in a classical dynamical study of the excimer dynamics of rare gas clusters. In particular, they found reactive molecular-type behavior in small clusters and nonreactive solid-state-type behavior in a large cluster. One can generalize that reactive vibrational predissociation is characteristic of vibrational energy flow in small clusters, while nonreactive vibrational energy redistribution is typical in condensed phases. (We will focus on vibrational relaxation pathways in the following paragraphs.)

Similar results were found in other studies. For example, Amar (1987) modeled the dynamics of  $\text{Br}_2^- \cdots \text{Ar}_n$  clusters following photodissociation of  $\text{Br}_2^-$ , and he found a correlation between structure and recombination mechanism similar to what had been observed (Amar and Berne 1984) for the corresponding neutral cluster; in particular, argon atoms approximately collinear with the diatomic axis were especially effective in promoting recombination. Alimi and Gerber (1990) used the hybrid quantum-classical method mentioned above to study the dynamics of the cage effect, corresponding to H chattering between heavy atoms, in the photodissociation of HI in clusters of the type  $\text{Xe}_n\text{HI}$  with  $n = 1-12$ . They found that a cage effect exists for all the clusters, including  $n = 1$ . For  $n = 1$ , these resonances are short lived, about 40 fs, and relatively unimportant, but, for  $n = 5$ , they are long lived, about 0.5 ps, and they dominate the process. As in the studies discussed in the previous paragraph, the larger cluster behavior already shows strong quantitative similarity to the corresponding condensed-matter reaction (Gerber and Alimi 1990).

Perera and Amar (1989) found more detailed support for the structural control of caging in classical dynamics calculations on a model of  $\text{Br}_2^-$  in large clusters of Ar and  $\text{CO}_2$ . The dissociation channel was found to become closed, as a function of cluster size, between 11 and 12  $\text{CO}_2$  molecules in the  $\text{Br}_2^-(\text{CO}_2)_n$  clusters, correlating with the appearance of double-capped minimum energy structures. This correlation was found in the  $\text{Br}_2^- \text{Ar}_n$  clusters as well. Collisions between a vibrating diatomic molecule in a cluster and the solvent particles may cause V-T energy transfer and rapid evaporation of the cluster.

Amar and Perera (1991) have also performed classical trajectory simulations of the photodissociation dynamics of  $\text{I}_2^-$  in  $\text{I}_2^-(\text{CO}_2)_n$ . Papanikolas et al. (1991) interpreted their experimental results on the same system in terms of these simulations. Their calculations showed that  $\text{CO}_2$  molecules first cluster around the  $\text{I}_2^-$  waist to form a solvent cylinder. Within this cylinder, the products of  $\text{I}_2^-$  photodissociation can undergo large-amplitude motion along the internuclear axis. This type of large-amplitude motion was also observed in the classical trajectories for  $\text{Br}_2^-(\text{CO}_2)_n$  (Perera and Amar 1989). During this motion, one or more of the  $\text{CO}_2$  molecules could slip between the dissociating iodine atoms, thereby creating a solvent-separated pair and hindering recombination.

Structural effects have also been observed in  $\text{Ar}_n\text{HCl}$  clusters with  $n = 1$  and 2 (García-Vela et al. 1994). In this case, the effect of cluster size on the cage effect depends on the excitation energy of HI and on the specific region of the potential surface that it accesses.

### 1.3.4. Energy Transfer in Exchange Reactions

As discussed previously, most work studying reaction dynamics in clusters by means of theoretical simulations has been directed to photoinduced unimolecular reactions of molecules in van der Waals or hydrogen-bonded clusters. Fewer simulations have been carried out on the effect of van der Waals or hydrogen-bonded clustering on bimolecular reactions. However, Hurwitz et al. (1993) have recently published a classical trajectory simulation of the hydrogen transfer reactions between an O(<sup>3</sup>P) atom and a hydrocarbon molecule weakly bound to an argon atom. The authors concluded that the Ar is not boiled off early in the reaction process. Rather, the solvent atom remains attached to the R group throughout the reaction. The O + H-R...Ar reaction is not direct, and throughout the lifetime of a collision complex several hydrogen chattering events occur. Coupled by an anisotropic interaction to the transient H bending mode in the O...H-R subsystem, the Ar takes part of the collision energy, which leads to substantially colder energy distributions for the OH product than were found for the corresponding reaction with the free hydrocarbon. The complexing with Ar also leads to considerably longer collision complex lifetimes, and the OHR subsystem explores a larger portion of the phase space in the cluster reaction than in the unclustered one.

The initial capture steps of the exchange reactions  $I + IAr_n \rightarrow I_2 + Ar_n$  with  $n = 12$  and 54 have been studied by trajectories by Hu and Martens (1993).

Kaukonen et al. (1991) reported classical trajectory calculations for  $[Na_4Cl_3]^+ Ar_n + Cl^-$  with  $n = 12$  and 32 and for  $[Na_{14}Cl_{12}]^{+2} Ar_{30} + Cl^-$ . Their results showed that it is possible to "tune" the relative probabilities for different product isomers by varying the initial vibrational temperature of the reactants and relative translations energy between collisional partners and/or the number of embedding Ar atoms.

## 1.4. MODELING CLUSTER REACTIONS WITH TIGHT TRANSITION STATES

In this section, we discuss studies where specific cluster reactions with tight transition states are modeled in terms of multidimensional potential energy surfaces or force fields (which, for practical purposes, we take here to be synonymous). In the last few years, there has been a considerable growth in the number of applications of potential energy surfaces to the study of chemical reactivity (Casavecchia 1990; Dunning and Harding 1985; Duran and Bertrán 1990; Gianturco 1989; Kaufman 1987; Kuntz 1985; Schatz 1989; Slanina 1986; Stone 1990; Truhlar 1981; Truhlar et al. 1985a, 1986, 1987; Truhlar and Gordon 1990). This now includes a number of applications of potential surfaces to reactive dynamics in and on clusters. As for other sections of this chapter, we will discuss selected examples from the literature. Examples chosen for discussion are especially concentrated on cluster reactions related to solvent effects.

Potential energy surfaces can be built starting from experimental data (e.g., bond strengths, geometries, infrared and fluorescence spectra, molecular beam scattering cross sections, viscosity, diffusion coefficients, line broadening

parameters, ultrasonic dispersion, or data on chemical reaction rates, cross sections, activation energies, threshold energies, kinetic isotope effects, or product energy distributions). They can also be built starting from theoretical calculations of the electronic structure of the system of interest, since the Born–Oppenheimer electronic energy plus the nuclear coulomb repulsion is the potential energy surface for interatomic motion. The pure theoretical approach, in which no experimental data are used, is called *ab initio*. *Ab initio* electronic structure calculations can be carried out at the self-consistent field molecular orbital level or, more accurately, including electron correlation. Various basis sets, differing greatly in size and quality, may also be employed. The empirical and theoretical approaches can be combined into a mixed approach, yielding semiempirical methods which combine experimental and theoretical data to construct potential energy surfaces. Within the semiempirical realm, we can distinguish general parameterizations (Dewar et al. 1985; Pople and Segal 1966; Stewart 1989), based on fitting the parameters to data for many molecules (but not usually to data for reaction rates), and specific models, designed to represent a single range of compounds or even only a single reaction; and in the latter case, often involving data for that specific reaction—for example, its activation energy. Examples of all these types of potential energy applied to the study of reactivity of clusters are given in the following.

In modern work, the simplest level of examination of a potential energy surface by electronic structure theory consists in at least optimizing the geometries and calculating the energies of the reactant and transition state stationary points (the former being a minimum, the latter a first-order saddle point). Successively more complete studies include the product stationary point, Hessians (second derivatives of the potential with respect to geometry) and vibrational frequencies at stationary points, steepest-descent reaction paths, vibrational frequencies along such paths, and, finally, a semiglobal (valid only near the reaction path) or even completely global analytic representation of the potential energy surface.

Theoretical interpretation of bimolecular nucleophilic substitution ( $S_N2$ ) reactions has a long history (de la Mare et al. 1955; Dostrovsky et al. 1946; Shaik et al. 1992). Anion-neutral  $S_N2$  reactions that are characterized by activation energies in the range 15–30 kcal mol<sup>-1</sup> in solution often proceed with no or small barriers in the gas phase. Because this large solvation effect is very interesting, and because of their simplicity,  $S_N2$  processes have become the prototype for recent work on solvent effects. We have previously mentioned (in the Introduction and in subsection 1.2.1.b.i) some of the experimental work designed to follow the transition in the kinetics due to the stepwise hydration of the nucleophile or proton acceptor, bridging the gap between the gas phase and solution. Theoretical studies have also explored this transition, as discussed next. We center attention on anion-neutral  $S_N2$  reactions exhibiting Walden inversion.

In particularly thorough examples of the traditional physical organic approach, Parker (1969) and Abraham (1974) interpreted solvent effects on Walden inversion reactions by using thermodynamic transfer functions. However, in order to explain the reaction rate decrease upon solvation from a microscopic point of view, quantum mechanical electronic structure calculations must be carried out. Microsolvated  $S_N2$  reactions were initially studied in this way, with the CNDO/2 semiempirical molecular orbital (MO) method, by using the supermolecule

approach, which was applied to  $F^-(H_2O)_n + CH_3F(H_2O)_m$  with  $n = 4, 6,$  and  $8$  and  $m = 4$  and  $7$  (Cremaschi et al. 1972). The authors carried out partial optimization of the stationary points and found that solvation stabilizes the transition state much less than the reactants. In the absence of solvent, some of the transition states were calculated to have negative energy barriers (preceded and followed by wells, so that the barrier is a local maximum). In other work, Morokuma (1982) tried to explain the gas phase data obtained by Bohme and Mackay (1981) by performing *ab initio* MO calculations with the 3-21G basis set. In particular, he studied the symmetric chloride exchange reaction  $Cl^-(H_2O)_n + CH_3Cl$  with  $n = 1$  and  $2$ . The calculated energy profile reproduces the double-well potential postulated by Olmstead and Brauman (1977), as discussed in subsection 1.2.1.b.i. A noteworthy aspect of Morokuma's work is the analysis of several reaction paths. For  $n = 2$ , for instance, Morokuma found that the most favorable path is the initial migration of one  $H_2O$ , with little or no barrier to form an intermediate complex, followed by a transition state corresponding to the  $CH_3$  inversion, and finally followed by migration of the other  $H_2O$  molecule. For the paths studied, the energy barrier was found to increase gradually when  $n$  changes from 0 to 2. Ohta and Morokuma (1985) carried out *ab initio* MO calculations with a flexible basis set to examine the potential energy surfaces for the  $S_N2$  reactions  $OH^-(H_2O)_n + CH_3Cl(H_2O)_m \rightarrow HOCH_3 + Cl^- + (n + m)H_2O$ , where the reactants are complexed with up to two water molecules. Although the water transfer process was found to be a part of the rate determining step in the symmetric reaction studied previously (Morokuma 1982), in these reactions it was found to take place after the transition state of the rate determining step. In general, in highly exothermic reactions such as  $OH^-(H_2O)_n + CH_3Cl(H_2O)_m \rightarrow HOCH_3 + Cl^- + (n + m)H_2O$ , water transfer is not likely to be involved at the dynamical bottleneck of the rate determining step, because the transition state for exothermic reactions is early. Thus,  $CH_3$  inversion precedes water transfer. In many cases, for exothermic reactions, the water never transfers (Hierl et al. 1986b), a feature not only of the  $S_N2$  mechanism, but also of cluster reactions involving proton transfer, where a propensity rule was proposed (Hierl et al. 1986a): "The most efficient channel is the least exothermic, yielding the ionic product with the minimum number of solvate molecules."

According to Magnera and Kerbale (1984),  $S_N2$  reactions with transition states that are more stable than reactants may exhibit a negative temperature dependence. However, adding even one or two water molecules of microsolvation may be enough to create a positive barrier. For example, Hirao and Kebarle (1989) found by *ab initio* electronic structure calculations that the gas phase energy profile along the reaction coordinate for the reaction  $Cl^-(H_2O)_2 + CH_3Br$  is very much closer to that for aqueous solution than to that for the unhydrated gas phase case. In contrast, Kong and Jhon (1986) determined, with a simpler potential energy surface, that about 60 water molecules are needed for representing solution-like behavior in the chloride exchange reaction and the  $S_N2$  process  $F^- + CH_3Cl$ . Thus, convergence toward the bulk limit may be considered fast or slow, depending on one's point of view.

Marcus (1956) and Levich (1970) have shown that nonequilibrium solvent relaxation plays an important role in homogeneous outer-sphere electron transfer

reactions. Marcus' equation can also be applied to the interpretation of nucleophilic substitution reactions in the gas phase and in solution (Albery 1980; Albery and Kreevoy 1978; Lewis and Slater 1980; Pellerite and Brauman 1980, 1982; Wolfe et al. 1981), which is not surprising since this equation is a quadratic free energy relation that may be derived under fairly general assumptions (Kreevoy and Truhlar 1986), involving either equilibrium or nonequilibrium solvation. Thus, it is hard to infer from phenomenological application of the Marcus equation how important nonequilibrium solvation effects are. Analyses based on reorientation of water dipoles indicate that bulk electric polarization of the solvent may sometimes be significantly out of equilibrium with the reaction coordinate in  $S_N2$  reactions in bulk water (Lee and Hynes 1988, Truhlar et al. 1993). What about the micro-solvated case? Several studies have been carried out to investigate this question.

Jaume et al. (1984) studied the contribution of solvent relaxation to the reaction coordinate of the  $F^-(H_2O) + CH_3F(H_2O)S_N2$  reaction. Potential energy calculations were performed using the *ab initio* MO method with the 3-21G basis set. The authors found large variation of the solvation parameters along the reaction path and concluded that solvent coordinates are an important part of the reaction coordinate. They showed that the solvent acts not only as a medium for the reaction but also as a reactant. Thus, the solvent does not adjust its position to the changing chemical system but rather takes part in it.

The Menshutkin reaction (Abboud et al. 1993) is a special case of the  $S_N2$  reaction where the reactants are uncharged but the products are charged, in contrast to the more usual  $S_N2$  reactions where both reactants and products are charged. The difference in charge states translates into an opposite effect of the solvent on these two types of reactions. Usual  $S_N2$  reactions are slowed down by solvent because charge is delocalized at the transition state, whereas the Menshutkin reaction is favored by the presence of the solvent because charge separation is created. Microsolvation effects on the reaction between ammonia and methyl bromide, which was taken as a prototype for the Menshutkin reaction, were analyzed by Solà et al. (1991). In this study, two water molecules were considered, one solvating the bromine atom in  $CH_3Br$  and the other solvating the ammonia. The effect of including the two water molecules is twofold: first, there is a decrease in the energy barrier; second, the transition state occurs earlier along the reaction path. As the system advances along the reaction path in an  $H_2O$  solvent, the N-O and Br-H distances shorten so there is a contraction of the solvation shell around both fragments. This is opposite to what happens in typical  $S_N2$  reactions, where one solvent shell is contracted and another one is expanded. The coordinates of the two solvent distances make significant contributions to the transition vector, which is the normal-mode eigenvector associated with the imaginary frequency at the saddle point, and this again indicates participation of the solvent in the reaction coordinate.

Theoretical studies of the microsolvation effect on  $S_N2$  reactions have also been reported by our coworkers and ourselves (González-Lafont et al. 1991; Truhlar et al. 1992; Tucker and Truhlar 1990; Zhao et al. 1991b, 1992). Two approaches were used for interfacing electronic structure calculations with variational transitional state theory (VST) and tunneling calculations. We analyzed both the detailed dynamics of microsolvation and also its macroscopic consequences (rate coefficient values and kinetic isotope effects and their temperature

dependences). The first approach was applied to the study of the microhydrated  $S_N2$  reaction of a chloride ion with methyl chloride, where the microsolvation consisted of one or two water molecules, in both cases solvating the anion (Tucker and Truhlar 1990). A semiglobal analytical potential energy function was created for the unsolvated reaction, with a barrier height chosen to fit an experimental rate coefficient value and with a shape based on correlated *ab initio* calculations for the gas phase system. The potential function has reaction-coordinate-dependent force constants and partial charges for all atoms of the solute. The interaction potential for the water molecules was added by molecular mechanics. All degrees of freedom were included, and the resulting analytic potential energy surface is a function of 36 coordinates. With the addition of just two water molecules, a definite trend toward the solution phase reaction profile was observed. For example, the barrier height, relative to reactants as zero of energy, increases from a value of  $3.1 \text{ kcal mol}^{-1}$  in the gas phase, to  $5.4 \text{ kcal mol}^{-1}$  for the monohydrated reaction, and to  $10.7 \text{ kcal mol}^{-1}$  for the dihydrated reaction, as compared with the accepted value of the solution phase barrier of about  $26\text{--}27 \text{ kcal mol}^{-1}$ . To go beyond classical transition state theory, the potential surface was used (Tucker and Truhlar 1990) to calculate, for both  $n = 1$  and  $2$ , the minimum energy path (MEP) in isoinertial coordinates (Shavitt 1969; Truhlar et al. 1985b; Truhlar and Kuppermann 1970, 1971), also called the intrinsic reaction coordinate (IRC) (Fukui 1981; Morokuma and Kato 1981), or, more suitably, the intrinsic reaction path (IRP). In contrast with the simpler approaches to defining a reaction coordinate used in previous cluster modeling studies (Jaume *et al.* 1984; Morokuma 1982; Ohta and Morokuma 1985), the MEP is an intrinsic property of the system, independent of the theoretician's model or choice of isoinertial coordinate system. For both the monohydrated and the dihydrated reactions it was found that, as the reaction proceeds, the water molecules migrate from the approaching chloride to the leaving chloride. Because the reaction under study is thermoneutral, the unsolvated ion is less likely to be a significant product than it is in the exothermic reactions typically studied experimentally. Rate coefficients were calculated by canonical variational transition state theory (CVT) (Lu et al. 1992; Truhlar et al. 1985b) for a tight dynamical bottleneck with a quantum tunneling correction based on a semiclassical approximation (Skodje et al. 1981), assuming small curvature of the reaction path. The rate coefficients decrease with increasing hydration of the system, as expected from the increasing barrier height that results from better solvation of the reactant than the transition state.

Since these calculations treat all 36 degrees of freedom on an equal footing, they include nonequilibrium solvation to the extent it is present. For comparison, the rate coefficients for the monohydrated reaction were also evaluated under the equilibrium solvation approximation. The extent of nonequilibrium solvation was evaluated by comparing calculations in which the degrees of freedom of the water molecule participate in the reaction coordinate to those in which they do not. Two different methods for defining the generalized transition state theory dividing surface under the equilibrium solvation approximation yielded quite different values for the rate coefficient. The most appropriate approximation, as shown by the variational transition state criterion, was found to give an increase of only 10% compared with the nonequilibrium approach. From this result, one may



conclude that strong solute-solvent coupling does not necessarily mean that nonequilibrium solvation effects are important. The different estimate of the nonequilibrium effects observed with the less accurate equilibrium approach indicates that one must distinguish the failure of the equilibrium solvation approximation from the failure of a less than optimum way of implementing it.

A second approach that we have used (González-Lafont et al. 1991) to interface electronic structure calculations with VTST and tunneling calculations is "direct dynamics" (Baldrige et al. 1989; González-Lafont et al. 1991; Liu et al. 1993), by which we mean basing the dynamics calculations directly on the output of the electronic structure calculations without explicit fitting or interpolation. This methodology was applied to the  $\text{Cl}^-(\text{H}_2\text{O})_n + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^-(\text{H}_2\text{O})_n$  reaction with  $n = 0, 1,$  and  $2$ . Instead of using an analytical potential energy function, the energy and gradient were calculated whenever needed by neglect-of-diatomic-differential-overlap (NDDO) semiempirical MO theory with parameters adjusted, starting from the general AM1 (Dewar et al. 1985; Zuebisch and Dewar 1988) parameterization. The method was labeled NDDO-SRP to denote NDDO with specific reaction parameters. Thus, rather than use one of the general parameterizations available for NDDO semiempirical molecular orbital theory as a completely predictive theoretical tool, this study used the NDDO molecular orbital framework as a partly predictive and partly fitting tool, resulting in an implicit potential energy function for a specific reaction. The results were compared, in detail, with previous calculations (Tucker and Truhlar 1990; Zhao et al. 1991b) based on the explicit (analytic) multidimensional semiglobal analytic potential function. Comparison with the results obtained with the analytical surface revealed some important differences that could be tested by future work; for instance, the structures of the saddle points for both  $n = 1$  and  $n = 2$  are rather different on the two surfaces. Perhaps more significantly, in many respects the two quite different approaches agree remarkably well. From an energetic point of view, the potential energy barriers on the implicit surface increase with stepwise hydration, as found earlier with the explicit surfaces.

The correspondence between the two sets of calculated  $\alpha$ -deuterium secondary kinetic isotope effects (KIEs), as well as heavy water microsolvant kinetic isotope effects, and their interpretation in terms of specific modes is very encouraging. For instance, both approaches predict an inverse secondary  $\alpha$ -deuterium KIE for  $\text{CD}_3\text{Cl}$ , approximately independent of the extent of solvation of  $\text{Cl}^-$ . [In general, vibrational frequencies and zero point energies are larger for lighter masses, because light particles are more quantum mechanical and have more widely spaced energy levels. Typically, the vibrations of a system become looser (i.e., have lower frequencies and hence lower zero point energies) as a system passes from reactants to the transition state, because force constants usually go down (since half bonds of transition states have weaker force constants than whole bonds of reactants). Thus, typically zero point energies go down in passing to the transition state, which would release energy *into* the reaction coordinate. Since zero point effects are, as just discussed, larger for lighter masses, this release typically is larger for lighter systems, and thus isotopically lighter systems typically react faster. This result is called a normal KIE. In the case under discussion, the effect of isotropic substitution is dominated by modes that increase in frequency so we get an inverse

effect.] The effect on the vibrational contribution to the  $CD_3$ KIE of adding a single water molecule is traceable almost entirely to a single transition state mode—the  $CH_3$  or  $CD_3$  internal rotation around the Cl–Cl axis. The differences between the two approaches are more significant in comparing microsolvant kinetic isotope effects—that is, the effect on the rate coefficient of changing  $D_2O$  to  $H_2O$  in the microsolvant. In particular, the NDDO-SRP surface predicts an inverse microsolvant KIE for  $n = 1$  and  $n = 2$ , while the microsolvant KIEs calculated from the earlier analytic surfaces are normal in both cases. However, while in the analytic approach the vibrational contribution to the global solvent KIE was also found to be normal for  $n = 2$ , the vibrational factor was inverse for  $n = 1$  (the normal global KIE resulted from the rotational contribution). In order to achieve a more detailed understanding, the vibrational contribution to the global KIE was further factored into contributions from individual vibrational modes. From this analysis, it was concluded that mid-frequency modes are not bystanders but have an important normal contribution, and the inverse microsolvant kinetic isotope effects are primarily due to the low frequency vibrations for this reaction.

The calculations carried out with the two approaches mentioned above showed the sensitivity of solvent KIEs to the low frequency vibrations associated with the coupling of the solute to the solvent. To treat this coupling more accurately, a new potential energy function for  $Cl(H_2O)^-$  was calibrated (Zhao et al. 1991a). The parameters of the new potential were determined to improve agreement with experiment for the dipole moment of water, with new-extended-basis-set correlated electronic calculations for the dissociation energy, geometry, and frequencies of the complex, with 369 *ab initio* interaction energies (Dacre 1984), and with one calculation for a geometry close to the  $Cl(H_2O)^-$  configuration at the previously calculated saddle point of the reaction  $*Cl(H_2O)^- + CH_3Cl \rightarrow CH_3^*Cl + Cl(H_2O)^-$ . We also attempted to converge the individual and total vibrational contributions to the equilibrium isotope effect for  $Cl(H_2O)^- + D_2O \rightarrow Cl(D_2O) + H_2O$ . New calculations of rate coefficients and secondary kinetic isotope effects for the microsolvated  $S_N2$  reaction  $Cl(H_2O)^- + CH_3Cl$  were then carried out (Zhao et al. 1992) based on the new chloride–water potential energy function combined with a more accurate internal potential function for the water molecule and the original analytic solute potential. At all temperatures, the microsolvant KIE is inverse with the new potential in contrast to the normal KIE calculated with the original potential, but is in agreement with the result obtained with the NDDO-SRP direct dynamics approach. The change in the direction of the predicted microsolvant kinetic isotope effect can be understood in terms of the effects of the solvent–solute interaction on coordinates other than the reaction coordinate; comparison of the vibrational contributions to the microsolvated KIEs indicates that the stronger interaction of the solvent and solute enhances the inverse tendency. The dominant effects on this microsolvant KIE ( $\mu$ SKIE) come from the low frequency and high frequency modes (in particular, the symmetric stretch mode), and it is their inverse contributions that convert the normal microsolvated KIE to an inverse one.

The contributions to the microsolvant KIE from various classes of mode are illustrated in Table 1-1. These factors indicate that the primary error in the original study was to miss the effect of about 10% in the high frequency modes, with a

**Table 1-1.** Factors Contributing to the Predicted Rate Coefficient Ratio  $\mu\text{SKIE} = k[\text{Cl}^-(\text{H}_2\text{O}) + \text{CH}_3\text{Cl}]/k[\text{Cl}^-(\text{D}_2\text{O}) + \text{CH}_3\text{Cl}]$ 

Potential function	Modes					$\mu\text{SKIE}$
	Translation	Rotation	Low frequency vibrations	Mid-frequency vibrations	High frequency vibrations	
1 (Tucker and Truhlar 1990)	1.03	1.41	0.43	1.67	1.00	1.04
2 (González-Lafont et al. 1991)	1.03	1.43	0.46	1.61	0.85	0.93
3 (Zhao et al. 1992)	1.03	1.41	0.40	1.67	0.90	0.87

difference in the same direction of about 7% in the low frequency contribution. The final conclusion is that the inverse microsolvant kinetic isotope effect ( $\mu\text{SKIE}$ ) for this reaction is primarily due to a very significant contribution from low frequency modes, almost, but not quite, compensated by "normal" contributions from rotation and mid-frequency modes, and helped by a small, but significant, contribution from high frequencies.

In light of these new results, it is interesting to review the available theories for bulk solvent kinetic isotope effects. Two fundamentally different models have been put forth to explain bulk solvent kinetic isotope effects. Swain and Bader (1960) proposed a model in which the librational frequencies of solvent molecules are responsible for solvent isotope effects. Each librational frequency in pure water is controlled by its coordination to four surrounding water molecules which make up the solvent "cage." The cage is the source of the structure of liquid water. The change in librational frequencies due to introduction of a solute is associated with the change imposed on the water librations in the four-coordinate cell. This theory, originally developed for equilibrium isotope effects (Swain and Bader 1960), was later applied to solvent KIEs (Swain et al. 1960; Swain and Thornton 1961a,b). In this case, it was assumed that transition states that are larger in size cause more breakdown in the structure of water, but effects due to "electrical" differences (changes in partial charges) of the solute at the transition state and in its reactant state were neglected (Swain et al. 1960).

Arnett and McKelvey (1969) presented a review of thermodynamic properties of highly dilute solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  and strongly emphasized the issues of structure breaking and structure making. Laughton and Robertson (1969) reviewed work on equilibrium and kinetic solvent isotope effects in terms of structural reorganization associated with librational degrees of freedom and the structural stability of hydrogen-bonded structures adjacent to the solute, and they concluded that solvent KIEs in  $\text{S}_{\text{N}}2$  solvolyses are related to "solvent reorganization about the developing anion." Thornton and Thornton (1971) reviewed both equilibrium and kinetic solvent isotope effects and differentiated among several factors, including changes in internal vibrations of solvent molecules strongly coupled to the solute, changes in water structure (especially for small ions), changes in librational frequencies, and exchange effects.

The second model of solvent isotope effects, due to Bunton and Shiner (1961a,b) concentrates on the hydrogen stretching frequencies of internal O-H vibrations in hydrogen-bonded solvent molecules and ignores the contributions of bending modes and librations. This model does not require any considerations of water structure, and it would be expected to be applicable to microsolvation without substantial modification. Bigeleisen (1960), Newton and Friedman (1985), Friedman and Newton (1986), and Kneifel et al. (1994) also emphasized the significant change in the O-L stretch frequency of ion-L<sub>2</sub>O complexes upon the substitution of L = D for L = H. For cations, Newton and coworkers (in the latter three references) found no support for the libration-dominant Swain-Bader model as far as the first-shell hydration is concerned, but, for bulk solvation, they concluded that libration appears to be more important.

Mitton et al. (1969) discussed both models in the context of methanolysis rates in CH<sub>3</sub>OH vs. CH<sub>3</sub>OD and found the argument involving solvent librations provided a more understandable explanation of the magnitudes of the effects than changes in the internal vibrational frequencies of the solvent molecules, but the argument involving hydrogen bonding explained the direction of the substituent effects.

Gold and Grist (1972) concluded that strongly basic anions perturb the water molecules that are hydrogen bonded to them, thereby contributing to inverse solvent kinetic isotope effects, but they did not provide evidence for a molecular explanation.

Schowen (1972) used the Swain-Bader theory to explain solvent kinetic isotope effects on S<sub>N</sub>2 reactions involving halides, in terms of the number of water molecules solvating a halide ion in the transition state (assumed to be three) vs. the number solvating it in the bulk (four). The contribution of a single halide-water hydrogen bond was also taken to depend on the partial charge on the halide, which could be consistent with either theory.

In this light, the single-water microsolvant KIE is very illuminating. The inverse character of this effect is consistent with the direction predicted by the solvent-structure argument, but for only one water it is clear that water structure breaking is impossible, and this indicates that the cell model of water structure breaking is probably not the sole reason for the inverse KIEs observed in bulk solvent KIEs. Water molecule O-H vibrations and water molecule librations are both involved in the microsolvant KIE, and they clearly must both be assessed for understanding cluster and bulk solvent KIEs. We must keep in mind, though, that bulk solvation may lead to a change in the structure of the reactant and/or transition state hydrogen bonds, causing a different effect to dominate the solvent KIE in the gas phase and in aqueous solution.

The prediction of an inverse  $\mu$ SKIE, even for a single water molecule, has recently been strikingly confirmed by experimental studies of the reaction F<sup>-</sup>(D<sub>2</sub>O) with several methyl halides (O'Hair et al. 1994). One of these, F<sup>-</sup>(H<sub>2</sub>O) + CH<sub>3</sub>Cl, has also been studied theoretically (Hu and Truhlar 1994) using transition state theory for a tight dynamical bottleneck whose properties were estimated using high level electronic structure calculations (electron correlation by Møller-Plesset second-order perturbation theory and an aug-cc-pVDZ basis set). The theoretical  $\mu$ SKIE is 0.65, and the calculated value is 0.65 as well. The need for high level

theory for quantitative results was demonstrated by repeating the calculation with PM3 semiempirical molecular orbital theory, which yielded  $\mu\text{SKIE} = 0.78$ . Factorization of the high level calculated isotope effect yields 1.05, 1.35, 0.74, 1.14, and 0.55, respectively, for the same classification of mode types as in Table 1-1. Thus, for this reaction, the high frequency modes provide the dominant effect. The isotope effect is dominated by the O-H stretching mode of the hydrogen bond between  $\text{F}^-$  and  $\text{H}_2\text{O}$ , in accord with the seminal analysis of Bunton and Shiner (1961a,b). In passing from reactants to the transition state, the zero point energy requirement of this mode increases by 1.2 kcal in the  $\text{F}^-(\text{H}_2\text{O})$  case but by only 0.9 kcal  $\text{mol}^{-1}$  in the  $\text{F}^-(\text{D}_2\text{O})$  case. In either case, this energy becomes unavailable for overcoming the barrier. Since 0.3 kcal  $\text{mol}^{-1}$  more energy is tied up in this vibration at the transition state for the  $\text{F}^-(\text{H}_2\text{O})$  case than for the  $\text{F}^-(\text{D}_2\text{O})$  case, less energy is available for crossing the barrier in the former case. Since less energy is available for crossing the barrier in the  $\text{F}^-(\text{H}_2\text{O})$  case, its rate is slower.

Why does the critical frequency go up? The answer is like a double negative. The hydrogen bond to  $\text{F}^-$  weakens the internal O-H bond of water. The hydrogen bond is stronger in reactants than in the transition state (because there is a full charge on  $\text{F}^-$ , rather than a partial charge) so the O-H bond is weakened more in reactants than in the transition state—that is, the O-H bond is stronger in the transition state, so it has a higher force constant, a higher frequency, and a greater zero point energy requirement at the transition state than at reactants.

It would be interesting, in future work, to examine the effect of anharmonicity on the calculated results.

At the transition state for the  $\text{F}^-(\text{H}_2\text{O}) + \text{CH}_3\text{Cl}$  reaction, the hydrogen bond from water is entirely to the F—that is, there is no evidence for water transfer at the methyl transfer transition state (see Figure 1-1), which is consistent with the propensity rule mentioned above, in that the water does not migrate. However, it is also consistent with the possibility that water migrates after the transition state is passed.

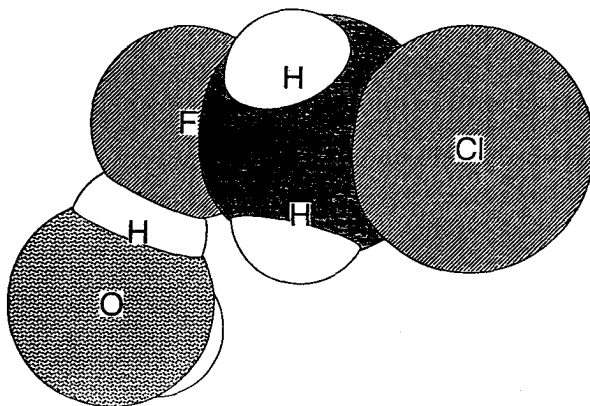


Figure 1-1. Space-filling view of the transition state structure for the  $\text{F}^-(\text{H}_2\text{O}) + \text{CH}_3\text{Cl}$   $\text{S}_{\text{N}}2$  reaction.

Several other studies have been concerned with cases where the solvent molecules intervene in specific ways in chemical reactions, such as acting as bifunctional catalysts (e.g., Bertrán 1989; Buckingham et al. 1986; Field et al. 1984; Lledós and Bertrán 1984, 1985a,b, 1986; Lledós et al. 1986; Moreno et al. 1987; Nguyen et al. 1991; Nguyen and Ha 1984; Nguyen and Hegarty 1984; Nguyen and Ruelle 1987; Ohta and Morokuma 1987; Peeters and Leroy 1991; Ruelle 1986, 1987a,b; Ruelle et al. 1985, 1986; Ventura et al. 1987; Weiner et al. 1985; Williams 1987; Williams et al. 1983; Yamabe et al. 1984). It has been shown that the potential barrier of the 2-hydroxypyridine  $\rightarrow$  pyridone process decreases noticeably when one or two water molecules intervene in the hydrogen transfer process (Field et al. 1984; Lledós and Bertrán 1986). Similar results have been obtained for *cis*-hydroxyimine  $\rightarrow$  formamide (Lledós and Bertrán 1984), and keto-enol tautomerization (Ventura et al. 1987; Weiner et al. 1985). The barrier to decarboxylation of a series of organic acids is decreased noticeably by intervention of a water molecule as a bifunctional catalyst (Lledós et al. 1986; Nguyen and Ruelle 1987; Ruelle 1986, 1987a,b; Ruelle et al. 1985). The presence of a second solvent molecule, which acts as a bifunctional catalyst, clearly favors numerous hydrolysis processes (Buckingham et al. 1986; Nguyen and Ha 1984; Nguyen and Hegarty 1984; Nguyen and Ruelle 1987; Williams 1987; Williams et al. 1983).

To illustrate these specific effects, consider the vinyl alcohol  $\rightarrow$  acetaldehyde tautomerization process. In this reaction, a chain containing two water molecules is needed to connect the hydrogen to be transferred and the nonsubstituted carbon. As compared with the gas phase transfer process, the barrier in the two-water cluster (Lledós et al. 1986; Ventura et al. 1987) is dramatically lowered, in good agreement with experimental results. However, the barrier is still sufficiently high to cast some doubt on the feasibility of such a mechanism. To understand how the energy is decreased by the two-water chain, one can look at the transition state: the hydroxylic hydrogen has been transferred to the first water molecule, whereas this molecule simultaneously begins to transfer one hydrogen to the second water molecule, and this, in turn, is hydrogen bonded to carbon. Thus, the hydrogen is transferred in a concerted way with the two-water group acting as a bifunctional catalyst, since it simultaneously accepts and releases a proton. A similar behavior was reported by Williams et al. (1983) on the assistance of a second water molecule to the addition of water to formaldehyde (Williams et al. 1980) and by Williams (1987) for the effect of one or two waters on the addition of ammonia to formaldehyde. In contrast, in a molecular orbital calculation carried out by Bouchoux and Hoppilliard (1990), the acid-catalyzed dehydration of ethanol via solvated complexes was found to be increasingly disfavored as the number of polar solvent molecules increases.

A question of great interest in the kinetics of reactions with cluster wells along the reaction path is the accuracy of transition state theory. Some classical trajectory calculations have indicated the possibility of large breakdowns (Cho et al. 1992), but these potential errors may be overestimated by the classical mechanical method employed, as discussed elsewhere (Truhlar et al. 1992; Wladkowski et al. 1992).

Tunneling effects on the microsolvated  $S_N2$  reactions studied so far are small. Processes dominated by tunneling are excited state proton transfer in

$C_{10}H_9OH \cdot NH_3$  and  $C_6H_5OH(NH_3)_5$  clusters, and these processes have been treated theoretically by Hineman et al. (1992) and by Syage (1993), respectively. Syage compared two models, one employing the Marcus theory of condensed phase reactions (Cohen and Marcus 1968; Marcus 1964, 1968) and one (Hineman et al. 1992) corresponding to an isolated solute, and, considering both his own data and those of Hineman et al. (1992), found better agreement with the latter. It would be interesting to repeat this kind of analysis using a full potential energy surface. Further discussion of proton transfer in the naphthol/ammonia and phenol/ammonia systems is provided in chapter 5 in this volume by Bernstein.

### 1.5. CONCLUDING REMARKS

A wide variety of dynamical approximations have been applied to cluster dynamics and kinetics. Most calculations to date are based on simplified potentials and classical mechanics or statistical methods. In the near future, we can expect to see more work with detailed potential energy surfaces (both analytic and implicitly defined by electronic structure calculations) and progress in sorting out quantum effects and treating them more accurately.

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