

TRANSITION STATE THEORY AND EXPERIMENTS IN CHEMICAL REACTIONS

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1. Introduction

The transition state theory of chemical reactions has proven to be a formidable tool for analyzing chemical reaction rates of a wide variety of reactions. In the present article some of its developments, extensions, and applications are described.

Transition state theory was developed in its current form by Eyring¹ and Evans and Polanyi² in 1935, only about a half a dozen years after the quantum mechanical description of potential energy surfaces by London³ for chemical reactions. The advances in the understanding of the dynamics in the 1930s were rapid, particularly by Hirschfelder, Wigner, and O.K. Rice, among others. A number of the problems, concepts, and themes that are currently discussed were considered at that time, and even some classical trajectory calculations were made then by Hirschfelder.

There was another thread in chemical reaction rate theory, unimolecular reaction rate theory, which developed earlier in the 1920s, the initial work being that of Hinshelwood,⁴ followed by the more detailed theory of Rice and Ramsperger⁵ and of Kassel,⁶ which became well known as the RRK theory. That theory was applied to and stimulated extensive experiments on the unimolecular decomposition of organic molecules during the 1920s and early 1930s. However, such experiments revealed that those reactions had complex mechanisms: They were found to proceed via a series of elementary steps involving free radicals as intermediates, rather than occurring in a single step. A new field of study, reaction rates and mechanisms, and later the direct spectral observation, of gas phase free radicals was born. The use of unimolecular theory went into decline—there were practically no systems to which it could be applied and which could stimulate its further growth. During 1939-45 there was a general lull, however, in all these activities because of the Second World War.

Interest in unimolecular theory resumed in the late 1940s with N. B. Slater's⁷ sophisticated and exciting extension of earlier ideas of Polanyi and Wigner and Peltzer.⁸ His work was based on treating the decomposing or isomerizing molecule as a collection of harmonic oscillators. The neglect of the effects of anharmonic coupling, and the results of various incisive experiments, led later to its abandonment as a method for

treating the emerging experimental data on these reactions. Nevertheless, it introduced new and refreshing ideas into the field.

In 1949, as a postdoctoral with O.K. Rice, I blended ideas drawn from transition state and RRK theories and formulated a molecular structure-based statistical theory for these reactions.⁹ The time was ripe for this development. New molecular ideas, such as potential energy surfaces, had developed only after RRK theory had been formulated, and post-war research was beginning to flourish. My own interest stemmed from the experimental work I had done on the unimolecular decomposition of the $\text{CH}_3\text{OCH}_2^\bullet$ free radical^{10a} and on the recombination of methyl radicals^{10b} in the laboratory of E.W.R. Steacie in Canada.

This unimolecular theory, known since the 1960s as RRKM theory, is in current use today.¹¹ To treat reactions for which the reverse reaction of bimolecular association has no energy barrier, the defining the position of the transition state (TS) becomes a problem. A variational form of the theory was subsequently developed to determine the TS,¹² and has been extensively applied.

In the present paper I comment on a number of types of reactions investigated with transition state theory and on some of the features which arise when specific aspects of the reaction or of the potential energy surfaces are introduced. They include electron transfers, energy dependence of unimolecular reaction rates in the gas phase, unimolecular reactions in clusters, including solvent dynamics, global contour plots for reactions, $\text{S}_\text{N}2$ reactions, and extensions of transition state theory which include, in addition to reaction rates, the distribution of quantum states of the reaction products of unimolecular dissociations. In the latter we again consider dissociations in which there is no energy barrier for the reverse reaction, the recombination of the fragments.

A striking feature in this history is that some sixty years after the development of transition state theory it continues to be a useful tool for chemists, to which additional concepts can be added. The field of chemical reaction rates itself has been stimulated by the new types of data which are becoming available with ultrafast techniques, as well as by the earlier classical techniques applied to interesting systems.

2. The transition state

2.1 Early developments and Wigner's no recrossing criterion

We recall briefly the formulation of TS theory, in which a quasi-equilibrium was assumed between reactants and the transition state.^{1,2} This quasi-equilibrium was mysterious, unsatisfying, and probably caused chemical physicists who later entered into the dynamics field in the 1950s and 1960s to be dubious about the theory. However, in 1937-1938 Wigner had pointed out that in a classical description the quasi-equilibrium

condition could result directly from the classical dynamics instead of being an *ad hoc* assumption.¹³

This idea of Wigner's is a consequence of Liouville's theorem: Suppose we consider a set of trajectories, each with an energy in $(E, E+dE)$, occupying some "tube" in phase space that passes through the TS hypersurface in the forward direction. Suppose further that these trajectories are traced backward in time to the phase space region occupied by the reactants and that none recross the TS. The density of phase space points is constant along this streamline (Liouville's theorem). Suppose that many other "tubes" of trajectories, each with energy in $(E, E+dE)$, are considered, so that the ensemble of all of these tubes passes through every part of the TS hypersurface lying in $(E, E+dE)$, and that none recrosses the TS hypersurface. In that case the density of points in $(E, E+dE)$ on TS hypersurface is the same as the density of points in the part of the reactants' region which is reached by the backwards-in-time trajectories. If the reactants' region has an equilibrium density of points in phase space, the forward traveling points on the TS hypersurface must also therefore have an equilibrium population. Thus, the no-recrossing of the TS hypersurface, in conjunction with the equilibrium distribution in the reactants' region, implies an equilibrium distribution on the TS hypersurface, as a consequence of Liouville's theorem. Such is Wigner's idea.

For many reactions the TS can be or has been defined in terms of a hypersurface in the coordinate part of phase space. One simple example is that of a reacting system whose potential energy surface has a saddle-point about which it can be expanded harmonically. One of its curvatures is negative, namely the one corresponding to the reaction coordinate. The TS is a multidimensional plane (hyperplane) perpendicular to this coordinate and passing through the saddle-point. Examples exist, given later, where the TS hypersurface also involves momentum-like variables because of the dynamics, e.g., either because of adiabaticity or of centrifugal effects. The TS hypersurface then crosses momentum axes in the phase space, rather than being independent of them.

Although Wigner's 1938 article was itself frequently cited in the literature (it was part of a celebrated Faraday Discussion), this particular and not very prominent feature went unnoticed until called to the community's attention by J.B. Anderson¹⁴ in the mid 1970's. Anderson used and tested it, initially to some skepticism, by making classical trajectory calculations which began at the TS instead of at the reactants.^{14,15} In reactions for which the reaction probability is small, this procedure reduced the computer time considerably.

Wigner's idea on the definition of the TS hypersurface also gave rise to a classical variational TS theory.^{15,16} The hypersurface with the least flux crossing it has, it can be shown, the fewest recrossings and so is the best hypersurface. Quantum variational theory (choosing a TS with the lowest quantum-calculated rate)^{1b} has been extended and extensively applied in recent years.¹⁷

The study of TS theory also had, as undoubtedly do other areas, its unusual moments. For example, several well known early papers (1931-1932),¹⁸ including a famous one of Eyring and Polanyi (used in defining the LEPS potential energy surface),

gave potential energy contour plots for the $\text{H}+\text{H}_2 \rightarrow \text{H}_2+\text{H}$ reaction, using the now standard mass-weighted skewed-axes coordinates, but with an obtuse angle instead of the correct and, after 1935, standard acute angle. As long as one did not study the mechanics (and trajectories) it was only a diagram and didn't matter. The correct angle was used by J.O. Hirschfelder in his Ph.D. dissertation,¹⁹ where he thanks O.K. Rice for pointing out the error. This incident is in a sense characteristic of O.K. Rice. I remember vividly his especially careful analyses of problems, of which this one would be a trivial but not unimportant example. (Others in the early days include refs 20 [cf ref 21] which also bring out his special physical insight.) In those early days the classical dynamics on the potential energy surface was also explored by using mass-weighted coordinates and a physical model of the potential energy surface and rolling a ball on it.^{1b}

The analysis of Wigner mentioned above is classical, and one can inquire as to what a corresponding quantum description might be. One approach begins with the "vibrationally adiabatic" one, a term I introduced²² in 1965 but whose key concept was clearly known earlier to Hirschfelder and Wigner²³: one can see it in an almost buried paragraph of their well known 1939 article.²³ If the reacting system remains in the same quantum state for the remaining coordinates during its motion along reaction coordinate s from the reactants to the TS (and on to products' region), they recognized, TS theory would follow as a consequence. This idea was again enunciated in later papers by Hirschfelder and coworkers²⁴ and was rediscovered in a much more detailed and specific form by several of us,^{22,25,26} each unaware of that earlier paragraph. For vibrationally adiabatic systems there is clearly no recrossing of the TS, but the position of the TS occurs at the maximum of the energy for that quantum state along the reaction coordinate, and will differ from state to state. We return later to this state-dependent position of the TS, and describe its classical analog.

Some or most of the vibrations of the reactants or reactant may be largely vibrationally adiabatic in the TS region. In approximately thermoneutral reactions some vibrations may even be vibrationally adiabatic all the way from reactants to products. There have since been many tests of this now widely used concept, particularly in calculations, and also in some experiments. In highly exothermic reactions, on the other hand, the vibrations may be adiabatic from the reactants to the TS but then highly nonadiabatic afterward, i.e., change their quantum state significantly during the motion from the TS to the products, because of a large repulsive (downhill) force acting on the vibrations in the exit channel. Nevertheless, this subsequent post-TS motion is so downhill that the trajectories don't recross the TS, and the validity of TS theory (little or no recrossing of the TS hypersurface) remains unaffected by this nonadiabaticity. Further, for the reverse reaction, the rate can be calculated from TS theory, using an equilibrium constant and TS theory for the forward rate constant, even though there now is considerable vibrational nonadiabaticity *before* reaching the TS. We return to this point later. Another interesting and related theory, the statistical adiabatic channel model (SACM), is one in which all vibrations and rotations are treated as adiabatic.²⁷

2.2 Vibrational adiabaticity/nonadiabaticity and reaction Hamiltonians

I would like to consider in somewhat more detail the mechanics of this vibrational adiabaticity. Perhaps with ultrafast techniques the adiabaticity can be observed directly in real time, rather than only by experiments comparing the final vibrational quantum states with the initial ones. To explore the dynamics further theoretically, one needs to consider the time-evolution of a vibration during the reaction. For this purpose, a coordinate system appropriate to such a continuous description is needed, and it may then be used also to explore possible major departures from adiabaticity.

Such a coordinate system was introduced in my 1966 articles,²⁸ by adapting it from a coordinate system used in a physics text to describe the motion of a particle in an accelerator: In the adaptation a curve is drawn from the reactants' to the products' region in the mass-weighted skewed angle space, as in Figure 1. For example, in a potential energy surface contour plot, the curve could proceed along the valley of the reactants, over a saddle-point, and into the valley of the products. The coordinates of any point were obtained by drawing a perpendicular from the point to the curve. The (signed) distance of this perpendicular segment was the vibrational coordinate and the distance along the curve from any arbitrary point on it to the foot of the perpendicular was the reaction coordinate.

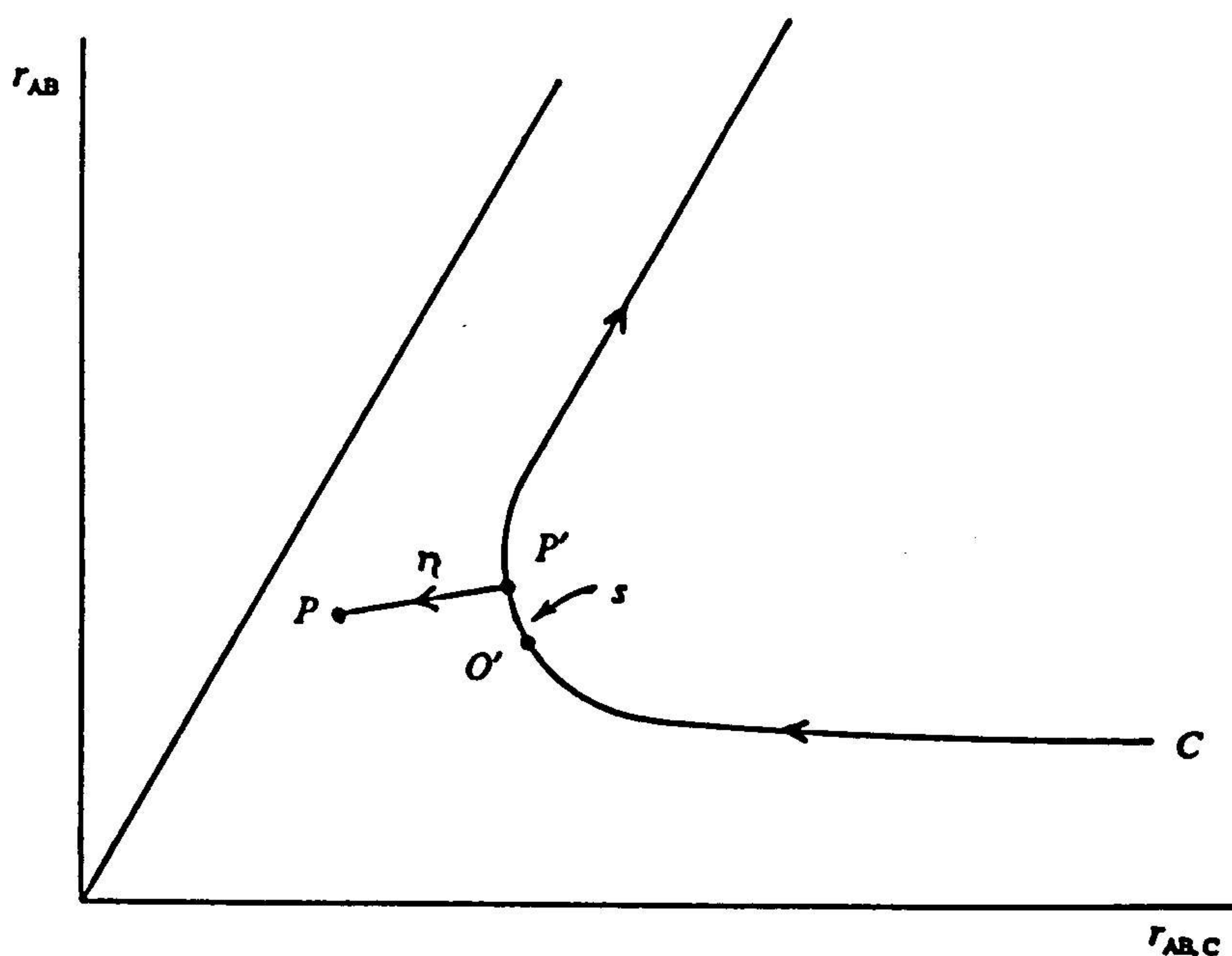


Figure 1. Coordinates (s , n) leading smoothly from reactants to products.²⁸

A Hamiltonian was then written and contained an internal centrifugal term, because of the curvature of the path.²⁸ The vibration of H_2 in the $H+H_2$ reactants smoothly became, with these coordinates, a symmetric stretching vibration of H_3 in the TS, and then became the vibration of the H_2 product. In this way vibrational adiabaticity could be defined throughout the reaction. Using the Hamiltonian one could also identify two sources of vibrational nonadiabaticity: A rapid change in vibrational frequency along the path induces changes in the vibrational quantum number, as does a large curvature of the path.²⁸ The analysis and the Hamiltonian were extended to three dimensions, using body-fixed axes with the appropriate internal (rotational-vibrational) coupling terms²⁹ and later, elegantly with more vibrational coordinates, to polyatomic molecules, by Miller, Handy and Adams,^{30a} omitting several rotational-vibrational coupling terms. They aptly termed it a reaction path Hamiltonian. Other developments are given in refs. 30b and 30c.

It should be noted that for some reactions, for example the transfer of a light atom between two heavy atoms, $AH+B \rightarrow A+HB$, the skewed-axis angle is so small that the path curvature becomes so large in the TS region and with it nonadiabatic transitions so great that a different starting approximation, and a different coordinate system is needed, instead, as a basis for a simple analysis. Polar coordinates,³¹ or for more than two internal coordinates (i.e., more than a linear description of a triatomic system) hyperspherical coordinates,^{32,33} are the appropriate ones to use, and an angle variable can be seen or shown to be, especially for a thermoneutral reaction, the reaction coordinate in the immediate vicinity of the TS. One can see this motion in a trajectory given in Figure 2. In a normal mode analysis of the AHB in the TS, this reaction coordinate at the TS would be the asymmetric stretching vibration. Hyperspherical coordinates have been extensively used in the well known and extensive numerical calculations of Kuppermann^{33a} and others. A detailed survey of the field is given by Manz.^{33b}

If the reaction were very exothermic, instead of being thermoneutral as in Figure 2, any sudden jump of the H from the reactants' to the products' valley would yield a highly vibrationally excited product: A "Franck-Condon" principle would be approximately applicable because of the difference in time scales of the H-motion and that of the heavy nuclei. An example is the formation of the vibrationally hot OH in the $H+O_3 \rightarrow HO+O_2$ reaction.

To see the connection between classical concepts, such as employed above by Wigner, and a quantum description, old quantum theory, or in its quantum mechanical version, Wentzel-Kramers-Brillouin (WKB) theory, or the corresponding many-coordinate semiclassical theory^{34,35} of the 1970's provides a key insight: The quantum number n corresponds to the classical action variable $\oint pdq$, q being a coordinate and p the corresponding momentum (e.g., $\oint pdq = (n + \frac{1}{2})h$ for a vibration). Adiabaticity of a vibrational coordinate corresponds to constancy of a vibrational action coordinate during the motion along the reaction path. The nature of the vibration can change considerably along the path, as we have seen in the $H+H_2$ reaction.

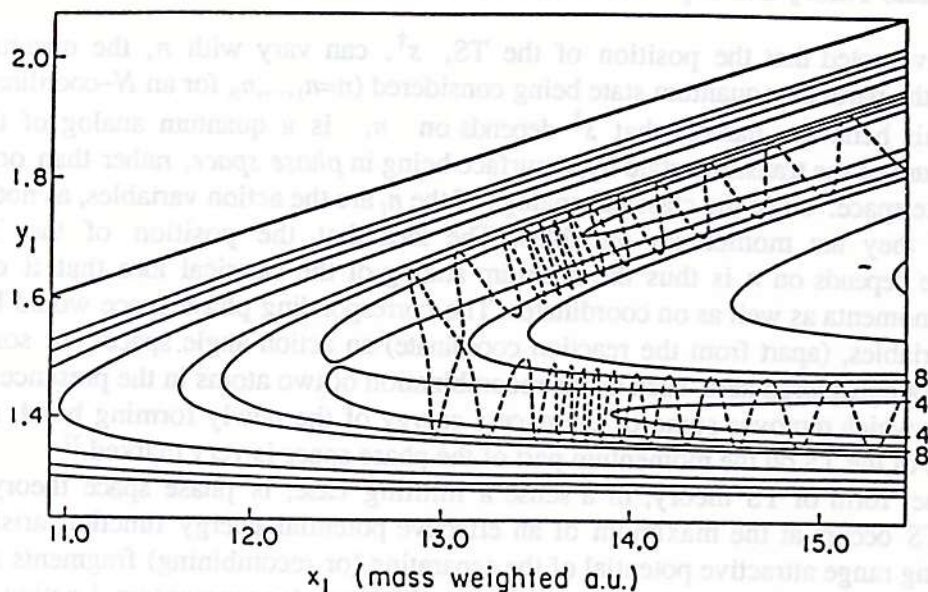


Figure 2. Classical trajectory for an H atom transfer.²⁴

The vibrationally adiabatic dynamics provides one way of translating Wigner's no recrossing idea from a classical to (apart from the reaction coordinate s) a quantum version. However, it has been shown that one need not have strict vibrational adiabaticity for this no-recrossing criterion to be satisfied:³⁶ An example above was one such illustration and, indeed, since adiabaticity was not required one would not expect it to be required in the quantum case. In general, vibrationally nonadiabatic transitions can occur at individual "avoided crossings" of the vibrational energy vs s curves for each vibrational quantum state, and there may be overlapping avoided crossings. However, as long as the individual avoided crossings do not occur at the TS, TS theory remains valid.³⁶

While vibrational adiabaticity may apply to some vibrations, particularly those of high frequency, it probably does not apply to very low frequency ones, for example to the hindered rotations in the TS which evolved from bending vibrations in the parent molecule during the dissociation. Their frequencies in the TS sometimes become roughly comparable with the reciprocal of the time for passage through the region near the TS, and in that case their behavior would be rather nonadiabatic. Indeed, almost statistical, behavior can then occur among that limited set of coordinates. Further, modes with low frequencies in the TS region could, as a first approximation, be treated classically. In that case, with a combination of Wigner's classical arguments applied to those coordinates and to the reaction coordinate, and with a vibrationally adiabatic model for the higher frequency coordinates at the TS, one can see how there could be no or few recrossings of the TS.

We have noted that the position of the TS, $s^\dagger$, can vary with n , the quantum number for the particular quantum state being considered ($n=n_1, \dots, n_N$ for an N -coordinate system). This behavior, namely that $s^\dagger$ depends on n , is a quantum analog of the general picture of the transition state hypersurface being in *phase space*, rather than only in coordinate space: since the classical analogs of the n_i are the action variables, as noted above, and they are momentum variables. The idea that the position of the TS hypersurface depends on n is thus the quantum analog of the classical idea that it can depend on momenta as well as on coordinates. The corresponding phase space would be, in these variables, (apart from the reaction coordinate) an action-angle space. In some reactions, not considered here, such as the recombination of two atoms in the presence of a third body which removes some of the excess energy of the newly forming bond, the dependence of the TS on the momentum part of the phase space is very marked.³⁷

Another form of TS theory, in a sense a limiting case, is phase space theory.³⁸ The PST TS occurs at the maximum of an effective potential energy function arising from the long range attractive potential of the separating (or recombining) fragments and a centrifugal potential. The latter depends on the orbital angular momentum l acting on the radial separation distance of the two fragments. Since l is a momentum variable (specifically an action variable) the position of the PST TS hypersurface depends, with this choice of variables, on both momenta and coordinates. There are no exit channel forces in PST other than the long range attraction and no torques.

Recently Klippenstein developed a method for finding the best TS hypersurface among a class of hypersurfaces.³⁹ (For example, should one use the length of the dissociating bond as the reaction coordinate, or the distance between the centers of mass of the two separating fragments, or some other distances, as the reaction coordinate?)

Experimentally there have been major developments in the unimolecular reaction field since its rebirth around 1960, depicted in Figure 3. One of these has been the time-resolved measurement of energy-dependent unimolecular rate constants $k(E)$, using a combination of molecular beams and picosecond lasers.⁴⁰ In this method molecules are excited to particular energies E , followed by internal conversion to the ground electronic state and dissociation from that state. The results showed that phase space theory was applicable in the immediate region of the threshold. At higher energies an inner TS becomes dominant. The data were treated with variational RRKM theory^{12c-12e} and, in the process two TS were identified variationally at any E , an inner TS and an outer TS, the PST TS.^{12d}

Indeed, the entire problem is also related to the "TS switching" concept which occurs in the treatment of the unimolecular dissociation of ions.⁴¹ The use of variational RRKM theory to calculate rates as a function of the vibrational energy of the dissociating molecule is depicted in Figure 4. The movement of the TS with increasing energy to shorter separation distances, being PST-like near the threshold, has been inferred in such work and in a number of other studies, cited in refs 12e and 41b. This effect is well illustrated in the bimolecular reaction of CN with O₂.^{39c}

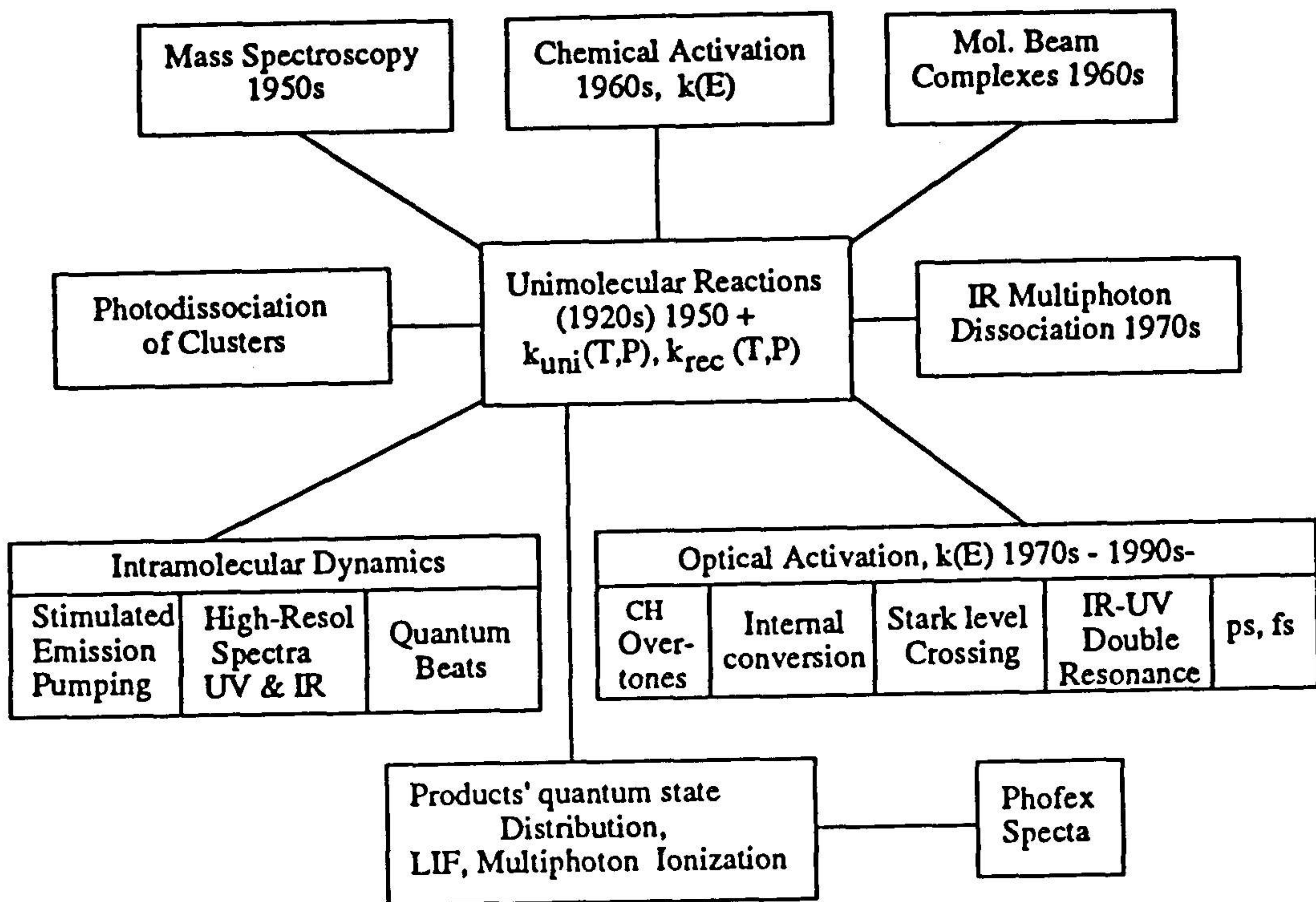


Figure 3. Developments in the field of unimolecular reactions since the late 1950s.

Another feature which has been incorporated into TS theory for some reactions is nuclear tunneling, particularly when an H is being transferred. Tunneling paths which "cut the corner" between reactants' and products' valleys in the skewed-axes potential energy surface and satisfy a least action principle, have been introduced.^{17,42} Nuclear tunneling has been incorporated into the flux expression for microcanonical systems by summing over nuclear tunneling factors in the state sum, instead of over states⁴³.

A new topic which has arisen involves the statistical fluctuations in rates from the RRKM value, both experimental and theoretical,⁴⁴ *when nuclear tunneling occurs*. Of particular interest next in ultrafast studies will be fluctuation in rates in the nontunneling region, due to inadequate mixing of states. Also of particular interest has been the step structure in rate *vs* E plots, accompanying the stepwise accessibility of new vibrational states of the TS.⁴⁵

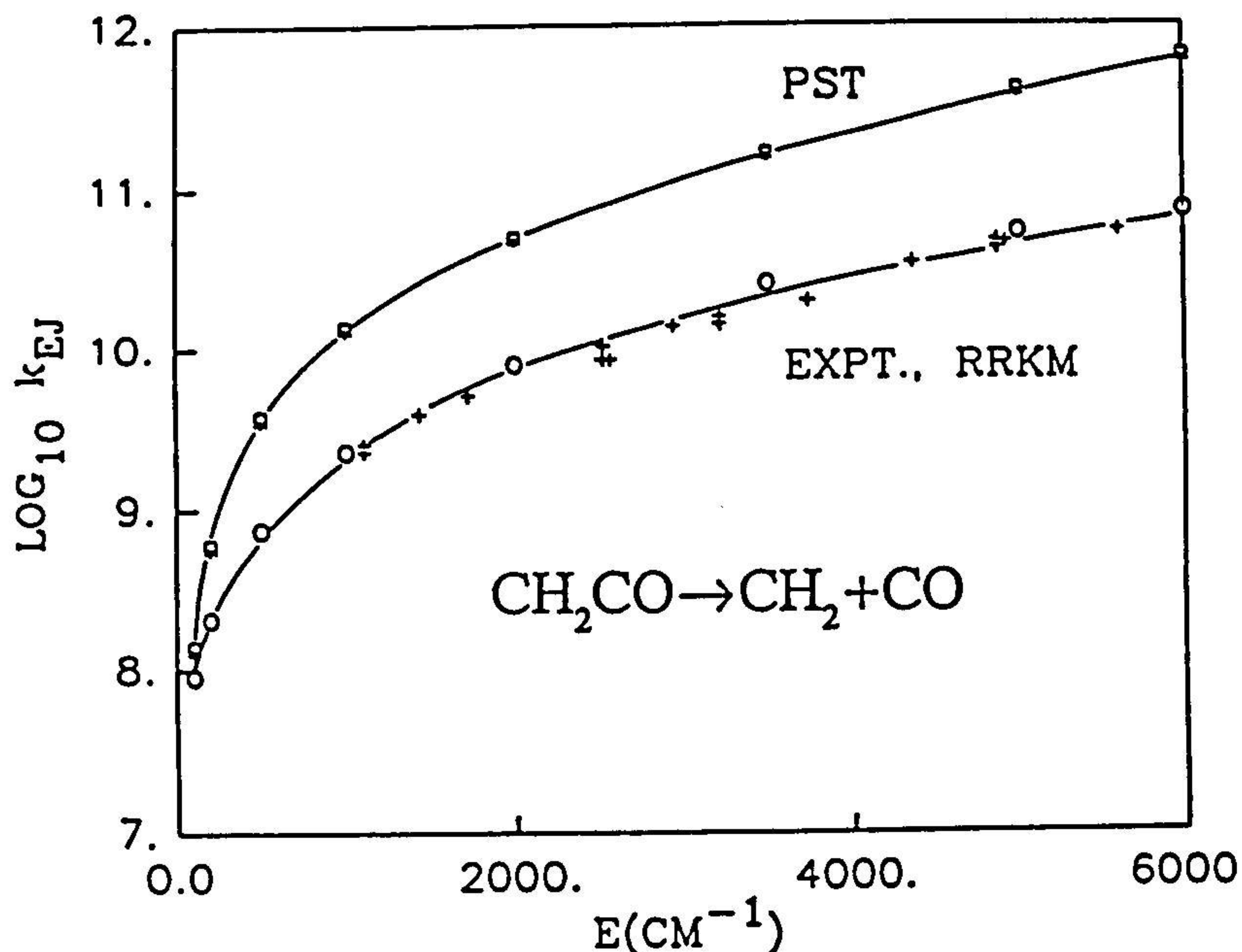


Figure 4. Unimolecular rate constant $k(E)$ vs E .^{12d}

2.3 Two questions. Quantum state distribution of products. Transient behavior

We next address the following questions.

1. Can one add some assumption to TS theory to predict the quantum state distribution of the reaction products of a unimolecular dissociation, in addition to its being a theory for the calculation of energy-dependent reaction rates?
2. When a dissociating molecule is hurtling down a potential energy repulsive surface to form products, do the intervening "states" satisfy the criterion for a transition state?

We consider the first, the distribution of quantum states of reaction products, for the case that there is no downhill force after passing through the TS, i.e., no "exit channel effect." The latter force would induce transitions in the vibrational states and, via torques, in the rotational states of the separating fragments, which become the reaction products. In the absence of this repulsive exit channel effect, the distribution of vibrational quantum states of the products should be similar to that which occurs in the TS. That is, such coordinates behave vibrationally adiabatically. However, for the lower frequency motions (hindered rotations) one expects changes of state between the TS and the phase space theory TS.

A dynamical approximation is needed to relate the distribution of the quantum states of the TS to those of the PST TS, through which the system subsequently passes en route to the dissociation. The distribution of the rotational-vibrational quantum states in the reaction products is then the same as that in the PST TS. In developing a treatment for the quantum state distribution of the reaction products we assumed that along the reaction coordinate s *between the two TS's* there is a statistical equilibrium between the reaction coordinate motion and the hindered rotations ("transitional coordinates") that were originally bending vibrations in the dissociating molecule.⁴⁶ This approach yielded encouraging agreement^{13e,46b,46c} with the experimental results⁴⁷ for the quantum state distribution of the products for the appropriate system (e.g., Figure 3). The rotational-vibrational quantum state distribution of the separated fragments was determined using laser induced fluorescence.⁴⁷ A separate statistical ensembles^{47b} method was also successful in treating the products' quantum state distribution.

Another experiment involves photofragmentation excitation spectra (PHOFEX) (Figure 5) and the determination of the distribution of quantum states of a product as a function of energy⁴⁸. These data are more sensitive to the two-transition state behavior than the $k(E)$ data. Variational RRKM, with the additional exit channel assumption mentioned earlier (adiabatic vibrations, nonadiabatic hindered rotations), and using Miller's analysis of the two TS problem⁴⁹, applied now to individual vibrationally adiabatic states instead of to the entire ensemble, was successful in treating the data.^{13e,47b,47c,48c}

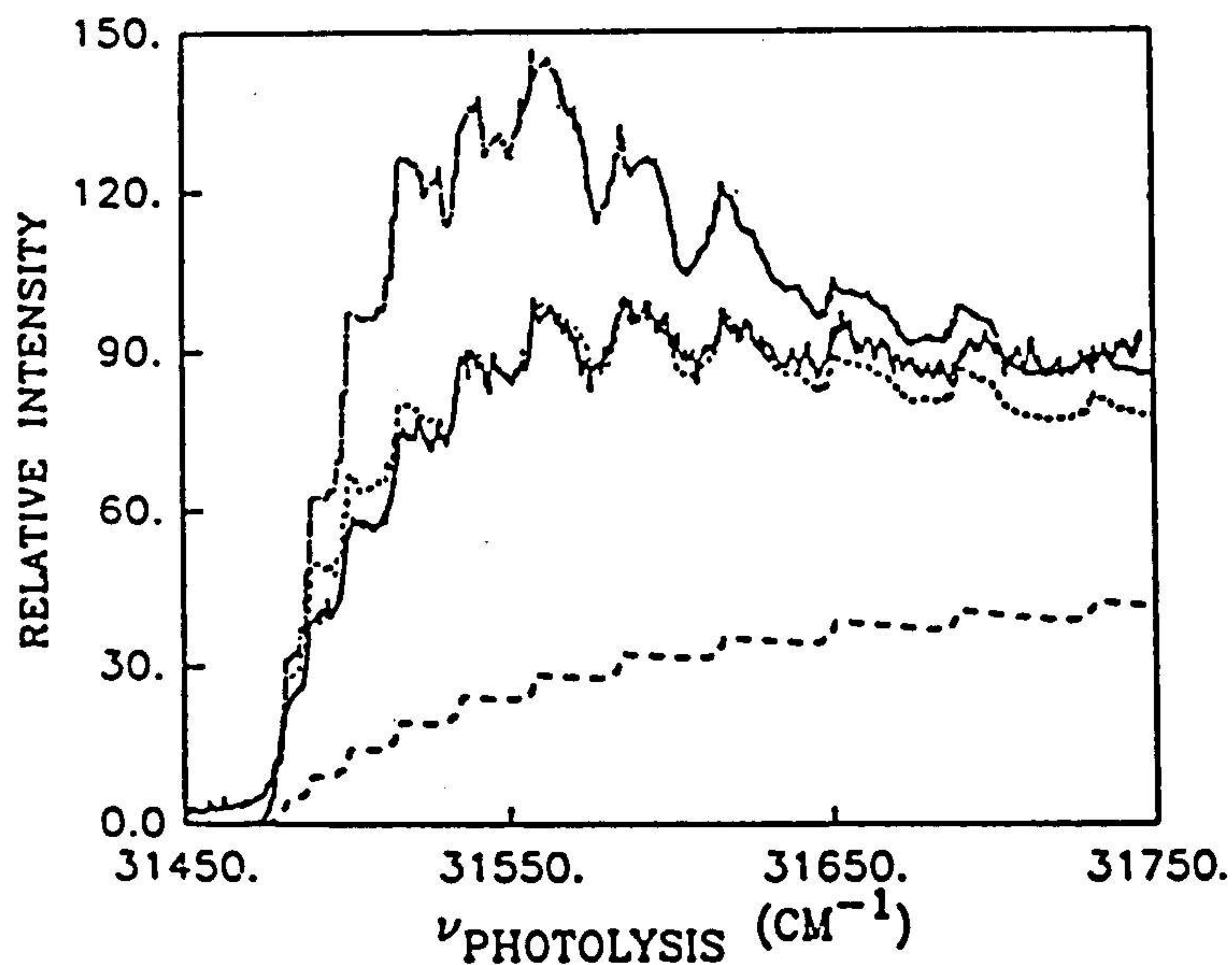


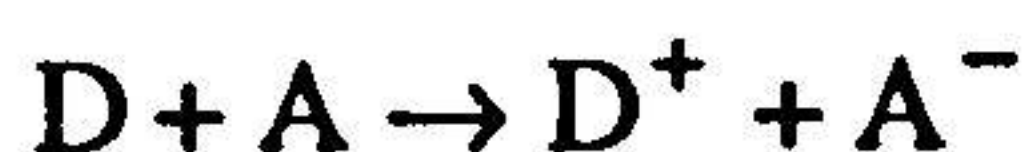
Figure 5. PHOFEX results.^{46b}

We turn next to the second question, which involves the definition of the TS. Because of the no-recrossing criterion, one may consider the TS as the hypersurface of no return. If we now examine a system photoexcited to some region on a downhill slope of a potential energy surface, we may apply this recrossing test to see if the "states" along the way constitute a transition state: There is, indeed, no recrossing for systems moving in the forward direction. However, essentially all trajectories in the reverse direction will recross this hypersurface, because they are subsequently reflected by the repulsive wall. In other words, these intervening states are not a transition state. A true transition state, produced at the top of a barrier (saddle-point), has been observed in a number of cases, in real time for a reaction (HgI_2 dissociation) in an electronically excited state⁵⁰ and spectroscopically for reaction in the ground state ($\text{F} + \text{H}_2$, $\text{OH} + \text{H}_2$ and $\text{O} + \text{HCl}$ reactions).⁵¹ (See also Ref. 52 re: an O_3 dissociation in an electronically excited state.) The especially strong and very striking feature of the ultrafast observation of chemical reactions is the observation of chemical bonds actually rupturing and/or forming in real time. The $\text{H} + \text{OCO} \rightarrow \text{HO} + \text{CO}$ reaction⁵³ was an early example. Applications of the ultrafast technique to numerous other reactions are reviewed in ref. 54, and include organic, inorganic, and charge transfer processes.

2.4 Free energy and potential energy diagrams

We consider next the topic of free energy plots, often used in conjunction with TS theory. They have been very helpful on many occasions in the visualization of the reaction process. We inquire as to whether there are also occasions when such plots might be misleading. For example, a free energy *vs* reaction coordinate curve is plotted for some reaction and, on the same plot, the free energy curve for a competitive path leading to the same products may also be plotted for comparison. One example is that of two ethylenes, which can form a cyclobutane directly or via a diradical intermediate. While these alternative paths can be depicted on a one-dimensional plot, one path to the left and the other to the right, such a plot doesn't describe the geometric relation of the two paths. Instead, such geometry is described by making a two- (or even three-) dimensional free energy or potential energy contour plot. At times a free energy *vs* reaction coordinate plot even for a single reaction path can also be incorrect. One example occurs in electron transfers involving the use of such a curve for reactants and one for products, unless one is especially careful in defining the ensemble for which the free energy is calculated. These topics are considered next, beginning with the latter.

For an electron transfer reaction which occurs between an electron donor D and an acceptor A,



plots were made in earlier years of the free energy of the thermally equilibrated reactants *vs* the DA separation distance r_{DA} and similarly the free energy of the thermally

equilibrated products was plotted versus r_{DA} on the same graph. D and A might each have a charge of any sign, or either or both might be uncharged. The electron transfer was then assumed to occur at the intersection of the two curves. Such a plot turns out not to be meaningful, and even the intersection can be fictitious: The details are intimately bound with concepts which were employed in the development of electron transfer theory:⁵⁵

Numerous nuclear coordinates of the solvent and often of the reactants themselves are involved in a reaction in a polar solvent, the orientations and polarized vibrations of the solvent molecules, for example. For the plots of a free energy vs r_{DA} curve for reactants and one for products to be compared in a meaningful way, they must be a reactants' ensemble which has at each r_{DA} the same distribution of all other coordinates as that in the products' ensemble. The distribution itself varies with r_{DA} . The construction of free energy plots constrained in this way was an important feature in the visualization of electron transfer theory, as in Figure 6.

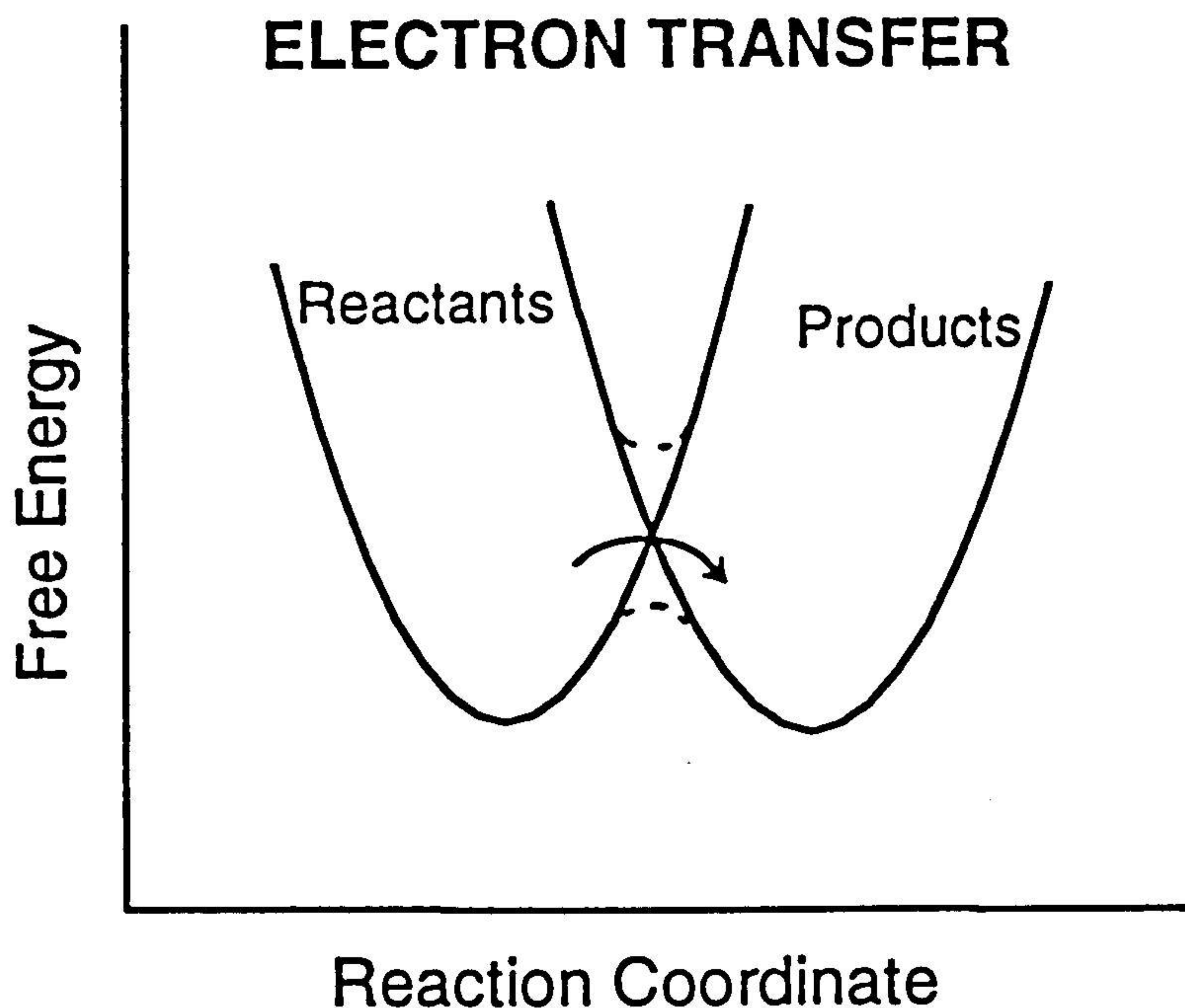


Figure 6. Free energy vs reaction coordinate for the reactants and for the products of an electron transfer

In the earlier publications I depicted profiles of the many-dimensional potential energy surface of the reactants and that of the products, holding all other nuclear coordinates fixed,^{55b} and gave the equations for the free energy profiles.⁵⁵ In later publications,⁵⁶ the constrained free energy *vs* reaction coordinate (typically not simply an r_{DA}) curves were plotted. Thus suitably constrained, two free energy curves could be plotted in a meaningful way *vs* the reaction coordinate. The coordinate used was ΔE , the energy difference of products and reactants,^{55b,57} or a related coordinate. Thereby, a hypersurface containing the set of coordinates that have the same ΔE was used to calculate a free energy of the reactants for that ensemble. Similarly; the free energy could be calculated for the products using the same ensemble. In this way free energy curves such as those in Figure 6 could be legitimately plotted *vs* the reaction coordinate *s*. The field of electron transfer is an example of the many applications of TS theory which has itself developed into numerous areas, ranging from biological to electrochemical and physical as well as organic systems. A chart which describes some of this development is given in Figure 7.

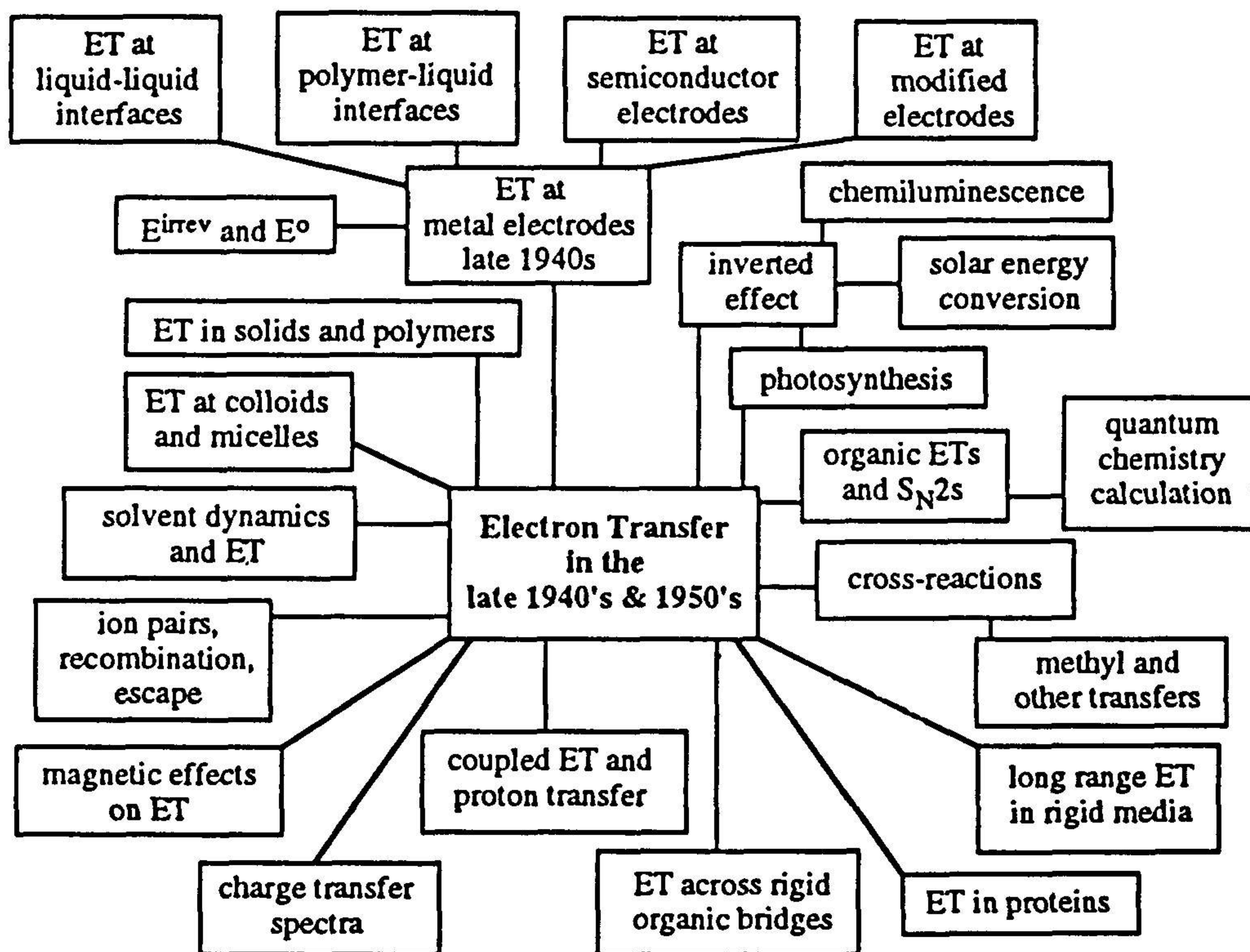


Figure 7. Growth of the electron transfer field.

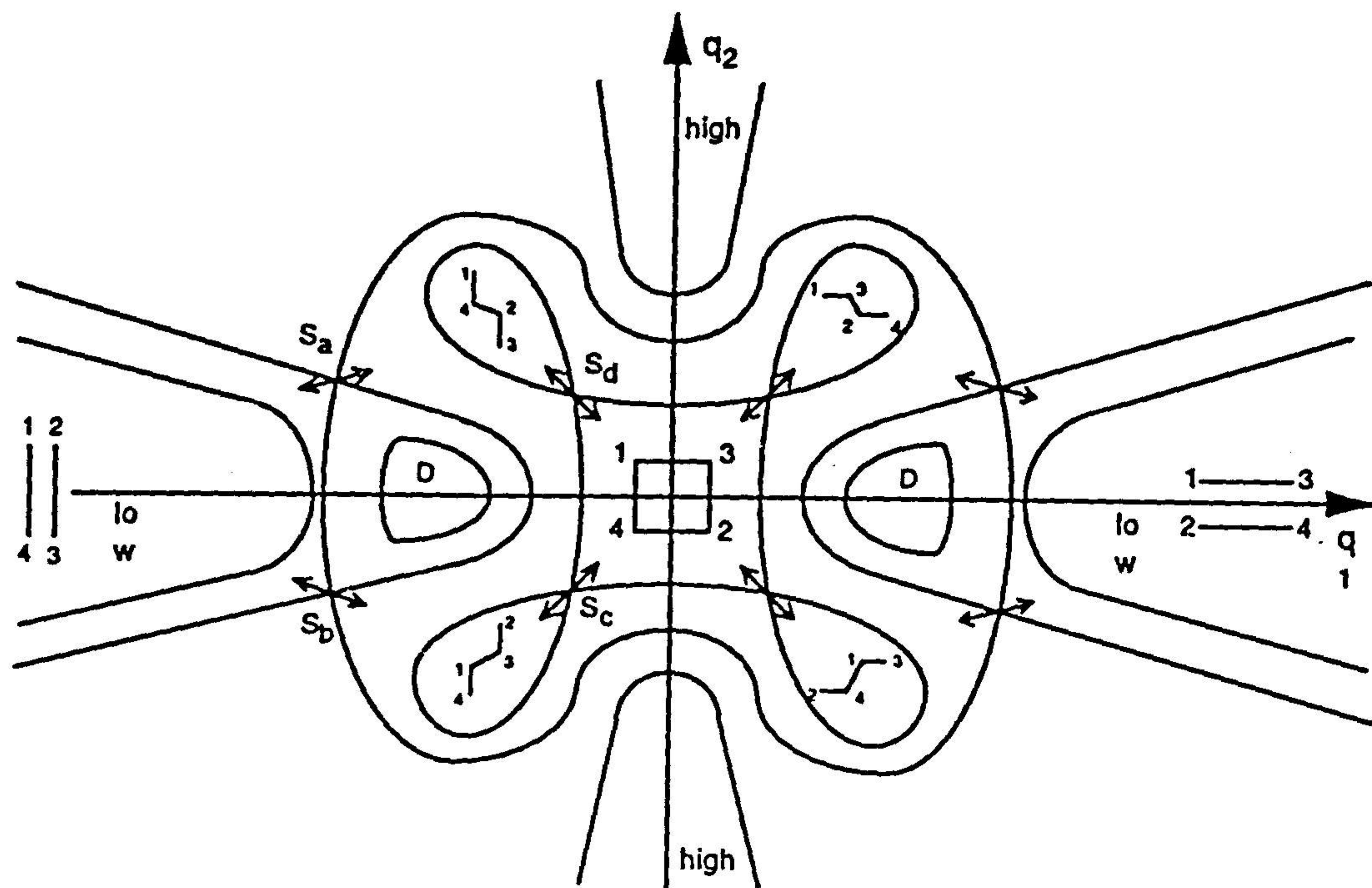
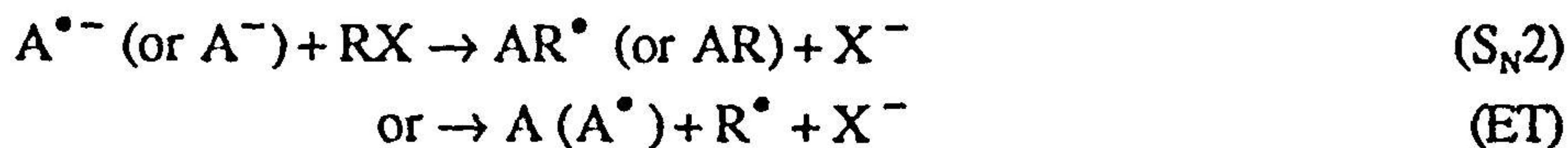


Figure 9. Global energy contour plot for an ethylene pair/diradical/cyclobutane system.⁶⁰

Another and very recent example involving free energy or potential energy contour plots and TS theory are the S_N2 and concerted bond rupture/electron transfer reactions. There are many such examples:



where $A^{\bullet-}$ is an aromatic anion radical and A the corresponding aromatic molecule, R is an alkyl or other group, X^- typically a halide, and A^- may be a carbanion or other nucleophile or, in the ET case, an electrode. Previously, the electron transfer theory had been extended by Savéant⁶¹ so as to include concerted electron transfer/bond rupture reactions (the above ET reaction). Experimentally, the S_N2 path is in some cases competitive with and frequently faster than the ET path, as judged by stereochemical or kinetic data. Recently, using a free energy contour diagram with $(A^{\bullet-} \cdots RX, R \cdots X)$ or $(A^- \cdots R, R \cdots X)$ as a pair of coordinates, and for various reactions, for example with $A^{\bullet-}$ being an aromatic radical anion,⁶²⁻⁶⁴ metal porphyrins,⁶⁵ or A^- being a substituted pyridine carbanion⁶⁴ or indeed with many others, it was shown how both the

substituted pyridine carbanion⁶⁴ or indeed with many others, it was shown how both the S_N2 and ET reaction paths could be depicted in a single diagram (Figure 9). The TS involved is, in the first approximation, the intersection of the zeroth-order electronic states on the left and right hand sides of the above equations (Figure 9a). An S_N2 path corresponds to crossing this intersection in a region where the above distances are both small, while the ET path corresponds to crossing where the $A^{\bullet-}$ (or A^-)...RX distance is relatively large ("gas kinetic").

Using this plot it was shown⁶⁶ how it was possible to construct a variational unified approach which includes both types of reaction as limiting cases and which offers the possibility for an intermediate case (Figure 10). The intermediate case may explain some observed intermediate values of the activation entropy. This S_N2 /ET bond rupture field, with its many sources of data, stereochemical, kinetic, interesting entropic effects, driving force effects ($-\Delta G^\circ$), comparisons of relative rates of the two paths and their dependence on the reactions (varying from being comparable to differing by 20 orders of magnitude) has offered a rich source of information obtainable by classical experimental techniques. It will be interesting to see in what form ultrafast technology will add to this knowledge. For example, in a DA pair, photoexcited to yield some charge transfer state D^+A^- , can it be constructed so as to react with another molecule in a van der Waals' pair via one or both of the two mechanisms above?

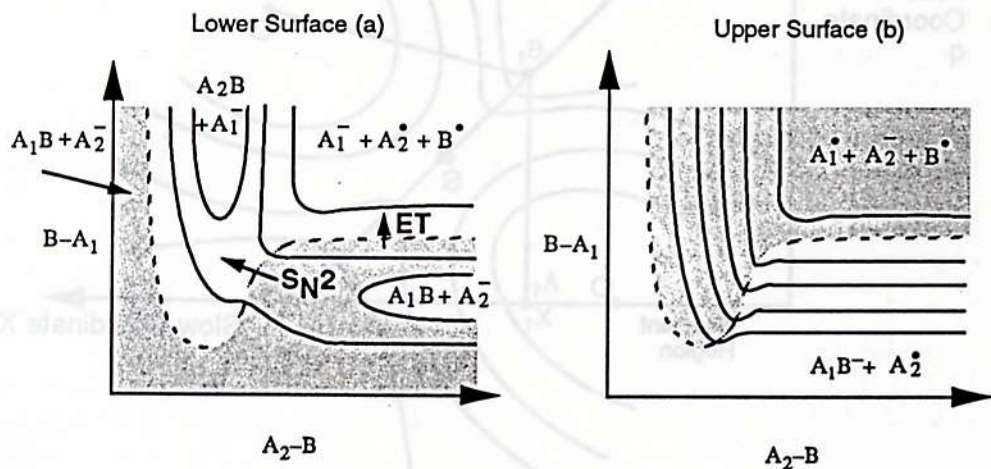


Figure 10. Free energy surfaces for concerted ET/bond rupture and S_N2 reactions of the ET type.⁶⁶

Another type of bimolecular reaction involving the rupture of one bond and formation of a new one, with no charge transfer, and where the cross-relation has been successfully applied, involves the transfer of a methyl group, with no accompanying charge transfers.⁶⁷ The range of reactions which exhibit the influence of "intrinsic" and "driving force" factors is seen in this and in other examples to be particularly large.⁶⁸

Among the many other areas involving the transition state theory of chemical reactions is solvent dynamics. There have been numerous studies, both experimental and theoretical, on the effects of solvent dynamics on reaction rates, for systems at a constant temperature.⁶⁹ There have been two principal theoretical approaches, one stemming directly from Kramers' classic 1940 article,⁷⁰ largely overlooked in the chemical literature for more than three decades. It is a one-coordinate approach (the reaction coordinate), and involves a phenomenological internal or external (solvent viscosity) viscous coefficient. The theory was extended by Hynes⁷¹ to include a frequency-dependent friction (memory effects). A different approach, typically two-coordinate, involves a vibrationally-assisted passage across the TS hypersurface,^{72,73} and permits the system to bypass the saddle-point region when it is profitable to do so (Figure 11).

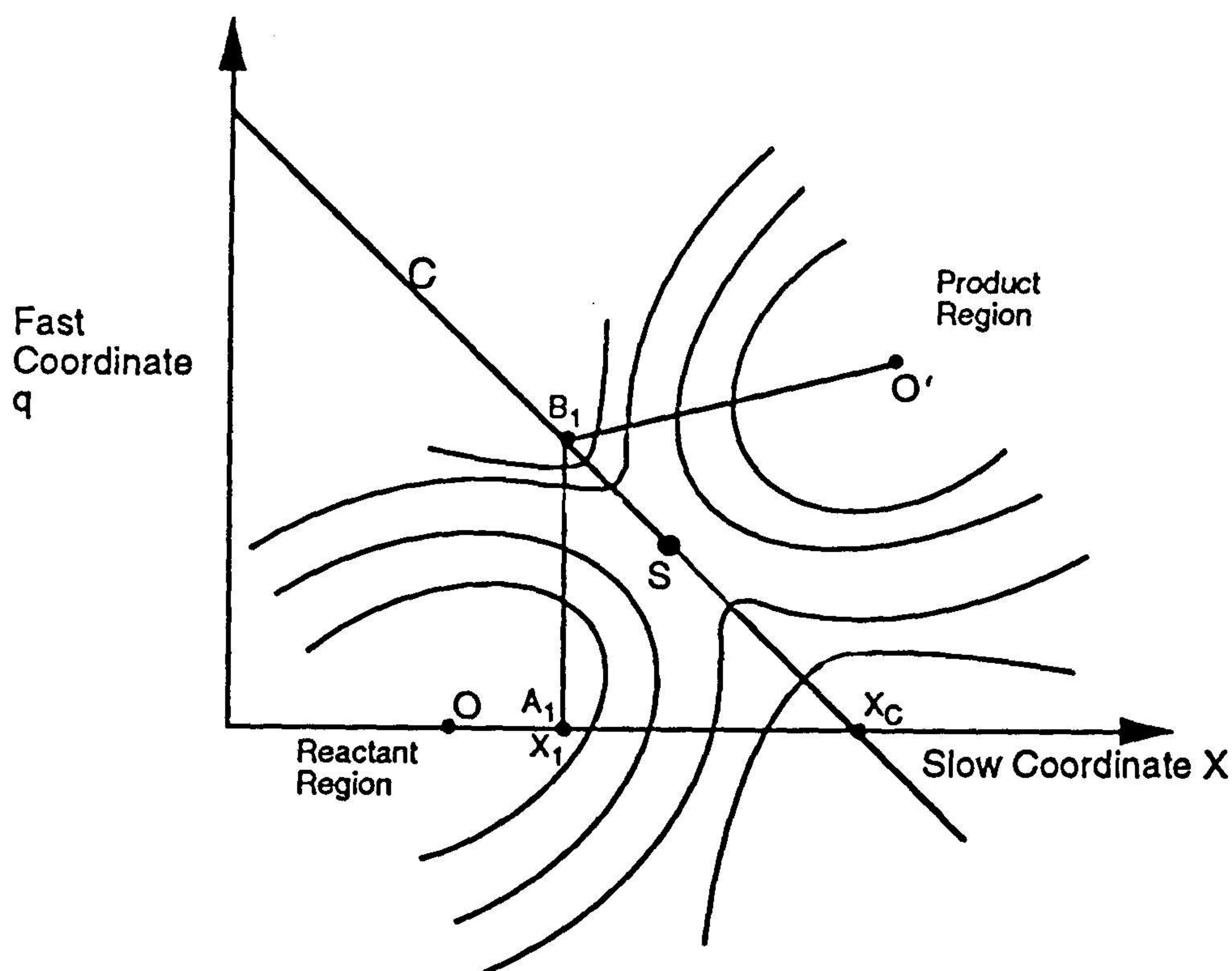


Figure 11. Solvent dynamics and a bypass of the saddle-point. 75b

Such an extension was essential for ET reactions.⁷³ Recently, the experimental study of rapid isomerization of *t*-stilbene in hexane clusters in a molecular beam at this Institute,⁷⁴ and the dependence of its reaction rate on energy and cluster size, prompted me to formulate a microcanonical version of the solvent dynamics so as to treat unimolecular reactions in clusters.⁷⁵ Various questions which the experimental and theoretical work posed have been discussed elsewhere,⁷⁵ in particular whether the observed effects with cluster size were due to the expected decrease of $k(E)$ with increasing size at a given E or to a frictional effect, or to both. Experiments were considered there for addressing this issue.^{75c}

Interestingly enough, reactions with dissipative effects have been described in terms of a TS theory of the reactant in a conservative system, namely a harmonic oscillator bath.⁷⁶ When a sufficiently large number of oscillators is used, the properties of the bath simulate a dissipative medium.

We conclude with some remarks on solvent response (relaxation), in part, because solvent dynamics can play a role, we have seen, in TS theory. The use of fast and particularly ultrafast techniques has permitted the study of the polar solvent response to a sudden change in the charge distribution.⁷⁷ The experimental result for the dependence of the spectral maximum $S(t)$ on time was highly nonexponential,⁷⁷ and has been treated theoretically.^{77c,78} It was possible, using continuum theory and the full dielectric dispersion behavior of the solvent to obtain results, without adjustable parameters which parallel the experimental curve for $[S(t) - S(\infty)]/[S(0) - S(\infty)]$ vs time surprisingly well,⁷⁸ as in Figure 12. One difference was in the behavior at very short times:⁷⁸ The calculated decrease at short times was more sudden than the reported experimental one, which showed an initial rapid decay in about 50 fs. On the other hand the experimental technique used, up-conversion, appears to have a resolution of about 50 fs. It would be useful, therefore, to see if a shorter time technique, a pump-probe optical absorption, could be used, some absorption interference notwithstanding. The system investigated was coumarin 343 in water.

We have seen that the transition state theory developed in 1935 has been subsequently extended, by making it variational, or microcanonical so as to treat unimolecular reactions, or by including solvent dynamics as well, or adding solvent and vibrational reorganization so as to treat electron transfers, or by adding an assumption to make predictions on the quantum state distribution of the reaction products, when there is no "exit channel effects." Some of the interesting new horizons can be expected to be in phenomena which are nonstatistical. It has been pointed out for many years that nonstatistical effects are expected for sufficiently short-time behavior: Rabinovitch estimated from his results of the order of 100 fs to 1 ps.⁷⁹ When the energy is added to a molecule in rather a delocalized way, e.g., by collision, or by other means when enough time has elapsed for there have been more delocalization of the energy, statistical theory, which transition state theory is, then the TS theory has proved to be a very useful tool. With ultrafast events being investigated, deviation from statistical behavior are being

studied in real-time, experimentally⁸⁰ and theoretically, e.g., refs. 81, and the future for new theories looks bright and challenging.

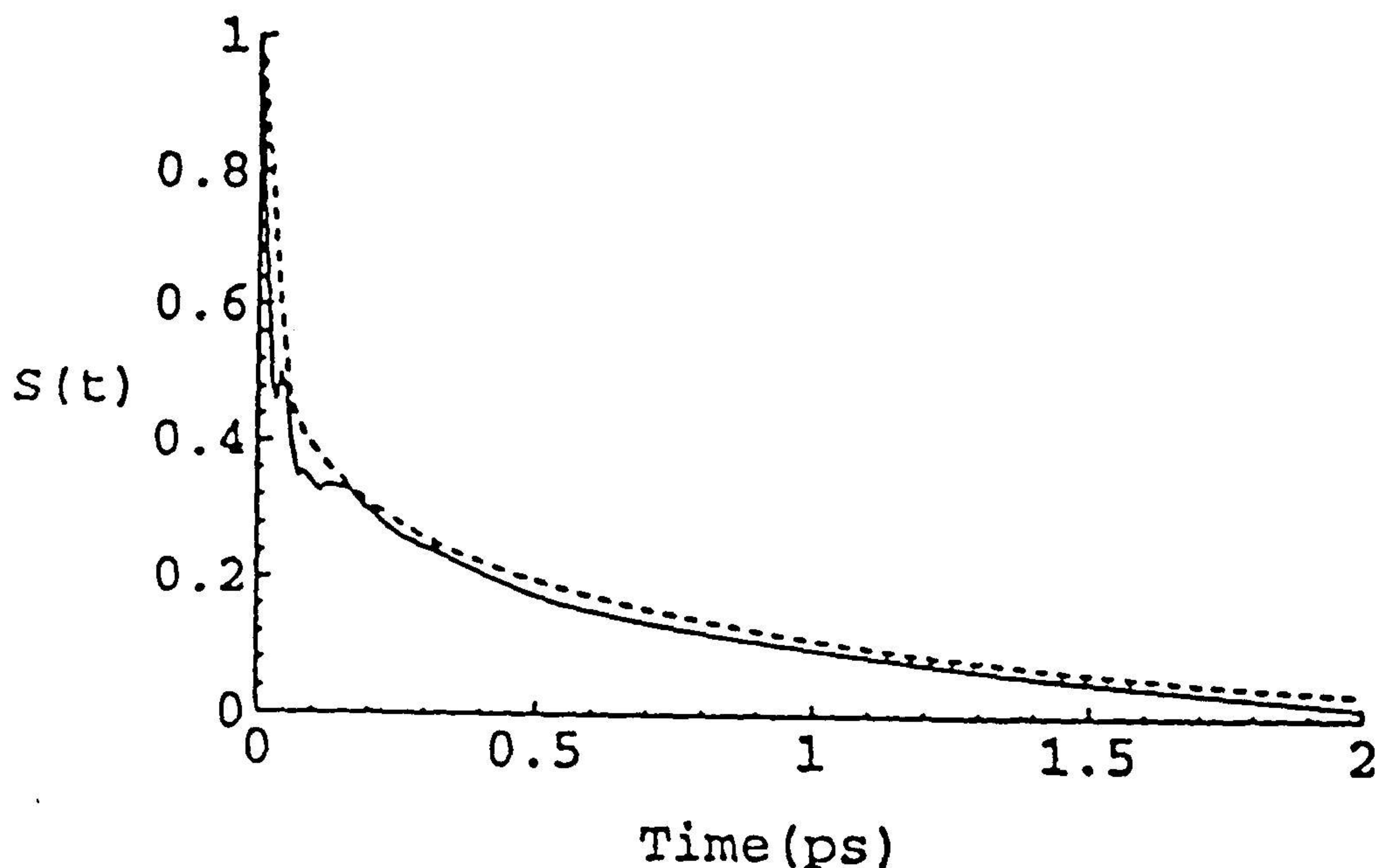


Figure 12. Time-dependent Stokes shift: experimental (dashed) and calculated (solid).⁷⁸

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