FAST CHEMICAL REACTIONS: Theory Challenges Experiment

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INTRODUCTION

The view commonly held by many chemists is that chemical reactions in the gas phase have rate constants that have a temperature dependence of the Arrhenius form

\[ k(T) = A \exp\left(-\frac{E_a}{RT}\right) \]

where the activation energy, \( E_a \), can be related approximately to the barrier height in the potential energy surface for the reaction. What is not generally realized is that there are many simple reactions of wide current importance that do not have rate constants of this form and, indeed, have rate constants that decrease in magnitude when the temperature is increased (1-4).

These reactions can have rate constants that are orders of magnitude larger than those obtained for reactions with activation energies, and it has not been easy to make accurate measurements of their rate constants, as highly reactive species such as free radicals and ions are usually involved. Furthermore, the rate constants can show interesting temperature dependences, which can also be hard to measure, especially for low temperatures (1). Due to significant improvements in techniques, however, some of these difficulties are being overcome and a wealth of experimental data is now being produced on the rates of fast chemical reactions that appear to have zero or negative activation energies (1, 2). This advance has come about not only through the sophisticated use of laser and mass-spectrometric
techniques for measuring the concentrations of highly reactive species, but also through the use of new types of apparatus for measuring reaction rates at very low temperatures. For the purpose of this review, fast two-body reactions are classified as those having rate constants larger than $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at room temperature. Association reactions are not discussed, although it should be realized that the rate constants for these reactions can also show negative temperature dependences (5).

The need for rate constant data for fast reactions over a range of temperatures becomes obvious when it is realized how important these reactions are in a variety of environments. For example, interstellar clouds can have very low temperatures (<20 K), and the only reactions that will be significant at these temperatures will be those without activation energies (6, 7). Furthermore, accurate data on the temperature dependence of the rate constants for fast reactions are crucial for understanding the chemistry of the atmosphere (8), where free radical reactions are commonplace and the temperatures can be quite low also.

With this large amount of experimental data becoming available for fast reactions, it is clearly important for theoreticians to turn their attention to the study of these reaction types. A large number of approximate theories have been proposed, particularly for the reactions of ions with molecules, where even analytical methods can be used with success (9). Although there has been much progress recently in the development of new quantum-mechanical methods for performing calculations on the three-dimensional reactions of atoms with diatomic molecules (10–12), most of these accurate quantum studies have been applied to systems having potential energy surfaces with barriers and reasonable activation energies.

What is not often realized is that fast chemical reactions can be easier to treat by quantum theory than reactions with barriers in the potential energy surface. The reason for this is that these reactions often have rates dominated by the longer-range part of the potential energy surface, and this part of the potential can usually be obtained quite accurately from knowledge of the multipole moments of the individual reacting molecules (particularly the charge, dipole moment, and quadrupole moment) and other molecular properties (13). Furthermore, the region of the dynamics of the reaction that often controls the reaction rate constant is in the long-range part of the entrance channel to the reaction, and it is not necessary to solve the Schrödinger equation over the whole of the reaction space from reactants to products to obtain rate constants (14).

For these reasons, it is possible to make quite accurate predictions of rate constants for a wide variety of fast reactions from first principles. Given the significant recent improvements in the experimental data becom-
ing available and the variety of theories being developed from accurate quantum methods to the most simple of analytical theories, this field is one where there is very close interaction between theory and experiment. Indeed, several predictions from theory have been verified in subsequent experiments. Furthermore, some exciting predictions from theory remain to be confirmed in experiments. The aim of this review is to illustrate this interaction by giving examples of where theory has challenged experiment.

First the simplest theoretical approach for the rates of reactions without barriers in the potential energy surface is outlined. This one-dimensional analytical "classical capture" method neglects the rotational states of the reactant molecules and rarely gives accurate results, although it does give useful predictions for the temperature dependences of the rate constants. Then a description is given of how accurate three-dimensional (3D) quantum mechanical calculations can be performed that provide benchmark results for testing the accuracy of more approximate theories that can give more physical insight. Several examples of comparisons of theoretical predictions with experimental data for reactions between ions and molecules are included, and the fast reactions of neutral species are also considered. Finally description is given of how the theoretical methods, developed originally for calculating rate constants, can be extended to other areas, including the calculation of isotopic branching ratios for chemical reactions and even to the calculation of the spectra for the photodetachment of electrons from dipolar anions.

CAPTURE THEORY IN ONE DIMENSION

It is assumed that the interaction potential between two molecules has a leading term for large separations that depends on the attractive term \(-C/R^n\). Here, \(C\) is a constant and \(R\) is the distance between the centers of mass of the molecules. As an initial approximation, the angles of orientation of the molecules are ignored. In classical mechanics, the effective potential is then

\[
V_{\text{eff}}(R) = \frac{bE}{R^2} - \frac{C}{R^n},
\]

Here, \(b\) is the impact parameter for the interaction and \(E\) is the energy of collision. This effective potential has a maximum that allows a classical capture approximation to be applied. This assumes that reaction occurs with unit probability for impact parameters that give a maximum in \(V_{\text{eff}}(R)\) lower than the collision energy, and with zero probability otherwise. A
typical diagram of the effective potential for a fast chemical reaction is shown in Figure 1.

It is also assumed that once the incoming particle has passed over the effective barrier to reaction, then reaction always occurs. Therefore, the theory is restricted to exothermic reactions and to reactions that have no secondary barriers in the potential energy surface. The cross section for reaction is then obtained from

\[ \sigma = \pi b_{\text{max}}^2(E, C) \]

where \( b_{\text{max}}^2 \) is the maximum value of the impact parameter that leads to reaction. The rate constant \( k(T) \) can then be obtained by Maxwell-Boltzmann averaging over the cross section, and has the temperature dependence of \( T^{(1/2-2/n)} \).

It is possible to do a similar calculation using quantum mechanics. Here we have a collision for fixed angular momentum quantum number \( l \) and collisional reduced mass \( \mu \). Thus the effective potential that contains the centrifugal term is

\[ V_{\text{eff}}(R) = \frac{l(l+1)}{2\mu R^2} - \frac{C}{R^n} \]

and the quantum mechanical capture collisional cross section is given by

\[ \sigma = \frac{\pi}{k^2} \sum_l (2l+1) P_l(E) \]

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**Figure 1** Potential profile (unbroken curve) and effective potential that contains the centrifugal term (broken curve) for a fast reaction. The arrows indicate the region that determines the capture rate constant.
where $k = (2\mu E)^{1/2}$ and $P_j(E)$ is the probability for passing through the centrifugal barrier, with boundary conditions applied at points displaced from either side of the potential barrier.

If the classical approximation is now applied so that the reaction probability is unity for angular momenta with a maximum in the effective potential less than $E$ and zero otherwise, then the cross section is

$$\sigma = \frac{\pi}{k^2} (l_{\text{max}} + 1)^2$$

where $l_{\text{max}}$ is the maximum angular momentum that gives a unit reaction probability. Comparison with the purely classical formula and identifying $(l_{\text{max}} + 1)$ as $kb_{\text{max}}$ gives the identical rate constant to the classical expression.

**QUANTUM CAPTURE THEORY IN 3D**

The above ideas can be extended to the calculation of rate constants for reactions in three-dimensions (14). Considering an atom + diatom reaction

$$A + BC \rightarrow AB + C$$

as the simplest example, it is now necessary to consider the rotational motion of the diatomic molecule BC. In most fast reactions, the vibrational states of the reacting molecule are not important and can be omitted from the calculations. This is because the long-range potentials are normally not very sensitive to the vibrational coordinates of the reacting molecules (14).

A full quantum close-coupling expansion of the wavefunction, $\Psi$, can be carried out in terms of basis functions, $y_j^l$. For a given value of the total angular momentum $J$, these functions couple together the rotational angular momentum quantum numbers $\{j\}$ of the molecule BC and “orbital” basis functions with quantum numbers $\{l\}$ that describe the rotation of the center of mass vector $R$ for the atom + diatom system. For a fixed value of the total angular momentum $J$, an appropriate expansion is (16)

$$\Psi = \sum_j \sum_l g_{jl}(R) y_j^l.$$ 

It is then possible to solve the close-coupling equations from very large separations through to a point well inside the centrifugal barrier where boundary conditions can be applied (14, 17). By summing over probabilities into all possible hindered-rotor states at this inner boundary point, a probability is obtained for reaction from a particular initial rotational state of the reactant molecule summed over all energetically available product states. Once again, it is assumed that there are no secondary
barriers in the short-range region of the potential that can cause reflection of reactive flux back to the reactants. By repeating the calculations for different values of \( J \), a capture cross section \( \sigma_j(E) \) is obtained that can be Maxwell-Boltzmann averaged over collision energy to obtain rate constants \( k_j(T) \) state-selected in the initial rotational states \( j \). In turn, the \( \{k_j(T)\} \) can be Boltzmann averaged to give the final rate constant \( k(T) \).

This quantum capture method is a powerful and general approach for calculating rate constants for fast reactions (14, 17). Since the close-coupling equations are solved only in the long-range region, coordinates appropriate for nonreactive scattering can be used and complicated coordinate transformations do not have to be carried out. As the theory of rotationally inelastic nonreactive scattering has been well developed for atom-diatom (18), diatom-diatom (19), atom-symmetric top, and atom-asymmetric interactions (20, 21), the theory can be readily applied to reactions of all of these types, providing enough computer time is available. The method, therefore, is instantly applicable to reactions more complicated than atom + diatomic systems.

Furthermore, it is easy to construct the leading terms in the long-range potential for such systems by using the classical electrostatic interaction potential, which requires knowledge of the principle multipole moments (dipole and quadrupole) on the reacting molecules. Another powerful advantage of the theory is that it is also straightforward to include potentials calculated via ab initio techniques in the calculations. Furthermore, several very powerful approximations to the close-coupling calculations, particularly the coupled-states and infinite-order sudden approximations (22, 23), have been developed for nonreactive scattering problems, and they can also be applied to fast reactions (14) to simplify the computations and make them less expensive in computer time.

The infinite-order sudden approximation (IOSA) (18) leads to particularly simple formulae for capture rate constants for fast reactions (14). This theory assumes that cross sections can be calculated for fixed orientation angles of the colliding partners, and then an average over all possible orientation angles and collision energy gives the final rate constants. Table 1 gives the analytical rate constants predicted by this theory for several different types of long-range interaction potentials (ion-dipole, ion-induced dipole, dipole-dipole, and dipole-quadrupole). These formulae give a useful guide as to the types of temperature dependences expected for the different interactions. The more accurate calculations have shown that the IOSA for dipole-dipole and quadrupole-dipole interactions works quite well (14), although it is not very accurate for ion-dipole interactions where the potential is highly anisotropic (24). The IOSA ignores the effect of rotational energy on the rate constants, and the
Table 1  Rate constants for various long-range interactions from the infinite-order-sudden approximation (14)

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential function</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-dipole</td>
<td>$-\mu_0 \cos \theta / R^2$</td>
<td>$0.25 \mu_0 ((8\pi/\mu)^{1/2} (k_B T)^{-1/2}$</td>
</tr>
<tr>
<td>Ion-induced dipole</td>
<td>$-\alpha / (2R^4)$</td>
<td>$2\pi (\alpha/\mu)^{1/2}$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>$-\mu_1 \mu_2 [2 \cos \theta_1 \cos \theta_2$</td>
<td>$1.77 (\mu_1 \mu_2)^{2/3} (k_B T)^{-1/6}$</td>
</tr>
<tr>
<td>Dipole-quadrupole</td>
<td>$3\mu_1 Q_2 \cos \theta_1 (3 \cos^2 \theta_2 - 1) - 2 \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2) / (4R^4)$</td>
<td>$0.86 \pi (\mu_1 Q_2 / \mu)^{1/2}$</td>
</tr>
</tbody>
</table>

$\mu_0$ is the dipole moment, $\mu$ the reduced mass, $\theta$ the angle that the ion-molecule center of mass vector $R$, makes with the direction of the dipole.

$\alpha$ is the isotropic molecular polarizability.

$\mu_i$ is the dipole moment on molecule $i$. The orientation of $R_1$ with respect to $R_2$ is defined by the angles $[\theta_1, \theta_2, (\phi_1 - \phi_2)]$.

$Q_2$ is the quadrupole moment of molecule 2.

rotationally selected rate constants $k_j$ are particularly sensitive to $j$ for the ion-dipole reactions.

A simple theory for fast reactions that is more accurate than the IOSA, but is still cheap in computer time and gives a useful physical picture, can be derived from the quantum capture theory described above (14, 24). In the close-coupling calculations, the intermolecular coordinate $R$ is divided into small sectors with midpoints $\{R_j\}$. In solving the close-coupling equations, it is necessary to find the local hindered-rotor energy levels for each of the $R_j$ values. For an atom-diatom system $A + BC$, this corresponds to finding the rotational levels of the molecule BC, in the presence of atom A for a fixed internuclear distance $R$, by diagonalizing the interaction potential with the basis set $\{\gamma_j\}$. This calculation yields a set of effective rotational energies as a function of $R$ that can be joined up to give “rotationally adiabatic potential energy curves.” The energy of each of these curves tends to the energy of a particular molecular rotational state $j$ for infinite separations. Thus, each rotationally adiabatic potential curve can be labeled by a rotational state $j$ of the reactant molecule BC.

These diagrams immediately suggest the approximation of calculating cross sections for each of these individual, $j$-selected, potential curves and identifying the capture reaction probabilities and cross sections so obtained with those for the particular initial $j$ state. If this theory is used in conjunction with the coupled states approximation (18, 26), where the simplified basis $\{Y_{\Omega}\}$ is used, then these calculations become very cheap to perform. Here, it is assumed that the projection, $\Omega$, of the rotational angular momentum along the intermolecular coordinate $R$ is conserved. In this case, the rotationally adiabatic curves are labeled by the pair of
$(j, \Omega)$ quantum numbers. Figure 2 shows an example of the rotationally adiabatic potential curves for an ion-dipole interaction.

A further simplification is to apply classical capture theory to the rotationally adiabatic potential curves (14, 24). This involves finding the largest value of the total angular momentum, $J_{\text{max}}(E, j, \Omega)$, such that the maximum in the rotationally adiabatic potential is still below the collision energy $E$. The cross sections are then obtained from

$$\sigma(j, E) = \frac{\pi}{k_j^2(2j+1)} \sum_{\Omega} [J_{\text{max}}(E, j, \Omega) + 1]^2.$$ 

Therefore, the numerical work reduces to performing a small number of matrix diagonalizations for a grid of $\{R_i\}$ values, and then performing very simple analyses on the rotationally adiabatic curves so obtained.

![Figure 2](image_url)

*Figure 2* Rotationally adiabatic potential curves for the $\text{C}^+ + \text{HCl} \rightarrow \text{CCl}^+ + \text{H}$ reaction with $J = 0$ (57).
These simplifications make this a cheap and general approach for treating all types of fast reactions. Several other types of rotationally adiabatic approaches have also been developed, and have been applied particularly to ion-dipole reactions (27–36). In the simple case of ion-dipole reactions, it is possible to derive approximate analytical formulae for the rotationally adiabatic potentials, which in turn lead to analytical formulae for the rate constants (31, 34).

The rotationally adiabatic capture theory has been thoroughly tested by comparison with benchmark cross sections calculated by using the full quantum close-coupling capture theory (14) discussed above. Comparisons of results for the He$^+ + $HCl (17) and O($^3P$)+OH (14, 37) reactions, where ion-dipole and quadrupole-dipole interactions are the potentials, respectively, show that the theory is highly accurate even for very low collision energies. Furthermore, these comparisons show that the coupled-states approximation, which assumes that the projection of the rotational angular momentum along the intermolecular vector is conserved during the collision, is also an excellent approximation. This is a finding that differs from that of a recent study in which the accurate calculations were not performed (38). In fact, the only fast reaction for which we have found the rotationally adiabatic-coupled states approximation to break down is that for the reactions of electrons with dipolar molecules (17, 39).

**ION–MOLECULE REACTIONS: COMPARISON WITH EXPERIMENT**

*Reactions of Ions with Polar Molecules*

The benchmark cross sections for the He$^+ + $HCl reaction (17) have also been used to test the accuracy of other theories proposed for the rate constants of ions with dipolar molecules and other fast reactions. These comparisons (40, 41) show that the statistical adiabatic channel approach used by Tröe (31–33), the adiabatic invariance method of Bates & Morgan (34–36), the perturbed rotational state approximation of Sakimoto & Takayanagi (27–30), classical trajectory calculations (42–47), and various types of transition state methods (48–51) all give quite good agreement with the quantum close-coupling results (41). Indeed, it is hard to find a theory that does not work well for ion-dipole reactions! As this review is concerned with illustrating the interaction between theory and experiment in the field of fast reactions, a detailed comparison of all these theories will not be given here. Rather, emphasis is placed on describing the results of those calculations that have produced new predictions that have been
verified in experiments or are likely to be tested by experiments in the near future.

One of the interesting predictions of all of these theories is the strong negative temperature dependence of the rate constants for the reactions of ions with dipolar molecules (24, 41). Until recently, there was little good experimental data for these reactions below room temperature. Then, Smith & Adams applied their selected ion flow tube (SIFT) apparatus to the measurement of rate constants for temperatures down to 200 K for proton transfer reactions such as

$$\text{H}_3^+ + \text{HCN} \rightarrow \text{H}_2 + \text{H}_2\text{CN}^+. $$

Their results confirm the theoretical prediction (24) of a sharp negative temperature dependence for the rate constant for this reaction and give excellent agreement with the theoretical predictions (52), as shown in Figure 3.

More recently, a remarkable series of experiments have been carried out at the Laboratoire d'Aérothermique in Meudon. Here, Rowe and co-

![Graph showing rate constants for the H₃⁺ + HCN → H₂ + H₂CN⁺ reaction.](image)

*Figure 3*  Rate constants for the $\text{H}_3^+ + \text{HCN} \rightarrow \text{H}_2 + \text{H}_2\text{CN}^+$ reaction. The curve gives results predicted with the rotationally adiabatic capture theory (24), and the error bars show subsequent experimental measurements (52).
workers have made use of an apparatus that involves a uniform supersonic jet as a flow reactor (53). This experiment requires using a rarefied gas wind tunnel to produce the conditions required to measure rate constants down to very low temperatures. The method is called CRESU, standing for “Cinétique de Réactions en Ecoulement Supersonique Uniforme.” It enables rate constants for a large variety of ion-molecule reactions to be measured down to temperatures as low as 8 K, which is in the interstellar temperature range (6, 7).

The CRESU experiments have confirmed the rate constants predicted from the rotational adiabatic capture theory for several ion-dipole reactions for temperatures down to 27 K (40, 53). An example of such an experimental/theoretical comparison is shown in Figure 4 for the

\[ \text{He}^+ + \text{HCl} \rightarrow \text{He} + \text{HCl}^+ \]

to charge transfer reaction, and it can be seen that the agreement is excellent. Similar good agreement is obtained for the charge transfer reactions of \( \text{He}^+ \) with \( \text{SO}_2 \) and \( \text{H}_2\text{S} \) (40).

This theoretical and experimental work has stimulated research by those who perform computer simulations of the chemical reaction networks in interstellar clouds. Some of these clouds are thought to have very low temperatures (\( \sim 10 \) K), and thus only fast reactions can be important (6,
Previous simulations had used rate constants for ion-dipole reactions based on room temperature measurements or highly approximate theories (9). New simulations with the ion-dipole rate constants appropriate for the lower temperatures have led to new explanations of some astronomical observations (54). For example, a large abundance of the HCS$^+$ ion is observed in several interstellar clouds and, for some time, the mechanism for production of this ion was unclear (55). The CS radical has a large dipole moment and hence the rotationally adiabatic capture theory predicts a large rate constant for the

$$\text{H}_3^+ + \text{CS} \rightarrow \text{H}_2 + \text{HCS}^+$$

reaction at low temperatures. Interstellar simulations with this rate constant give concentrations of the HCS$^+$ species in good accord with the astronomical observations (56).

Unlike proton transfer reactions, most fast reactions involve ions, atoms, or molecules that do not have electrons in closed-shells. This implies that a proper treatment requires consideration of the coupling of electronic spin and orbital angular momentum with the rotational motion of the molecule, and the reaction can often occur on more than one potential energy surface. Furthermore, spin-orbit coupling effects can play an important role in the temperature dependence of the rate constants. The C$^+(2P)$ and N$^+(3P)$ ions are good examples of atomic ions with non-zero electronic orbital angular momentum, and many rate constants have been measured for the reactions of these ions. Furthermore, it is found that the capture theories with a simple ion-dipole potential often significantly overestimate the measured rate constants for these particular ions (53).

Recently, several ab initio multiconfigurational self-consistent field (MCSCF) calculations have been performed on the potential energy surfaces for the reactions of C$^+$ and N$^+$ with dipolar molecules (57, 58). To take the C$^+$ + HCl reaction as an example, two A$'$ and one A$''$ potential energy surfaces are produced (57). For infinite separations of C$^+$ and HCl, these three surfaces become degenerate. The MCSCF calculations give both the lowest-energy A$'$ surface and the A$''$ surface as attractive, while the second A$'$ surface becomes strongly repulsive. These calculations enable a determination to be made of the factor $f$, which is the fraction of potential energy surfaces that become attractive in the entrance channel to the reaction. For C$^+$ + HCl, $f$ takes the value 2/3. Multiplication by $f$ of the capture rate constant $k_c$ obtained from the ion-dipole interaction gives good agreement with the Boltzmann averaged rate constants obtained from the three ab initio potential surfaces and with experiment for this reaction (40, 57). For the reactions of N$^+$, the MCSCF calculations give $f = 1/3$ as
the lowest $^3A''$ potential that is attractive whereas the second $^3A''$ and the $^3A'$ potentials are both repulsive (58).

These findings led to the proposal that the exact rate constants, $k$, for the exothermic reactions of open shell ions with molecules are bounded above by $k_c$ and below by $f k_c$ (58). These bounds arise because the capture rate constant $k_c$ should be an upper bound to $k$, as nothing that is omitted from the capture theory can lead to enhancement of the rate constant over $k_c$ except for tunneling through a classically disallowed centrifugal barrier. As is explained below, this tunneling effect cannot be significant except at very low temperatures ($< 1 \text{ K}$). If non-adiabatic transitions between the different potential energy curves are not allowed, the rate constant will be given by $f k_c$. If, however, the non-adiabatic transitions between the repulsive curves and attractive curves occur with unit probability, the rate constant will be given by $k_c$. In practice, the true rate constant will be between these two extremes and will be in the range $k_c > k > f k_c$. This relationship has been examined for all 34 exothermic reactions of C$^+$ and N$^+$ ions with molecules for which rate constant measurements have been made at room temperature and is found to be accurate in every single case (58). Table 2 gives a list of all these exothermic reactions. These reactions include those of polar, non-polar, and polyatomic molecules with C$^+$ and N$^+$.

It is important to emphasize that, once again, the theory described above only considers the entrance channel to the reaction and does not attempt to describe the potential energy surface all the way from reactants to products. Nor does the theory need to use correlation diagrams for the potential energy surfaces that require a linear transition state. For endothermic reactions, such as C$^+$ + H$_2$, extensive \textit{ab initio} calculations have shown that it is necessary to examine the potential energy surfaces all the way from reactants to products to understand the reaction cross sections (59).

**Solvated Ion-Dipole Reactions**

The above considerations all apply to reactions in the gas phase, but it is interesting to consider the effect of solvent molecules on fast reactions:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reactant Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$^+$</td>
<td>NO, O$_2$, HCl, H$_2$O, H$_2$S, HCN, CO$_2$, OCS, SO$_2$, NH$_3$, C$_2$H$_2$, H$_2$CO, CH$_4$, C$_2$H$_4$, CH$_3$CN, C$_2$H$_4$</td>
</tr>
<tr>
<td>N$^+$</td>
<td>H$_2$, CO, NO, O$_2$, HCl, H$_2$O, H$_2$S, HCN, CO$_2$, OCS, SO$_2$, NH$_3$, H$_2$CO, CH$_4$, C$_2$H$_4$, \textit{trans} C$_2$H$_2$Cl$_2$, \textit{cis} 1, 2 C$_2$H$_2$Cl$_2$, 1, 1 C$_2$H$_2$Cl$_2$</td>
</tr>
</tbody>
</table>
This is a vital link between gas- and liquid-phase reactions. An interesting series of experiments have been carried out on this subject by Henchman and coworkers (60–63). They have measured the rate constants for the reactions of the species OH\(^{-}(H_2O)_n\), \(n = 0, 1, 2, \text{ and } 3\), with several molecules, including HF, CH\(_3\)Cl, and CH\(_3\)CN. Flow-tube and ion-beam techniques are used for the temperature range of 200–420 K. The rate constants measured for these dipolar molecules have been compared with those calculated with the rotationally adiabatic capture theory (60–62). In these calculations, the water molecules only influence the calculations through their effect on the reduced mass for the collision; since they are solvating the ion, they are not affecting directly the dipole moment of the reacting molecule.

These measurements show that the proton transfer reactions

\[
\text{OH}^{-}(H_2O)_n + HF \rightarrow H_2O + \text{F}^{-}(H_2O)_n
\]

do go at the capture rate even when HF is solvated by three water molecules (60). The findings are different, however, for the nucleophilic displacement reactions (61)

\[
\text{OD}^{-}(D_2O)_n + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{OD} + \text{Cl}^{-}(D_2O)_n,
\]

where it should be noted that several different reaction products are possible. Here, it is found that the reaction OD\(^{-}\) + CH\(_3\)Cl, with no solvating water molecules, does have an experimental rate constant only slightly above that predicted from the rotationally adiabatic capture theory; however, the experimental rate constants fall well below the theoretical values for the reactions of the OD\(^{-}\)(D\(_2\)O) and OD\(^{-}\)(D\(_2\)O\(_2\)) species.

These results are explained through \textit{ab initio} calculations of potential energy surfaces that have been performed for these reactions (64). These calculations show that there are secondary barriers in the short-range region of the potential energy surfaces that increase in height with increasing number of D\(_2\)O molecules. These secondary barriers arise because the nucleophilic displacement reaction requires the sequential mechanism of attack of the CH\(_3\)Cl molecule by the OD\(^{-}\)(D\(_2\)O\(_n\)) unit at the end of the molecule opposite to the Cl atom, the inversion of the CH\(_3\) group to enable the OD\(^{-}\) to bond to the C atom, and the dissociation of the Cl\(^{-}\) ion. There is a barrier in the potential energy surface associated with the inversion of the CH\(_3\) group, and the height of this barrier increases with the number of solvent D\(_2\)O molecules, which cause steric hindrance. With an increasing number of solvent molecules, quite a large activation energy is produced,
and the long-range region of the reaction then becomes unimportant. This will be the general case for most reactions of ions in solution.

**Reactions of Ions with Non-Polar Molecules**

Most of the reactions discussed above involve dipolar molecules, but it is interesting to consider the reactions of ions with non-polar molecules. Here, if only the ion-induced dipole interaction is considered, the capture rate constant is given by Langevin form (65, 66)

\[ k_L = 2\pi(\alpha/\mu)^{1/2} \]

where \( \alpha \) is the polarizability of the molecule. Note that this predicts no temperature dependence of the rate constant. If the ion-quadrupole interaction is also included, then a very slight \( (T^{-1/6}) \) negative temperature dependence is predicted from a simple capture theory such as the average quadrupole orientation approximation (AQO) (9) and more sophisticated theories such as the adiabatic invariance method (36). These theories suggest that the ion-quadrupole effect will only become significant at very low temperatures.

To see whether these predictions hold, some CRESU experiments were performed (67) on the reactions of \( \text{He}^+ \), \( \text{C}^+ \), and \( \text{N}^+ \) with \( \text{C}_6\text{F}_6 \) and \( \text{c-C}_6\text{H}_{12} \), at 27 and 68 K. SIFT experiments were also carried out at 300 K on the same reactions (67). These molecules were chosen because they have very large quadrupole moments. It was found, however, that the measured rate constants were close to the Langevin values and did not show the small temperature dependence predicted from theory (9, 36). It is possible that the experiments would have to be performed at temperatures lower than 27 K to observe the temperature dependence significantly. To examine this point, CRESU experiments were performed (68) on the reactions of \( \text{He}^+ \) with \( \text{N}_2 \), \( \text{O}_2 \), and \( \text{CH}_4 \), and \( \text{N}^+ \) ions with \( \text{O}_2 \), \( \text{CO} \), and \( \text{CH}_4 \) for the lower temperature range of 28, 20, and 8 K. Yet again, no temperature dependence was observed in the rate constants. Although these non-polar molecules do not give rate constants that agree perfectly with theory, the temperature effects are much smaller than those observed for the ion-dipole case, and it might be necessary to go to temperatures lower than even 8 K to see a significant effect.

It should be mentioned here that there are problems in applying capture theory to the fast reactions of large polyatomic molecules. This is because these theories consider the reacting molecules to be point dipoles or point quadrupoles with the origin at the center of mass of the molecule. It is possible that the molecule becomes so large that the centrifugal barriers in the potential calculated from capture theory for higher energies are
actually in the repulsive region of the real potential energy surface. Considerations such as these put a question mark over the application of capture theory to larger molecules (41). A study on the reactions of $N^+$ ions with the three geometric isomers of $C_2H_2Cl_2$ emphasizes this point (69). Here it was found that the rate constant for the non-polar trans isomer of $C_2H_2Cl_2$ agreed with the Langevin rate coefficient measured in CRESU experiments at 27, 68, and 163 K, and with SIFT experiments at 300 K. However, although the measured rate constants for the polar isomers of $C_2H_2Cl_2$ did have a negative temperature dependence, their absolute values were about half that predicted from the rotationally adiabatic capture theory, although still within the range $k_c > k > f k_c$.

A recent paper in which a novel free jet expansion flow reactor was used reports the measurement of rate constants for reactions such as $C^+ + O_2$ for temperatures down to 0.6 K (70). The rate constant reported for the $C^+ + O_2$ reaction, however, was a factor of two larger than predicted from the adiabatic invariance theory (36). Even at this low temperature, it is difficult to find a mechanism that will enable a measured rate constant to be larger than that predicted by capture theory that includes a proper treatment of all the molecular moments and the anisotropy of the polarizability. Indeed, the comparison of the capture theory rate constants with experiment for the 34 reactions of $C^+$ and $N^+$ justifies this statement further (58). Given the dramatic improvements in the experimental techniques for measuring rate constants at very low temperatures, the rate constants calculated from capture theory should provide useful bounds and checks on those being measured.

**Predictions on Ion-Molecule Reactions**

One of the most interesting predictions that has arisen from several of the capture theories for ion-dipole reactions is that the rotationally selected rate constants $k_j$ decrease significantly as $j$ is increased for a given temperature (24, 27, 32). This is illustrated in Figure 5, where the $k_j$ are plotted for the $N^+ + NH_3(j, k = 0)$ reaction with a potential described by an ion-dipole plus an ion-induced dipole term (25). These results were computed with the rotationally adiabatic capture theory. Also shown in the Figure is the rate constant $k$, which is obtained by Boltzmann averaging over the $k_j$. It can be seen that $k$ has a stronger negative temperature dependence than any of the individual $k_j$. This is because the Boltzmann average brings in higher values of $j$ as the temperature is increased, and the $k_j$ decrease significantly as $j$ is increased. Thus, the strong negative temperature dependence of $k$ is intimately connected with the dependence of $k_j$ on $j$ (14). Physically, the decrease in $k_j$ on increasing $j$ is related to the fact that the ion-dipole potential forces a collinear geometry for the reaction, and initial
rotational angular momentum in the molecule makes it harder for this collinear geometry to be achieved.

Although there is excellent agreement between the theoretical and experimental rate constants \( k \) for temperatures down to 27 K for several ion-dipole reactions, there have been no measurements as yet of cross sections or rate constants selected in the initial states of the reactant molecule \( j \) for these reactions. The theoretical predictions present a clear and exciting challenge to experiment.

Another interesting prediction that remains to be verified in experiments on ion-molecule reactions is the limit of \( k \) as the temperature \( T \) approaches zero. Of course, in this limit the molecule will be in the \( j = 0 \) state and \( k_{j=0} = k \). Tröe applied the statistical adiabatic channel model to this limit for an ion-dipole reaction (32). His approach involves, essentially, obtaining analytical approximations to the rotationally adiabatic potential energy curves. For very low collision energies, the centrifugal barrier in the potential will occur at very large \( R \) values (\( > 100 \) Å). As the interaction potential is so weak at these \( R \) values, second-order perturbation theory is applicable for ion-linear dipole reactions. Then the \( 1/R^2 \) dependence of the ion-dipole interaction potential

\[
V(R, \theta) = -\mu_D \cos \theta/R^2
\]

provides a \( 1/R^4 \) dependence in the rotationally adiabatic potential with
the centrifugal \( J(J+1)/(2\mu R^2) \) term subtracted. Here, \( \mu_D \) is the dipole moment of the molecule and \( \theta \) is the orientation of the ion-dipole center of mass vector \( \mathbf{R} \) with respect to the direction of the dipole. In turn, this produces a rate constant that tends to a temperature independent function for very low \( T \). The formula derived by Tröe (32) is

\[
k(T \to 0) = 2\pi(\alpha/\mu)^{1/2}[1 + \mu_D^2/(3\alpha B)]
\]

where \( B \) is the rotor constant. Note that this formula contains a simple addition to the Langevin rate constant \( k_L \) that depends on the square of the dipole moment. With the rotationally adiabatic theory, we have verified the accuracy of the Tröe formula for the low temperatures between 0.1 and 1 K for the \( \text{H}_3^+ + \text{HCN} \) system (71). These new calculations also confirm that some computations we reported previously (24) for the \( \text{H}_3^+ + \text{HCN} \) reaction do not extrapolate down accurately to the very low temperature range (72).

For all except extremely low temperatures, so many angular momenta contribute to the cross section with unit reaction probability that tunneling through the centrifugal barrier for one extra classically forbidden angular momentum with a small probability will not contribute significantly to the cross section. In the limit very close to zero collision energy, however, even the \( J = 1 \) angular momentum will give a classically forbidden reaction probability, and the \( J = 1 \) partial wave has a weight of 3 compared to the \( J = 0 \) partial wave, so tunneling through the centrifugal barrier becomes important in this limit.

Vogt & Wannier analyzed analytically the quantum mechanical limit for \( E \to 0 \) of the cross section for the ion-induced dipole potential and found it to be exactly twice that obtained in the classical Langevin formula (73). This suggests that for extremely low temperatures, the Tröe formula for ion-dipole reactions is incorrect and should be multiplied by 2, as indeed should the Langevin formula. In the region where quantum effects are not important, however (i.e. when reaction with \( J > 0 \) is classically allowed), and where second-order perturbation theory is still applicable, the Tröe formula should be accurate. In practice, the temperature range for which this formula is valid will depend on the parameters for the problem, including the reduced mass, polarizability, dipole moment, and rotational constant.

As far as we are aware, the range of applicability of the Tröe formula has not yet been tested by using an accurate quantum theory that includes both tunneling and rotational coupling. Such calculations are hard to perform due to the very low collision energies that are required in the calculations. Given the recent experimental advances in trapping atoms, molecules, and ions at extremely low temperatures, it will be very inter-
testing if these experiments can be extended to the measurement of rate constants for ion-dipole reactions in the limit of \( T \to 0 \).

A formula for the rate constant of the exothermic reactions of electrons with dipolar molecules has been derived analytically by using a rotationally adiabatic quantum theory that incorporates tunneling (39). Here, simplifications arise compared to the ion-dipole interaction, as only one rotationally adiabatic potential curve becomes attractive due to the enormous bending zero-point energy in the electron-dipole complex that results from the very small mass of the electron. For molecules with large dipole moments and large rotor constants, the electron-dipole rate constant is predicted to depend on \( B^{1/2}/T \) for low temperatures (39). Unfortunately, there are not many reactions of electrons with molecules having large dipole moments that are exothermic, although the reactions of highly vibrationally excited HF or HCl with electrons should be good experimental candidates for illustrating this novel temperature effect.

CAPTURE CALCULATIONS FOR FAST NEUTRAL REACTIONS

There have also been many calculations of the rate constants for fast reactions of neutral species; however, the comparisons with experimental data have not been so outstanding as those for ion-molecule reactions. There are several reasons for this. First of all, it is much harder to measure accurate values for the rate constants for fast neutral reactions, as mass spectrometer techniques cannot normally be used to measure accurately the concentration of the reaction species. Furthermore, most fast neutral reactions involve two radicals, both of which have to be produced and detected.

From the point of view of theory, fast neutral reactions are further complicated by the fact that both reacting radicals can be open-shell species with non-zero electronic orbital angular momentum and the number of potential energy surfaces involved in the problem can be large (14). Furthermore, the long-range forces for neutral species are not so dominant as those for ion-molecule reactions, and short-range forces will be more important. Despite these drawbacks, the capture theory has provided some useful new results for the temperature dependence of fast neutral reactions.

The accurate close-coupled quantum theory has been applied (37) to the reaction,

\[
O(3P) + OH \rightarrow O_2 + H
\]

reaction, with a quadrupole-dipole potential, and gives cross sections in excellent agreement with those calculated by the rotationally adiabatic theory. The rate constants calculated for this reaction are also in quite
good agreement with experiment (74, 75). This reaction is important in both combustion (33) and interstellar chemistry (74). Several other capture theories that have been applied to this reaction also give good results. For example, Varandas has developed a classical capture theory that includes recrossing of the trajectories back to the reactants and uses a potential energy surface based on ab initio data connected to a long-range potential (76). Furthermore, Phillips has developed a simple analytical classical capture theory that includes parameterized short-range effects. This approach gives promising comparisons with experiment not only for the O + OH reaction but also for a range of fast reactions, including neutral and ionic species (45–47). Also, Markovic et al have applied a modified transition state theory to this reaction (50).

Graff & Wagner have given a careful analysis of the spin-orbit effects for the O + OH reaction that enables the IOSA capture theory to be extended to fast reactions of open-shell atoms (77). As has also been discussed by Graff (78), the negative temperature dependence of the rate constant for this reaction is largely connected with the population of the spin-orbit levels of the O(3P) atom. The atomic level with lowest energy, \(^3\)P\(_2\), has the largest quadrupole moment and hence has the largest cross section. Thus, the population of higher spin-orbit states for larger temperatures will produce a negative temperature dependence in the Boltzmann averaged rate constant (37) in a way analogous to that predicted for ion-dipole reactions where the rotational state dependence of the rate constant is important (24). Since the C(3P) atom has the level \(^3\)P\(_0\) as the lowest energy state, and this state has a zero quadrupole moment, the fast reactions of C(3P) are expected to be much slower than those for O(3P). These results have implications for interstellar chemistry (78).

For the interaction of two dipolar molecules, the IOSA gives a slight negative temperature dependence \((T^{-1/6})\) in the reaction rate constant (14). These results are in good agreement with those calculated with a theory in which the IOSA is used for one of the molecules and the coupled states approximation, which explicitly couples the rotational states in a basis set, is used for the other molecule (14, 79). Several fast reactions between dipolar molecules do give a slight negative temperature dependence in the measured rate constants (1). Interestingly, the rotationally adiabatic theory for dipole-dipole reactions gives individual \(k_j\) that increase with increasing temperature, in contrast to the ion-dipole case. The \(k_j\), however, decrease with increasing \(j\) for a fixed temperature, and this produces a decrease with increasing temperature in the rate constant \(k\) obtained by Boltzmann averaging over the initial \(j\) states. This is illustrated in Figure 6, where the rate constants \(k_j\) and \(k\) for the SO + OH\((j)\) reaction are plotted against temperature (79). Thus, analysis of the rotationally selected rate constants
once again gives new insight into the negative temperature dependence of
the rate constants observed for many fast reactions.

To achieve agreement of theory with measured absolute values of the
rate constants for these types of neutral reactions, however, a very careful
analysis of the electronic states involved will be needed. This will probably
require detailed \textit{ab initio} calculations of the different potential energy
surfaces for individual reactions, as was the case for the reactions of C$^+$
and N$^+$ discussed above. Furthermore, it might also be necessary to
calculate the non-adiabatic matrix elements for transitions between the
potential energy surfaces. It will then be possible to apply the quantum
close-coupling capture theory (14) to the calculation of reaction cross
sections state selected in the initial electronic and rotational states of the
reactant molecules.

**ISOTOPIC BRANCHING RATIOS FOR HD REACTIONS**

A major disadvantage of all the capture theories discussed above is that
they give no information on the products of the chemical reactions, as the
computed rate constants refer to a sum over all product states. Recently,
the rotationally adiabatic capture theory has been extended to calculate the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Rotationally selected rate constants, $k_j$, for the SO + OH($j$) dipole-dipole reaction calculated by using the rotationally adiabatic capture theory (14, 79). Also shown is the rate constant, $k$, obtained by Boltzmann averaging over the $\{k_j\}$.}
\end{figure}
isotopic branching ratio $F$ for the $O^+ + HD$ reaction (80). If the reactions

$$O^+ + HD \rightarrow OH^+ + D$$

and

$$O^+ + HD \rightarrow OD^+ + H$$

have cross sections $\sigma(OH^+)$ and $\sigma(OD^+)$, respectively, for a given temperature of HD, then we have $F = \sigma(OH^+)/[\sigma(OH^+) + \sigma(OD^+)]$. Highly accurate cross sections for both of these reactions have been measured as a function of collision energy with a guided ion beam mass spectrometer apparatus (81).

The dominant interaction here in the reactant channel is ion-quadrupole. The theory involves partitioning the hindered rotor wavefunction of the $[OHD]^+$ complex at the centrifugal barrier in the $O^+ + HD$ rotationally adiabatic potential curves for each value of $J$, and associating each partition with the $OH^+$ or $OD^+$ product channel (80, 82–84). Since the center of mass of HD is not equidistant between the H and D atoms, this gives an isotopic branching ratio that is not equal to 0.5. The agreement between this theory and experiment of the cross sections for reactions forming $OH^+$ and $OD^+$ is excellent, as is shown in Figure 7.

The theory also predicts an interesting temperature effect (80). It is found in the calculations that the rotationally selected isotopic branching ratio $F(j)$, where $j$ is the initial rotational state of the HD molecule, decreases significantly as $j$ is increased. This implies that $F$ will be larger for low temperatures of the HD molecule than for high temperatures, as the Boltzmann average over $j$ brings in higher $j$ states for larger temperatures. This effect is quite pronounced due to the large rotational spacings in HD. Recently, an experiment was carried out to test this prediction (85). The isotopic branching ratio $F$ of the $O^+ + HD$ reaction was measured for different temperatures of the HD molecule, and perfect agreement was obtained with the prediction (80). All of these results suggest that the capture theory can, in special cases, be modified to give reliable product-state information. Clearly, it will be worthwhile exploring the possibility of extending the rotationally adiabatic theory to the calculation of branching ratios for other types of chemical reactions.

**DETECTION OF ROTATIONALLY ADIABATIC POTENTIAL CURVES**

It should be clear from many of the above results that the rotationally adiabatic theory provides good results for fast reactions. This theory
assumes that each initial rotational state has its own rotationally adiabatic potential energy curve on which the reaction proceeds. This suggests at once that it might be possible to detect the rotationally adiabatic curves directly by spectroscopy on the complex formed in the reaction. Indeed, it is possible to prepare ion-dipole complexes (86, 87). The number of rotationally adiabatic potential curves for these complexes is enormous, however, and the spectroscopy will be very complicated (88).

One interaction that gives rotationally adiabatic potential curves of a particularly simple form is the electron-dipole interaction (39). As has been explained above, only one of the $j$-labeled curves becomes attractive for each value of the total angular momentum $J$, with all other curves being repulsive. This implies a very simple spectroscopy for electron-dipole complexes (89). This is illustrated in Figure 8, which presents some rotationally

---

**Figure 7** Cross sections for the O$^+$ + HD reactions forming OH$^+$ and OD$^+$. The triangles refer to rotationally adiabatic capture calculations (80) and the dotted line gives fits through the experimental data points (81). $E_c$ is the collision energy, and the temperature of the HD molecule is 305 K.
adiabatic potential curves for the $e^- + \text{CH}_2\text{CN} (j, k = 0)$ interaction. Furthermore, as is indicated in Figure 8, the one attractive rotationally adiabatic potential curve can also hold shape resonances, the lifetime of which is controlled by the width and height of the centrifugal barrier through which the electron must tunnel. For the interaction of electrons with linear or symmetric top molecules in their ground vibrational states, there is a maximum of one of these shape resonances for each pair of $(J, k)$ values (89), where $k$ is the symmetric top projection quantum number along the symmetry axis.

High-resolution spectra for the photodetachment of electrons from dipolar anions have been measured by Lineberger and coworkers (90–93). They have concentrated on molecules with large dipole moments and systems such as $\text{CH}_2\text{CN}^-$ and $\text{CH}_2\text{CHO}^-$ have produced particularly well-resolved rotational structure in the threshold region of the photodetachment spectra (90–93). These spectral lines show the normal
rotational spacings expected for the parent radicals. The linewidths show interesting patterns, as they are almost independent of the symmetric top projection quantum number $k$ for CH$_2$CN$^-$ but broaden significantly as $k$ is increased for CH$_2$CHO$^-$. 

The rotationally adiabatic theory gives a very clear picture for the origin of the structure in these photodetachment spectra and also provides quantitative predictions of the relative line positions and widths (89). For CH$_2$CN$^-$, each peak observed in the photodetachment spectrum corresponds to a shape resonance on the rotationally adiabatic potential curve for a particular value of $J$. Analytical approximations for these rotationally adiabatic potential energy curves also show that the shape resonances have energies that vary directly with the rotational energy of the parent CH$_2$CN radical, in agreement with experiment (91). Furthermore, this approximation also shows that the linewidths for CH$_2$CN$^-$ will increase with $J$, but are independent of $k$, which is also the experimental finding.

Unlike CH$_2$CN, CH$_2$CHO is not a near symmetric top molecule, and $k$ is not a good quantum number. This enables Feshbach resonances to occur corresponding to transitions from one rotationally adiabatic curve labeled by $(J,k)$ to one labeled by $(J,k-1)$, as shown in Figure 9. A perturbation theory analysis of this transition leads to a formula for the linewidth of the Feshbach resonance that depends on $(a-b)^2(2k-1)^2$, where $a$ and $b$ are rotor constants (89). This $k$ dependence of the linewidths agrees well with the experiment (91). Furthermore, the $(a-b)^2$ dependence suggests that the linewidths for photodetachment in CD$_2$CDO$^-$ will have magnitudes about a third of those for CH$_2$CHO$^-$. This prediction has recently been confirmed in experiments (92).

The rotationally adiabatic theory for photodetachment of dipolar anions has recently been extended by Simons (94), who developed a method that enables non-adiabatic transitions to occur between different rotationally adiabatic potential energy curves in the long-range region of the electron-dipole interaction. This gives linewidths for the photodetachment of CH$_2$CN$^-$ in even better agreement with experiment.

It is also interesting to make predictions on the photodetachment spectra when the dissociation rate of the electron can be enhanced by temporary vibrational excitation of the negative molecular ion during the photodetachment process (95). This is an equivalent process to vibrational predissociation of van der Waals molecules (96). An analytical theory has been developed for this problem based on the crossing of an attractive rotationally adiabatic curve for the vibrationally excited state with a repulsive curve for the ground vibrational state (95). It is assumed that the vibrational dependence of the dipole moment of the parent molecule drives the transition between these curves through the electron-dipole interaction.
This enables a simple Franck-Condon theory to be used to derive a formula for the photodetachment linewidth (95). An interesting prediction from this formula is that, for large values of the total angular momentum \( J \), the line widths decrease with increasing \( J \). This finding is in agreement with recent experimental results on the photodetachment of PtN\(^-\) (93), where measurements of spectra with isotopically substituted species showed that the PtN\(^-\) is vibrationally excited during the photodetachment process.

Given the fact that the rotationally adiabatic potential energy curves have now been detected in the spectroscopy of negative ions, it is also interesting to attempt to detect them in the spectroscopy of neutral species. Many of the complexes that are intermediates in neutral fast reactions will give very complicated spectra. It is worth mentioning, however, that the rotationally adiabatic potential curves have been useful in interpreting the spectra of simple van der Waals molecules such as ArHCl, ArHF, ArOH, and H\(_2\)HF (97–100), which are weakly bound through the long-range intermolecular forces. Indeed, a method was recently developed for invert-
ing high-resolution infrared spectra of van der Waals molecules to yield the rotationally adiabatic potential curves directly (98).

**CONCLUSIONS**

The aim of this review has been to illustrate the rich interaction that exists between theory and experiment in the kinetics of fast reactions in the gas phase. This interaction has stimulated a wide range of new experimental research, including the measurement of rate constants for reactions involving both ionic and neutral species at temperatures lower than had been the case before, the determination of the temperature dependence of isotopic branching ratios, and the measurement of spectra for the photodetachment of electrons from dipolar anions. In all of these cases, it was the unexpected predictions from theory that provided the incentive for the new experimental work.

Theory is so powerful in this field for several reasons: The relevant part of the interaction potentials are often known from the classical electrostatic interactions; only the entrance reactant channel of the problem needs to be considered in dynamics calculations; and calculations on polyatomic and molecule-molecule reactions are straightforward. Furthermore, the simple rotationally adiabatic potential energy curves provide clear explanations of many of the experimental results. These curves are derived from rigorous quantum mechanics and are obtained just by diagonalizing the interaction potential with a set of rotational basis functions. They reduce the problem to one of solving the dynamics for a range of one-dimensional potentials that retain the state-selectivity in the initial rotational states, and they provide a simple picture of the long-range dynamics. Furthermore, they enable quantitative calculations to be carried out on a wide range of processes. Indeed, it is now possible to detect the rotationally adiabatic potential curves directly in spectroscopic experiments. It is the strong anisotropy in the potential energy surfaces that often arise for fast reactions that produces the widely spaced, rotationally adiabatic potential curves that enables them to be applied so generally.

Several predictions from the theory of fast reactions will be a major challenge to experiments in the future. There have been no accurate measurements yet of the rotationally selected rate constants, $k_j$, for fast reactions, and the predicted strong decrease of $k_j$ with increasing $j$ for ion-dipole and dipole-dipole reactions remains to be confirmed in experiments. Furthermore, interesting results will be obtained if rate constants can be measured at temperatures very close to 0 K for ion-molecule reactions. Unusual temperature dependences are also likely to be observed if the rate
constants for the fast reactions of neutral species can be measured at lower temperatures.

The study of fast reaction kinetics in the gas phase is now established as a field on its own that requires new concepts, new theories, and new experimental methods as compared to those used for more traditional reactions with activation energies. This advance has come about through the development of methods for detecting very reactive species and through the formulation of theories that can make realistic predictions that challenge the experiments.

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